

Copyright is owned by the Author of the thesis. Permission is given for a copy to be downloaded by an individual for the purpose of research and private study only. The thesis may not be reproduced elsewhere without the permission of the Author.

Particle Size Effect on Caking in Sucrose

**A Thesis presented in partial fulfilment of the requirements for the degree of
Masters in Chemical Technology at Massey University**

Rebecca Clarke

B. Tech (Chem)

2005

- Abstract -

Caking, and the associated loss of flowability, have for a long time been a problem in the sugar industry, causing difficulties during conveying and making the product unacceptable to consumers. There are many factors that are thought to contribute to this problem, including relative humidity, compaction and packing of the crystals, and particle size.

In order to determine if particle size did have an effect, a series of samples containing different sized crystals, and different proportions of fine crystals were created. These samples then had their water vapour sorption isotherms measured by equilibrating samples over saturated salt solutions. Caking tests were also carried out using the friability test and the blowtest. No significant difference was found on either the isotherms or the friability test. The blowtest, however, was found to be much more sensitive to the small differences in caking occurring between samples. It was found that only fines less than 150 μm had any effect on caking, and even then, only when they were present in large quantities. In addition, the smaller the particles, the smaller the amount required for caking to occur. For example, the critical water activity for standard sugar was found to be 0.61. For a sample of 100% 212-315 μm particles this decreases to 0.55 and for a sample of 0-75 μm this decreases even further, to 0.22.

No additional effect was found to be caused by crystal damage, over and above the effect of decreased particle size.

It is proposed this increase in caking in fine particles is due to capillary condensation. The smaller the crystals, or the greater the proportion of fines small crystals present, the more contact points between particles. Between each of these contact points capillary condensation can occur, which means more moisture can be absorbed at a lower water activity, therefore, the amount of water needed for caking to occur is also reached at a lower water activity. This effect is very small, and neither the isotherms nor the friability test was able to detect these changes, but the blowtester was able to.

Some of these fine crystals will originate in the crystallisation process, however many of the fine crystals are a product of attrition. It was found that this was a problem when sugar was conveyed using a screw conveyor, but not when a redler chain conveyor was used. In addition, there were no differences found in the amount of attrition occurring when conveyors are run at less than full loads. It is recommended that in future construction and modification of the plant, chain redlers be considered rather than screw conveyors.

- Acknowledgements -

“However high we climb in pursuit of knowledge, we shall see heights above us, and the more we extend our view, the more conscious we shall be of the great immensity that lies beyond” – D.A. Wrangham

My pursuit of caking in sucrose started in Palmerston North, over a year ago. Since then I have spent nine months in Auckland – somewhere I’ve always vowed I never wanted to live, then a few weeks in Taranaki, before returning to the familiarity of Palmerston North. During this time there were many people who helped me in my pursuit.

Firstly, thank you to my supervisors Tony and Kylie, who have helped me understand the problem, made sure I kept on track with the project, made me think for myself, supported me, have given suggestions and given their time to this project. Without their support this thesis would never have been written.

Secondly, everyone at New Zealand Sugar, especially Allan Dobbie, my supervisor. Also, the laboratory staff for helping me find my way round the lab and allowing me the use of the equipment and cupboard space, the CPR team leaders for sharing their office, everyone who helped me get samples, and Warren, also for helping me get samples, and divulging information and stories about the plant.

Helen and Jay in the Food Chemistry lab at Massey, Albany for helping me get set up for my work there.

Fonterra, Kapuni, for allowing me the use of the isothermal microcalorimeter, Jeremy for showing me how to use this instrument. The Coastal View Relay Team for giving me a leg of the relay at short notice.

Lastly, a special thanks to everyone I met at Windsor Park, the Birkenhead Badminton Club and Auckland Central Ceroc, for making my time in Auckland bearable . . . and even enjoyable.

- Table of Contents -

ABSTRACT	i
ACKNOWLEDGEMENTS	iii
TABLE OF CONTENTS	v
LIST OF FIGURES	ix
LIST OF TABLES	xv
CHAPTER 1 PROJECT OVERVIEW	1-1
1.1 Introduction	1-1
1.2 Caking	1-2
1.3 Attrition.....	1-2
1.4 Project Objectives.....	1-3
CHAPTER 2 LITERATURE REVIEW	2-1
2.1 Introduction	2-1
2.2 Chemistry of Sucrose.....	2-1
2.2.1 Crystalline Sucrose	2-2
2.2.2 Amorphous Sucrose.....	2-4
2.2.2.1 Glass Transition Temperature.....	2-5
2.2.2.2 Determination of Amorphous Sugar Content	2-6
2.3 Moisture	2-9
2.3.1 Types of Moisture.....	2-9
2.3.1.1 Water Content Determination.....	2-10
2.3.2 Water Activity	2-11
2.3.3 Sorption Isotherms	2-12
2.3.3.1 Measurement of Sorption Isotherms	2-14
2.3.3.2 Hysteresis.....	2-14
2.3.3.3 Temperature Dependence of Isotherms.....	2-15
2.3.3.4 Crystalline Sucrose Sorption Isotherm.....	2-15
2.3.3.5 Amorphous Sucrose Sorption Isotherm	2-16
2.3.4 Capillary Condensation	2-17
2.3.4.1 Kelvin Equation	2-17
2.3.5 Size Relationships	2-18
2.4 Caking	2-20
2.4.1 Humidity Caking.....	2-21
2.4.1.1 Temperature Gradients	2-22
2.4.2 Caking in Amorphous Sugar.....	2-23

2.4.3	<i>Effect of Fines on Caking</i>	2-24
2.4.4	<i>Quantification</i>	2-26
2.4.5	<i>Caking at New Zealand Sugar</i>	2-28
2.4.6	<i>Prevention of Caking</i>	2-28
2.5	<i>Attrition and Particle Size Analysis</i>	2-29
2.5.1	<i>Affect of Fines on the Properties of the Sugar</i>	2-29
2.5.2	<i>Mechanisms of Attrition</i>	2-30
2.5.3	<i>Measurement/Quantification</i>	2-32
2.5.4	<i>Particle Size Analysis</i>	2-32
2.5.4.1	<i>Methods</i>	2-32
2.5.4.2	<i>Sampling</i>	2-34
2.5.4.3	<i>Sample Points</i>	2-35
2.5.4.4	<i>Subsampling</i>	2-36
2.6	<i>Conclusion</i>	2-40
CHAPTER 3 ISOTHERMS		3-1
3.1	<i>Introduction</i>	3-1
3.2	<i>Experimental</i>	3-2
3.3	<i>Results and Discussion</i>	3-6
3.3.1	<i>Effect of Crystal Size</i>	3-8
3.3.2	<i>Effect of Proportion of Fine Crystals</i>	3-10
3.3.3	<i>Comparison to Literature</i>	3-12
3.4	<i>Conclusions and Recommendations</i>	3-15
CHAPTER 4 DETERMINATION OF AMORPHOUS SUCROSE CONTENT		4-1
4.1	<i>Introduction</i>	4-1
4.1.1	<i>Thermal Activity Monitor</i>	4-2
4.2	<i>Experimental Methodology</i>	4-4
4.3	<i>Results</i>	4-6
4.4	<i>Conclusion</i>	4-12
CHAPTER 5 CAKING		5-1
5.1	<i>Introduction</i>	5-1
5.2	<i>Experimental</i>	5-2
5.2.1	<i>Liquid Bridging</i>	5-3
5.2.1.1	<i>Friability</i>	5-3
5.2.1.2	<i>Blowtester</i>	5-4
5.2.2	<i>Solid Bridging</i>	5-4
5.3	<i>Results and Discussion</i>	5-4
5.3.1	<i>Liquid Bridging</i>	5-5
5.3.1.1	<i>Friability</i>	5-5
5.3.1.1.1	<i>Comparison of Friability Measurements and Isotherms</i>	5-7
5.3.1.1.2	<i>Comparison of Results in This Study to Literature</i>	5-7
5.3.1.2	<i>Blowtester</i>	5-8
5.3.1.2.1	<i>Effect of Proportion of Fines</i>	5-8
5.3.1.2.2	<i>Effect of Size of Fine Particles</i>	5-11
5.3.1.2.3	<i>Comparison to Literature</i>	5-13
5.3.1.2.4	<i>Relationship Between Blowtester and Isotherm Measurements</i>	5-13

5.3.2	<i>Solid Bridging</i>	5-14
5.3.2.1	<i>Friability</i>	5-14
5.3.2.2	<i>Blowtester</i>	5-14
5.3.3	<i>Kelvin Radius</i>	5-16
5.4	<i>Conclusion and Recommendations</i>	5-23
CHAPTER 6 SIZE ANALYSIS.....		6-1
6.1	<i>Introduction</i>	6-1
6.1.1	<i>Different Methods for Describing Particle Size</i>	6-1
6.1.2	<i>Different Parameters Used to Estimate Average Particle Size</i>	6-2
6.1.2.1	<i>Mean Particle Size</i>	6-3
6.1.3	<i>Sieve Analysis</i>	6-4
6.1.4	<i>Laser Diffraction</i>	6-5
6.1.5	<i>Comparison of Sieving and Laser Diffraction</i>	6-7
6.2	<i>Experimental</i>	6-7
6.2.1	<i>Materials</i>	6-7
6.2.2	<i>Sieving</i>	6-9
6.2.3	<i>Laser Diffraction</i>	6-10
6.2.4	<i>Bulk Density</i>	6-10
6.2.4.1	<i>Poured Bulk Density</i>	6-11
6.2.4.2	<i>Tapped Bulk Density</i>	6-11
6.3	<i>Results and Discussion</i>	6-12
6.3.1	<i>Size of Different Products</i>	6-12
6.3.2	<i>Fines in the Plant at New Zealand Sugar</i>	6-14
6.3.3	<i>Redler vs Screw</i>	6-14
6.3.3.1	<i>Loading</i>	6-18
6.3.4	<i>Size in Relation to Isotherm</i>	6-21
6.3.5	<i>Bulk Density</i>	6-21
6.3.6	<i>Packing</i>	6-22
6.4	<i>Conclusions and Recommendations</i>	6-27
CHAPTER 7 EFFECT OF PARTICLE DAMAGE		7-1
7.1	<i>Introduction</i>	7-1
7.2	<i>Experimental</i>	7-1
7.3	<i>Results and Discussion</i>	7-3
7.3.1	<i>Isotherms</i>	7-3
7.3.2	<i>Friability</i>	7-5
7.3.3	<i>Blowtester</i>	7-5
7.3.4	<i>Kelvin Radius</i>	7-7
7.4	<i>Conclusion and Recommendations</i>	7-8
CHAPTER 8 CONCLUSIONS AND RECOMMENDATIONS		8-1
8.1	<i>Recommendations for Future Work</i>	8-3
REFERENCES		R-1

APPENDIX A-1

A1 Nomenclature	A-1
A2 Caking Figures	A-2
A3 Sample Points	A-8
A4 Calculations	A-9
<i>A4.1 Residence Time in Conveyors</i>	A-9
<i>A4.2 Packing If Small Crystals Fit Between Larger Crystals</i>	A-11
<i>A4.3 Packing If Small Crystals Form A Layer Around Large</i>	A-12
<i>A4.4 Estimation of Number of Crystals</i>	A-13
A5 Laser Diffraction Analysis Reports	A-14

- List of Figures -

Figure 2.1	Structure of sucrose (Pennington & Baker, 1990)	2-2
Figure 2.2	Single sucrose crystals (Pennington & Baker, 1990)	2-3
Figure 2.3	Solubility curve for sucrose	2-4
Figure 2.4	Literature data for glass transition temperature (Foster, 2000).....	2-6
Figure 2.5	Karl Fischer titration results for standard sugar, >850 μm (Roge & Mathlouthi, 2000)	2-11
Figure 2.6	Sorption isotherm for crystalline sucrose	2-16
Figure 2.7	Sorption isotherm for amorphous sucrose	2-17
Figure 2.8	Sorption isotherm for different sized crystals (Mathlouthi & Roge, 2003)	2-19
Figure 2.9	Humidity caking mechanism (Bronlund, 1997)	2-22
Figure 2.10	Amorphous caking mechanism (Bronlund, 1997)	2-23
Figure 2.11	Friability angle for samples containing different proportions of fine crystals (Roge & Mathlouthi, 2000)	2-25
Figure 2.12	Abrasion and fracture of a sucrose crystal	2-31
Figure 2.13	Screw conveyor and redler chain conveyor (Perry & Green, 1997)	2-31
Figure 2.14	Cross section of segregation in a heap (Allen, 1975)	2-35
Figure 2.15	Bad sampling technique and good sampling technique (Allen, 1975)	2-36
Figure 2.16	Coning and quartering (Allen, 1975)	2-37
Figure 2.17	Table sampler (Allen, 1975)	2-38
Figure 2.18	Chute riffler sampler (Allen, 1975)	2-38
Figure 2.19	Spinning riffler sampler (Allen, 1975)	2-39
Figure 3.1	Possible effects of fine crystals on the isotherm	3-2
Figure 3.2	Time taken for samples to reach equilibrium	3-5
Figure 3.3	Working isotherms for samples taken from around the factory	3-7
Figure 3.4	Comparison of results to published data	3-8
Figure 3.5	Working isotherms for samples composed of 100% fine crystals	3-9
Figure 3.6	Working isotherms for samples composed of 10% fine crystals, mixed with 600-850 μm crystals	3-9
Figure 3.7	Working isotherm for samples composed of varying proportions of 0-75 μm crystals, mixed with 600-850 μm crystals	3-10
Figure 3.8	Working isotherm for samples composed of varying proportions of 75-150 μm crystals, mixed with 600-850 μm crystals	3-11
Figure 3.9	Working isotherm for samples composed of varying proportions of 150-212 μm crystals, in 600-850 μm crystals	3-11
Figure 3.10	Working isotherm for samples composed of varying proportions of 212-315 μm crystals, in 600-850 μm crystals	3-12

Figure 3.11	Comparison of particle size isotherms with those published by Mathlouthi and Roge (2001)	3-13
Figure 3.12	Comparison of isotherms with varying percentages of fines with those published by Mathlouthi and Roge (2001)	3-14
Figure 4.1	The thermal activity monitor	4-2
Figure 4.2	Inside a calorimetric unit	4-3
Figure 4.3	Heat flow in the calorimeter	4-3
Figure 4.4	Glass ampoule and sample	4-4
Figure 4.5	Amorphous content vs integral peak curve (Billings, 2002)	4-6
Figure 4.6	TAM curve for standard sucrose sample, containing no amorphous content	4-8
Figure 4.7	TAM curve for 75-150 μm sample which may contain some amorphous sucrose	4-10
Figure 4.8	Effect of amorphous sucrose on the isotherm	4-11
Figure 4.9	TAM curve for sample containing 0.16% amorphous sucrose (Billings, 2002)	4-12
Figure 5.1	Rotating platform	5-3
Figure 5.2	Blowtester	5-4
Figure 5.3	Angle required to break liquid bridges in samples containing varying proportions of 0-75 μm crystals, mixed with 600-850 μm crystals	5-6
Figure 5.4	Angle required to break liquid bridges in samples containing varying proportions of 75-150 μm crystals, mixed with 600-850 μm crystals	5-6
Figure 5.5	Airflow required to break liquid bridges in samples containing varying proportions of 0-75 μm crystals, mixed with 600-850 μm crystals	5-9
Figure 5.6	Airflow required to break liquid bridges in samples of containing varying proportions of 75-150 μm crystals, mixed with 600-850 μm crystals	5-9
Figure 5.7	Airflow required to break liquid bridges in samples containing varying proportions of 150-212 μm crystals, mixed with 600-850 μm crystals	5-10
Figure 5.8	Airflow required to break liquid bridges in samples composed of varying proportions of 212-315 μm crystals, mixed with 600-850 μm crystal	5-10
Figure 5.9	Airflow required to break liquid bridges in samples containing 100% fine crystals	5-12
Figure 5.10	Airflow required to break liquid bridges in samples containing 10% fine crystals, mixed with 600-850 μm crystals	5-12
Figure 5.11	Airflow required to break solid bridges in samples containing 0-75 μm crystals, in 600-850 μm crystals	5-15
Figure 5.12	The relationship between the solid and liquid bridges for standard sugar	5-16
Figure 5.13	Capillary radius vs water activity at 20 °C	5-16
Figure 5.14	Kelvin radius vs airflow required to break liquid bridges in standard sugar	5-18
Figure 5.15	Kelvin radius vs friability angle required to break liquid bridges in standard sugar	5-18
Figure 5.16	Kelvin radius vs airflow required to break liquid bridges in 100%	

0-75 μm sample	5-19
Figure 5.17.... Kelvin radius, calculated from liquid bridging data vs average particle size of fine crystals for samples with varying proportions of fine crystals	5-22
Figure 5.18 Kelvin radius, calculated from solid bridging data vs average particle size of fine crystals for samples with varying proportions of fine crystals	5-22
Figure 6.1 Different methods of reporting the diameter of a particle	6-2
Figure 6.2 Normal distribution and bimodal distribution	6-3
Figure 6.3 Sieve analysis for different products	6-12
Figure 6.4 Laser diffraction analysis for different products	6-13
Figure 6.5 Particle size distributions before and after standard 1A crystals were conveyed in a chain redler post-graders	6-15
Figure 6.6 Particle size distributions before and after standard 1A crystals were conveyed in a screw conveyor to be packed	6-16
Figure 6.7 Particle size distributions before and after standard 1A crystals were conveyed in a screw conveyor post-grading	6-16
Figure 6.8 Particle size distribution before and after standard 1A crystals were conveyed in a chain redler conveyor at low levels	6-19
Figure 6.9 Particle size distributions before and after caster crystals were conveyed in a screw conveyor at low levels	6-19
Figure 6.10 Different packing conformations	6-22
Figure 6.11 Correlation between number of crystals and blowtest result at a water activity of 0.59	6-26
Figure 6.12 Correlation between number of crystals and blowtest result at a water activity of 0.65	6-26
Figure 6.13 Correlation between number of crystals and blowtest result at a water activity of 0.69	6-26
Figure 6.14 Correlation between number of crystals and blowtest result at a water activity of 0.75	6-26
Figure 6.15 Correlation between number of crystals and blowtest result at a water activity of 0.81	6-26
Figure 6.16 Correlation between number of crystals and blowtest result at a water activity of 0.87	6-26
Figure 7.1 Working sorption isotherms for process samples and recombined process samples	7-4
Figure 7.2 Working sorption isotherms for process samples and process samples with milled sugar added in place of fines	7-4
Figure 7.3 Liquid bridging strength for process samples and recombined process samples	7-6
Figure 7.4 Liquid bridging strength for process samples and process samples with milled sugar added in place of fines	7-6
Figure A1 Angle required to break liquid bridges in samples containing different proportions of 150 – 212 μm crystals, mixed with 600-850 μm crystals A-1	

Figure A2	Angle required to break liquid bridges in samples containing different proportions of 212-315 μm crystals, mixed with 600-850 μm crystals.....	A-1
Figure A3	Angle required to break liquid bridges in samples containing 0.1% fine crystals, mixed with 600-850 μm crystals	A-1
Figure A4	Angle required to break liquid bridges in samples containing 1% fine crystals, mixed with 600-850 μm crystals	A-1
Figure A5	Angle required to break liquid bridges in samples containing 10% fine crystals, mixed with 600-850 μm crystals	A-2
Figure A6	Angle required to break liquid bridges in samples containing 100% fine crystals, mixed with 600-850 μm crystals	A-2
Figure A7	Angle required to break solid bridges in samples containing different proportions of 0-75 μm crystals, mixed with 600-850 μm crystals	A-2
Figure A8	Angle required to break solid bridges in samples containing different proportions of 75-150 μm crystals, mixed with 600-850 μm crystals.....	A-2
Figure A9	Angle required to break solid bridges in samples containing different proportions of 150-212 μm crystals, mixed with 600-850 μm crystals.....	A-3
Figure A10	Angle required to break solid bridges in samples containing different proportions of 212-315 μm crystals, mixed with 600-850 μm crystals.....	A-3
Figure A11	Angle required to break solid bridges in samples containing 0.1% fine crystals, mixed with 600-850 μm crystals	A-3
Figure A12	Angle required to break solid bridges in samples containing 1% fine crystals, mixed with 600-850 μm crystals	A-3
Figure A13	Angle required to break solid bridges in samples containing 10% fine crystals, mixed with 600-850 μm crystals	A-4
Figure A14	Angle required to break solid bridges in samples containing 100% fine crystals, mixed with 600-850 μm crystals	A-4
Figure A15	Airflow required to break liquid bridges in samples containing 0.1% fine crystals, mixed with 600-850 μm crystals	A-4
Figure A16	Airflow required to break liquid bridges in samples containing 1.0% fine crystals, mixed with 600-850 μm crystals	A-4
Figure A17	Airflow required to break solid bridges in samples containing different proportions of 75-150 μm crystals, mixed with 600-850 μm crystals.....	A-5
Figure A18	Airflow required to break solid bridges in samples containing different proportions of 150-212 μm crystals, mixed with 600-850 μm crystals.....	A-5
Figure A19	Airflow required to break solid bridges in samples containing different proportions of 212-315 μm crystals, mixed with 600-850 μm crystals.....	A-5
Figure A20	Airflow required to break solid bridges in samples containing 0.1% fine crystals, mixed with 600-850 μm crystals	A-7
Figure A21	Airflow required to break solid bridges in samples containing 1% fine crystals, mixed with 600-850 μm crystals	A-7
Figure A22	Airflow required to break solid bridges in samples containing 10% fine crystals, mixed with 600-850 μm crystals	A-7
Figure A23	Airflow required to break solid bridges in samples containing 100% fine crystals, mixed with 600-850 μm crystals	A-7
Figure A24	Sample points – drying	A-8
Figure A25	Sample points – conditioning	A-8
Figure A26	Malvern report for standard 1A sugar, sample 1	A-14
Figure A27	Malvern report for standard 1A sugar, sample 2.....	A-14
Figure A28	Malvern report for standard 1A sugar, sample 3	A-15
Figure A29	Malvern report for manufacturers sugar, sample 1	A-15

Figure A30	Malvern report for manufacturers sugar, sample 2	A-16
Figure A31	Malvern report for Caster sugar, sample 1	A-16
Figure A32	Malvern report for caster sugar, sample 2	A-17
Figure A33	Malvern report for caster sugar, sample 3	A-17
Figure A34	Malvern report for fines free caster sugar, sample 1	A-18
Figure A35	Malvern report for fines free caster sugar, sample 2	A-18
Figure A36	Malvern report for standard 600-850 μm sugar, sample 1	A-19
Figure A37	Malvern report for standard 600-850 μm sugar, sample 2	A-19
Figure A38	Malvern report for standard 600-850 μm sugar, sample 3	A-20
Figure A39	Malvern report for 0-75 μm sugar, sample 1	A-20
Figure A40	Malvern report for 0-75 μm sugar, sample 2	A-21
Figure A41	Malvern report for 0-75 μm sugar, sample 3	A-21
Figure A42	Malvern report for 0-75 μm sugar, sample 4	A-22
Figure A43	Malvern report for 0-75 μm sugar, sample 5	A-22
Figure A44	Malvern report for 75-150 μm sugar, sample 1	A-23
Figure A45	Malvern report for 75-150 μm sugar, sample 2	A-23
Figure A46	Malvern report for 75-150 μm sugar, sample 3	A-24
Figure A47	Malvern report for 150-212 μm sugar, sample 1	A-24
Figure A48	Malvern report for 150-212 μm sugar, sample 2	A-25
Figure A49	Malvern report for 150-212 μm sugar, sample 3	A-25
Figure A50	Malvern report for 150-212 μm sugar, sample 4	A-26
Figure A51	Malvern report for 212-315 μm sugar, sample 1	A-26
Figure A52	Malvern report for 212-315 μm sugar, sample 2	A-27

- List of Tables -

Table 2.1	Reliability of selected sampling methods (60:40, coarse:fine, sand mixture; P=0.60) (Allen, 1975)	2-39
Table 3.1	Relative humidities of different salt solutions at 20 °C (Bell & Labuza, 2000)	3-5
Table 3.2	Change in moisture content in desiccators over time	3-6
Table 4.1	Amorphous contents of different samples	4-7
Table 4.2	TAM samples repeated at 53% RH	4-10
Table 5.1	Critical Kelvin radiuses and water activities for different samples	5-19
Table 5.2	Correlation between size of 'fines' and critical Kelvin radius	5-22
Table 6.1	Percentage of fine crystals in samples taken before and after conditioning, and product samples	6-14
Table 6.2	Results of one tailed t-test for different conveyors	6-18
Table 6.3	Results of one tailed t-test for different conveyors at low loading	6-19
Table 6.4	Poured and tapped bulk densities for isotherm and caking samples	6-21
Table 6.5	Actual and theoretical bulk densities for different packing conformations	6-23
Table 6.6	Formulae for correlations between number of crystals and blowtest result at different water activities	6-24
Table 7.1	Critical Kelvin radiuses and water activities for different samples	7-7

Chapter 1

- Project Overview -

1.1 Introduction

Caking in bulk sucrose is a major problem in the sugar industry. Not only are caking problems costly, but they also cause frustrations to customers, and with this, the potential loss of trade. At New Zealand Sugar it has been found that these adverse effects of caking are most severe when bulk sugar is transported to customers some distance from the refinery in Auckland. In extreme cases, 20 tonnes of bulk sugar has set into a single lump, requiring manual intervention to allow sugar to flow.

Recent studies at New Zealand Sugar have quantified the effects of temperature gradients on induced caking in bulk sucrose and it is now known what water activity the sugar needs to be when it is packed and transported in order to avoid caking problems (Billings, 2002). Caking problems can also be minimised by conditioning, the blowing of dehumidified air through the bulk sugar before packing, and also by insulating the walls of the sugar container after packing to minimise temperature gradients (Rastikian & Capart, 1998).

There is anecdotal evidence that fines are instrumental in the caking problem. Some of these fines are produced in the crystallisation process, however most are thought to be the result of attrition as the sugar crystals are conveyed.

1.2 Caking

Caking is the formation of solid lumps from formally free flowing powder. These lumps are caused by temperature gradients in the bulk material. This causes fluctuations in interstitial air relative humidity since warm air holds more moisture than cooler air. Moisture migrates to restore the equilibrium, creating moisture concentration gradients. In areas of high relative humidity, moisture is adsorbed and condenses onto particle surfaces. This causes the dissolution of the particle surface, and the formation of liquid bridges consisting of solution. As the equilibrium changes again these liquid bridges dry out, creating a solid bridge between crystals particles. In addition, capillary condensation caused by surface tension effects may cause caking to occur at a lower humidity.

There have been conflicting reports published in literature as to whether the presence of fine crystals in sucrose increases the potential for caking to occur (Roge & Mathlouthi, 2000, 2003), or whether the bulk sucrose is so soluble that this effect does not exist (Johanson & Paul, 1996).

1.3 Attrition

Attrition can be defined as the unwanted breakage of particles, resulting in a decrease in particle size. This breakage can take two forms – abrasion or fracture. The first of these, abrasion, occurs when edges or corners are removed, resulting in a number of very small particles and a slight decrease in size of the parent particle. Fracture, meanwhile, occurs when the parent particle splits into at least two particles that are of a comparable size.

Damage occurs to crystals when particles hit each other at high velocity, such as in a pneumatic conveyor, or when particles are subject to shear. At the New Zealand Sugar factory crystals are conveyed using both screw conveyors and chain redler conveyors. It is thought that the latter caused more damage, since particles are subject

to shear forces, both between the blades and the casing of the conveyor, and between the blades and other particles.

1.4 Project Objectives

The aims of this project were as follows:

- To identify if fine crystals have an affect on caking
- To determine what mechanism caking is occurring by
- To identify where in the New Zealand Sugar plant damage to crystals is occurring
- To identify if crystal damage has any affect on caking apart from that related to size

Chapter 2

- Literature Review -

2.1 Introduction

The objectives of this work were to determine the effect fine crystals have on caking of sucrose and to determine where in the manufacturing process at New Zealand Sugar these fine crystals are generated. In order to complete these objectives it was important to have an understanding of how moisture interacts with crystalline material and the mechanisms by which caking occurs. It was also important to have an understanding of attrition. The purpose of this chapter is to introduce these concepts.

The sugar refining process has changed little in the last hundred years. The first step of this process is to remove impurities from the raw sugar, by washing in hot water and centrifuging. The crystals are then dissolved in hot water and the resulting syrup screened. In the next step, lime and carbon dioxide are added. These precipitate, removing further impurities. The syrup is then filtered and put through a carbon decolourisation plant. The next step is to grow the crystals. This is done by boiling the water off in vacuum pans, creating a supersaturated solution, and thus nucleation of sugar crystals. When these crystals reach their desired size they are dried using dehumidified air, then graded into their different size fractions and packaged.

(Chelsea Sugar – New Zealand)

2.2 Chemistry of Sucrose

Sucrose, obtained from sugar cane or sugar beet, is a disaccharide, containing glucose and fructose moieties. Its molecular formula is $C_{12}H_{22}O_{11}$, giving a molecular weight

of 342.3g/mol. The IUPAC (International Union of Pure and Applied Chemistry) nomenclature for sucrose is β -D-fructofuranosyl- α -D-glucopyranoside. The structure of sucrose is shown below in Figure 2.1.

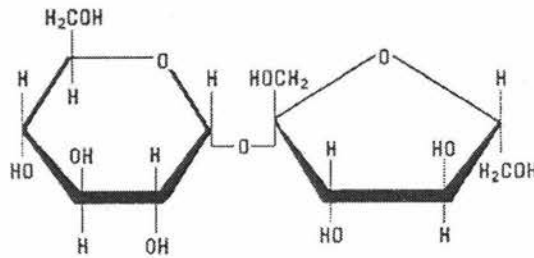


Figure 2.1 Structure of sucrose (Pennington & Baker, 1990)

Sucrose can exist in the crystalline or amorphous states or as a solution.

2.2.1 Crystalline Sucrose

Sucrose crystals can have three forms; single crystals, twin crystals or conglomerates. Single crystals, such as those shown in Figure 2.2, are the most common form and belong in the sphenoidic class of the monoclinic crystal structure. Twins are composed of two single crystals, rotated 180° to each other. Conglomerates form due to the random junction of two or more single crystals growing together. The latter two forms occur in liquors that contain a high impurity content (Vaccari & Mantovani, 1995).

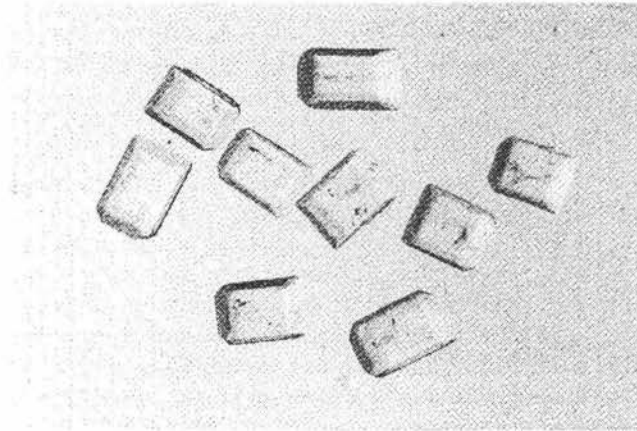


Figure 2.2 Single sucrose crystals (Mathlouthi & Reiser, 1995)

The density of crystalline sucrose is 1590 kg/m^3 (Mullin, 2001). The melting point is dependent on the purity of the sample, but usually occurs between 182 and 192°C (Pennington & Baker, 1990).

Sucrose is extremely soluble in water, and is also soluble in alcohol and other polar solvents. However, it is insoluble in most non-polar organic solvents such as benzene. The solubility can be expressed as percent water (g sucrose/100 g water) by the following equation:

$$S = 64.397 + 0.07251.t + 0.0020569.t^2 - 9.035 \times 10^{-6}.t^3 \quad \text{Equation 2.1}$$

where t is the temperature in degrees Celsius (Pennington & Baker, 1990). This is also shown in Figure 2.3.

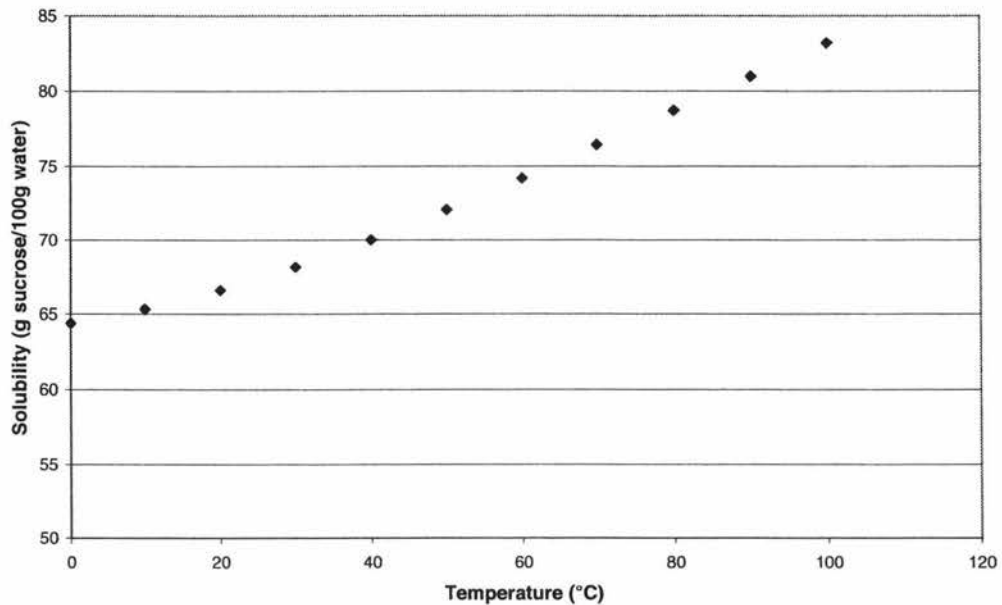


Figure 2.3 Solubility curve for sucrose

The specific heat capacity is a measure of the energy required to increase the temperature of 1kg of the material by 1 °C. For sucrose, at 20 °C, this is 1.8643 kJ/kgK (Bubnik *et al.*, 1995).

2.2.2 Amorphous Sucrose

In the amorphous form, the sucrose powder is in a disordered, non-equilibrium state (Roos & Karel, 1991a, 1993). This is due to the high viscosity of the amorphous sugar which limits molecular movement. It is then more difficult for the molecules to form the orderly alignment necessary for crystallisation (Bhandari & Howes, 1999).

Amorphous sucrose can be produced by dry-milling, quenching of the melt, freeze drying or by rapidly drying the solution, for example, by spray drying (Mathlouthi, 1995).

Amorphous sucrose is much more hygroscopic than crystalline sucrose due to a higher specific surface area and a possible change in conformation about glycosidic

linkages. Therefore, it has an increased affinity towards water (Bressan & Mathlouthi, 1994).

2.2.2.1 Glass Transition Temperature

The glass transition temperature is the temperature at which amorphous material begins to change from a solid 'glassy' state to a 'rubbery' state (Roos & Karel, 1993); this is characterised by a change in viscosity. This occurs at 56.6 °C for anhydrous amorphous sucrose at 0 % relative humidity (Labuza *et al.*, 1992), decreasing to 0 °C for a moisture content of 10 g/100g dry powder. This is shown graphically in Figure 2.4. This figure also shows that at an ambient temperature of 20 °C the critical moisture content at which recrystallisation will occur is 7 g/100g dry powder.

Over time an amorphous material will go through three different states if the temperature increases above the glass transition temperature, T_g . The first of these is the 'sticky point', T_s , the temperature at which the force required to stir the food powder increases sharply. The next is the 'collapse' temperature, T_c . This occurs when the powder can no longer hold its own weight, resulting in the loss of structure. If the temperature continues to rise the material will crystallise (Roos & Karel, 1991a, 1993; Chuy & Labuza, 1994). During recrystallisation free water is released, leading to a decrease in water content within the sugar crystal (Roge & Mathlouthi, 2003). This water cannot diffuse out as rapidly as it is produced which causes an increase in the water concentration and a decrease in viscosity of adjacent amorphous material. This increases the rate of recrystallisation in surrounding material (Makower & Dye, 1956; Chuy & Labuza, 1994).

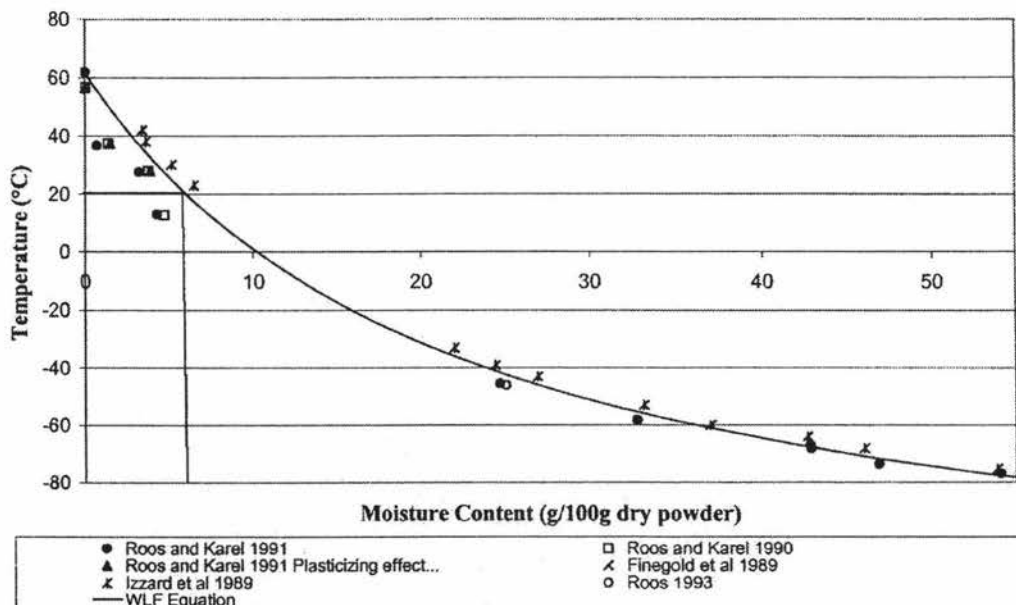


Figure 2.4 Literature data for glass transition temperature (Foster, 2000)

Moisture acts as a plasticiser which decreases the T_g , T_s , and T_c (Roge & Mathlouthi, 2003); therefore in the presence of a small amount of water the transformation from the amorphous to crystalline state can occur. This also explains why crystallisation occurs at high relative humidities.

2.2.2.2 Determination of Amorphous Sugar Content

It is important to know the amorphous content of sucrose samples because it can have a profound effect on both the sorption isotherm and on caking. Various methods can be used to determine the amount of amorphous sucrose present in a sample. These methods include gravimetric methods such as mass balances and dynamic vapour sorption (DVS), methods based on the heat of recrystallisation, such as isothermal calorimetry and differential scanning calorimetry (DSC), and methods based on crystal structure, such as x-ray analysis (Sebhatu *et al.*, 1994).

The simplest method for determining the amorphous content of a sucrose sample is based on the mass fraction balance for a sample containing both crystalline and

amorphous sucrose. This method has been used by Billings (2002), Bronlund and Paterson (2004) and Buckton and Darcy (1995).

$$X_{\text{amorphous}} = \frac{M_{\text{total}} - M_{\text{crystalline}}}{M_{\text{amorphous}} - M_{\text{crystalline}}} \quad \text{Equation 2.2}$$

The total mass, M_{total} , is the mass of water that is lost when the sample is dried. $M_{\text{crystalline}}$ is the mass of the crystalline component of the sample and $M_{\text{amorphous}}$ is the mass of the amorphous component. These can be found using the crystalline isotherm and the isotherm for the sample respectively, if the water activity of the sample is known before drying. This is only possible because crystalline sucrose absorbs very small amounts of moisture in comparison to amorphous sucrose (Makower & Dye, 1956). The main disadvantage of this method is that it can only detect amorphous sucrose down to the 1 % level (Billings, 2002). Further, this method cannot be used for this work because it is hypothesised that the isotherm for the finer particles will not be the same as for standard sugar, and as thus is unknown.

Dynamic vapour sorption (DVS) also uses the mass balance theory. This instrument consists of a microbalance housed inside a temperature-controlled cabinet. A few milligrams of sample is weighed into the DVS sample cup inside this cabinet. The relative humidity of the cabinet is then ramped using dry nitrogen bubbled through water and acetone. At each relative humidity the change in mass is measured, once equilibrium has been reached (Mackin *et al.*, 2002). This can then be related to the amorphous content using the amorphous and crystalline sorption isotherms.

The main advantages of this method are that it is quick, and a very small sample size is needed. In addition this method has been shown to be accurate to measure amorphous contents as low as 0.5 % (Mackin *et al.*, 2002).

Differential scanning calorimetry, (DSC), is generally the most commonly used thermal analysis method (Bergqvist & Soderqvist, 1999). By ramping the temperature while scanning it can detect and measure the heat evolved during transformation of an amorphous material to its crystalline state (Sebhatu *et al.*, 1994).

This method is limited to samples that contain a high amount of disorder (ie, amorphous material), and problems have been encountered in trying to measure small amorphous contents (Sebhatu *et al.*, 1994). A recent improvement on this method is modulated temperature differential scanning calorimetry (MTDSC), which uses the same standard theory, but in addition, a sinusoidal wave is superimposed over the conventional linear heating or cooling program (Guinot & Leveiller, 1999). This increases the sensitivity of this method, however, it is still not as sensitive as the DVS or isothermal microcalorimetry methods.

X-ray diffraction uses an x-ray beam that strikes a large number of random orientated crystals in a sample. Diffraction patterns are measured by sweeping a detector, creating a diffractogram (Sebhatu *et al.*, 1994). The diffractogram is different for crystalline and amorphous sugars (Bergqvist & Soderqvist, 1999). However, this method is not suitable for measuring samples containing only a very small amorphous content.

Billings (2002) used a thermal activity monitor (TAM), an instrument based on isothermal microcalorimetry. This instrument is capable of detecting very small heat flows produced or adsorbed by a chemical or physical reaction, and operates by measuring the heat flow between the reaction vessel and surrounding environment.

The major advantage of the TAM is that it is highly sensitive, so can be used to measure very small amorphous sugar levels. Other advantages are that it is non-invasive, non-destructive, and is not dependent on sample form, so it does not matter if the sample is a solid, liquid or gas.

The problem with most of the above methods is that they measure the average degree of disorder throughout the bulk (Sebhatu *et al.*, 1994), and therefore are not suitable to use to detect the small amorphous contents that could be present in the samples to be tested in this study.

Previously it was found that the sugar produced at New Zealand Sugar did not contain any amorphous content at the 0.1% level, using both the gravimetric method and a

thermal activity monitor (Billings, 2002). As shown in Figure 2.4 it is not expected that any amorphous material would be present at ambient temperatures.

2.3 Moisture

Water-sugar interactions concern three levels – the humidity of the atmosphere, the syrup surrounding the crystal and the water contained in the sucrose crystal itself (Bressan & Mathlouthi, 1994).

2.3.1 Types of Moisture

There are four distinct types of moisture associated with crystalline sugar. These are:

Interstitial – The water vapour found in the air that fills the gaps between the crystals (Ludlow & Aukland, 1990).

Free moisture – A layer of dilute sugar solution, which exists on the surface of the sugar crystals as they leave the centrifuges. It is not associated with caking and will either evaporate or become bound moisture (Bagster, 1970; Ludlow & Aukland, 1990).

Bound moisture – A supersaturated layer that is formed when free moisture evaporates. Crystallisation occurs on the surface of the syrupy coat as more water is evaporated, causing water molecules to become trapped. The water migrates to the outer surface with time, producing a thin syrupy layer (Ludlow & Aukland, 1990). The moisture concentration is approximately 0.02 % by mass of an average sugar particle, but the concentration in this layer is approximately 40 % (Leaper *et al.*, 2002). Bound moisture is more difficult to remove than other types of moisture

(Bagster, 1970), and is strongly linked to caking in sugar (Bagster, 1970; Ludlow & Aukland, 1990; Bressan & Mathlouthi, 1994).

Inherent Moisture – Found inside the sugar crystal as part of the crystal structure. Inherent moisture is not related to caking (Bagster, 1970; Ludlow & Aukland, 1990).

2.3.1.1 Water Content Determination

The most common methods used to determine water content in sucrose are desiccation, oven drying and the Karl Fischer titration. Desiccation is carried out over phosphorus pentoxide for at least one month and the difference in weight before and after the desiccation gives the moisture content. It is commonly used in food science research (Bronlund, 1997; Foster, 2002), but because of the long time requirements it is not suitable for routine measurements in industry. Oven drying uses one of three types of ovens: a vacuum oven at 508 – 635 mmHg and 80 – 85 °C, a forced draft oven at 105 °C or a convection oven at 105 °C. Samples are weighed before and after drying. The problem with oven drying is that volatile compounds as well as water can be evaporated (Mathlouthi & Roge, 2001). The Karl Fischer titration uses a special reagent, containing pyridine, methanol, sulphur dioxide and iodine, which reacts with water (Troller & Christian, 1978). It is possible to use the Karl Fischer titration method to differentiate between the different moisture types by first extracting the free water and measuring this, then grinding the crystals to release any internal water and repeating the titration (Hamano & Sugimoto, 1978; Roge & Mathlouthi, 2000). The water content in sucrose, measured by Roge and Mathlouthi (2000) using the Karl Fischer titration is shown below in Figure 2.5.

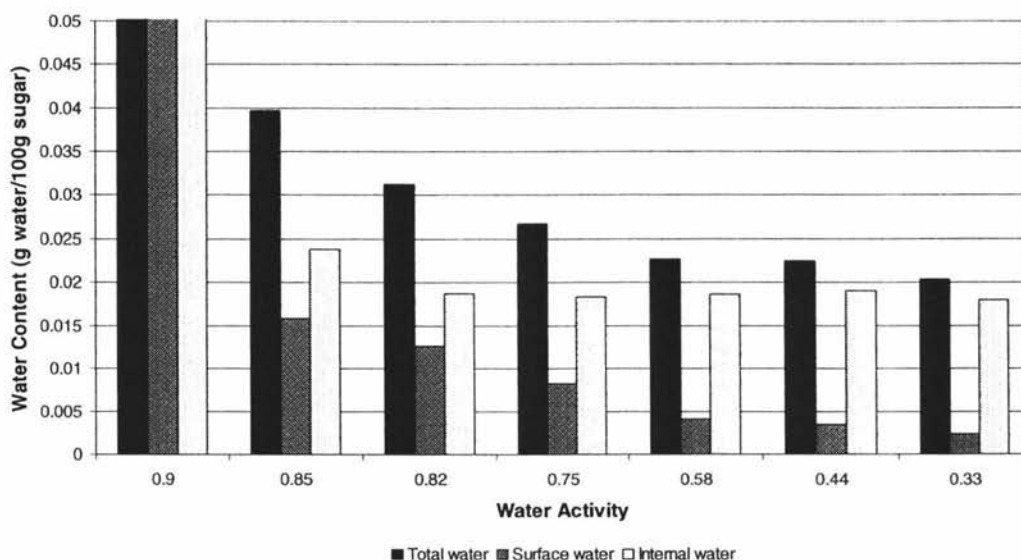


Figure 2.5 Karl Fischer titration results for standard sugar, >850 μm (Roge & Mathlouthi, 2000). The total water, surface water and internal water content at a water activity of 0.9 are 5.246, 5.0579 and 0.1881 g water/100g sugar respectively

Other possible methods used to determine water content include gas chromatography, thermal analysis, infrared spectroscopy and solvent extraction (Troller & Christian, 1978).

In this research oven drying at 105 °C in a convection oven is the most appropriate method because it is quick and does not require any special equipment, apart from the oven.

2.3.2 Water Activity

Water content is a measure of the total amount of water in a sample, but not all this water can be used in actions or reactions in the material. For this reason a more useful measure is the water activity, a_w , the amount of water that can be used (Troller, 1983). It is related to the free water content through the isotherm but is not related to the bound moisture content, which remains constant.

The relationship between water activity and the surrounding atmosphere, when at equilibrium, is:

$$a_w = p_v/p_w = RH(\%)/100 \quad \text{Equation 2.3}$$

where p_v is the water pressure exerted by the food material, p_w is the vapour pressure of pure water at the equilibrium temperature, and RH is the relative humidity of the system (Iglesias & Chirife, 1982).

There are many different methods for measuring water activity including the use of a vapour pressure manometer, where the vapour pressure of the sample is compared to that of pure water. Another common method is hygrometry, in which a standard curve is created from measuring the weight gain from the absorption of moisture onto a material such as cellulose or hair. A third method, the dew point measurement, uses an air stream in equilibrium with a sample directed at a mirror and the dew point is measured. This is then related to the equilibrium relative humidity through a nomograph (Troller, 1983).

2.3.3 Sorption Isotherms

Water vapour sorption isotherms are used to describe the behaviour of a product with respect to the humid air which surrounds it (Mathlouthi & Roge, 2003). The isotherms predict the relationship between the equilibrium moisture content and the water activity at a constant temperature (Bell & Labuza, 2000). They are therefore a useful mechanism for showing what desirable or undesirable levels of water activity are achieved at different water contents (Troller & Christian, 1978), for example, the saturation equilibrium, the water activity where caking begins to occur, is shown as a vertical line on the adsorption curve. This means the isotherms are useful in predicting caking.

There have been many different equations suggested to fit sorption isotherms. The GAB (Guggenheim – Anderson – De Boer) equation, Equation 2.4, was agreed to be

the best equation at the 1983 International Symposium on the Properties of Water (ISOPOW) because it accurately fits numerous food isotherms (Bell & Labuza, 2000). It is a true kinetic model formulated from first principles to describe the sorption of a gas to a free solid surface, then Langmuir type adsorption onto specific sites on the surface, with condensation on the subsequent layers (Bronlund, 1997). Another commonly used equation is the BET (Brunauer, Emmett and Teller) equation, Equation 2.5. This equation is based on the assumption that only the first adsorbed layer is attracted strongly by the surface, then the second layer is adsorbed onto this first adsorbed layer, then the third layer onto this second layer and so forth (Feldman & Sereda, 1965).

The GAB equation is

$$m = \frac{C_1 k m_0 a_w}{(1 - k a_w)(1 - k a_w + C_1 k a_w)} \quad \text{Equation 2.4}$$

where C_1 and k are constants and m_0 is the monolayer moisture content (Bell & Labuza, 2000).

The BET equation is

$$m = \frac{m_0 C a_w}{(1 - a_w)(1 + a_w(C - 1))} \quad \text{Equation 2.5}$$

where m_0 is the monolayer moisture content and C is a constant related to the excess enthalpy of sorption (Bell & Labuza, 2000).

For prediction purposes the best model to use is the one which describes the data the best. In addition some models are only applicable for a certain part of the isotherm (Iglesias & Chirife, 1982). Therefore, it is worthwhile checking the fit of a number of models.

2.3.3.1 Measurement of Sorption Isotherms

There are numerous different methods that can be used for the measurement of sorption isotherms (Troller & Christian, 1978). Most of these use one of three general approaches:

- measurement of moisture content of samples in desiccators containing saturated salt solutions, with or without vacuum
- measurement of vapour pressure of the air in equilibrium with a food at a given moisture content, with a sensitive manometric system
- inverse gas chromatography column packed with the food powder as the stationary phase (Bronlund, 1997)

These measurements take some time. It is important that equilibrium relative humidity between the product and the surrounding air is reached; rapid a_w methods give only an apparent value of the equilibrium relative humidity, which is the equilibrium relative humidity of the surface of the substance (Mathlouthi & Roge, 2001).

The desiccator method is the most straightforward method. In addition it is probably the most commonly used method (Bell & Labuza, 2000), which means the results obtained are directly comparable to other researchers. For these reasons, this method was used in this work.

2.3.3.2 Hysteresis

Sometimes the shapes of isotherms differ depending on whether they had been drawn from adsorption or desorption data. This difference is termed hysteresis (Bell & Labuza, 2000). Roth (1976) found that icing sugar displays a high level of hysteresis, whereas cane sugar displays none, however, this difference could be due to amorphous sucrose being present on adsorption but not desorption. Troller and Christian (1978) have demonstrated some hysteresis in crystalline sugar. They propose that this is predominantly due to capillary condensation, however, Chinachoti and Steinberg (1986) showed that hysteresis was caused only by amorphous sucrose.

2.3.3.3 Temperature Dependence of Isotherms

Rastikian and Capart (1998), showed that there is very little difference in crystalline sucrose isotherms at 22 °C and 35 °C. This means that small fluctuations in temperature are unlikely to have an effect on the isotherm.

2.3.3.4 Crystalline Sucrose Sorption Isotherm

The moisture sorption isotherm for crystalline sucrose is shown below in Figure 2.6. It can be seen from the figure that the moisture content is very low, until a water activity of approximately 0.85, when it becomes exponential, reaching an asymptote at a water activity of approximately 0.9. It is at this stage that caking becomes a problem. The crystalline isotherm can be predicted by the GAB model fitted to all the literature data, where the constants C_1 , k and m_0 are 0.3065, 0.9192 and 0.4104 g water/100g dry sugar respectively. The differences that are present could be because, apart from the data from Mathlouthi and Roge (2001; 2003), the sugar crystals used to generate the isotherms contained a wide particle size distribution. The crystals used by were all larger than 850 μm .

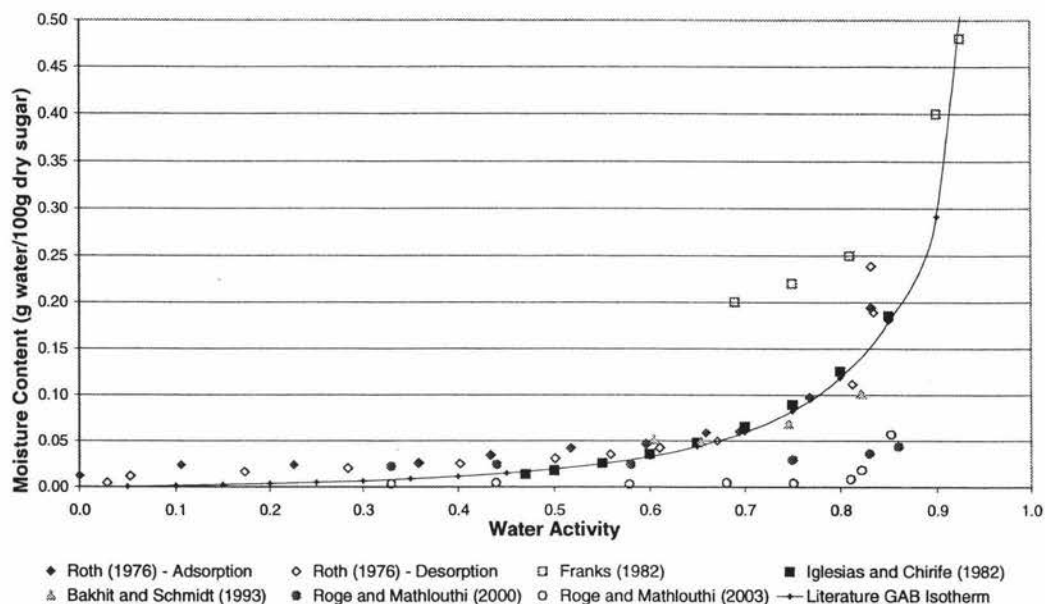


Figure 2.6 Sorption isotherm for crystalline sucrose

2.3.3.5 Amorphous Sucrose Sorption Isotherm

The moisture sorption isotherm for amorphous sucrose is shown below in Figure 2.7. It should be noted that at all water activities the moisture content of amorphous sucrose (as shown on the y-axis) is much greater than that of crystalline sucrose in Figure 2.6.

The amorphous isotherm can be predicted by the GAB model fitted to all the literature data, where the constants C_1 , k and m_0 are 11.68, 0.9334 and 1.881 g water/100g dry sugar respectively. This figure shows that amorphous sucrose absorbs much more water than crystalline at all water activities. Also, the exponential section, is much more gradual for amorphous sugar.

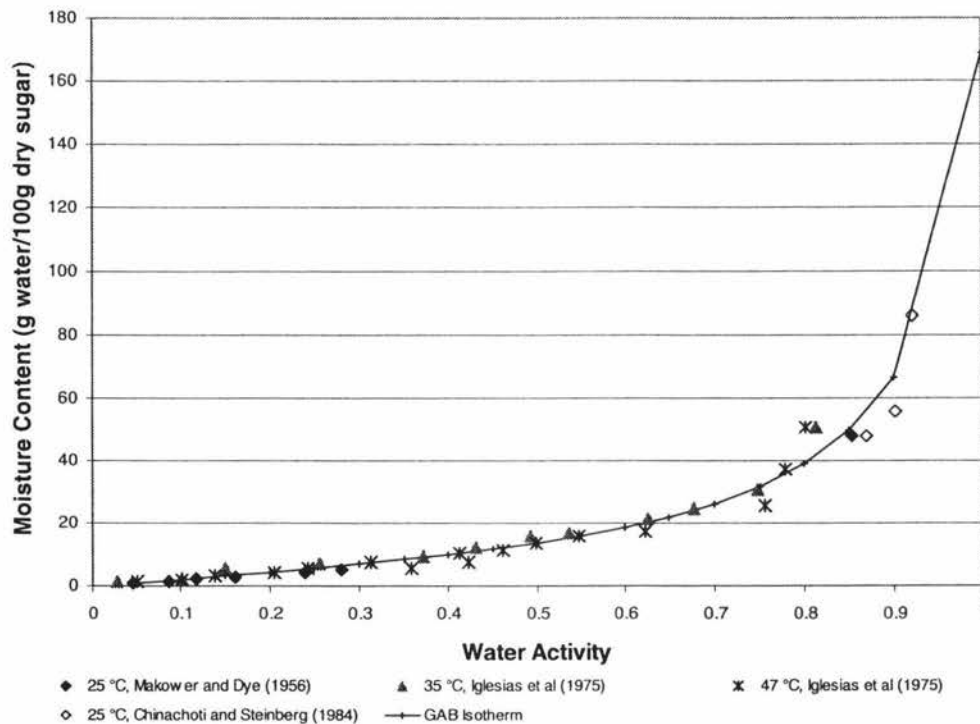


Figure 2.7 Sorption isotherm for amorphous sucrose

2.3.4 Capillary Condensation

Pores, or capillaries, are formed by contact points between particles in a packed bed. Surface tension effects cause the saturated vapour pressure of the air above the liquid surface inside these capillaries to be less than that of the bulk air. Capillary condensation will occur if the pressure is low enough to be greater than the saturated partial pressure above the capillary surface (Billings, 2002). Capillary condensation is one reason for the exponential increase in moisture content at high water activities.

2.3.4.1 Kelvin Equation

The Kelvin equation (Equation 2.6) can be used to predict the capillary radius, r_k , at which capillary condensation would occur, for any given water activity (Adamson, 1990).

$$a_w = \frac{p_v}{p_w} = e^{\frac{-2\sigma \cos \theta V_0}{r_k R T}} \quad \text{Equation 2.6}$$

Where P_v is the vapour pressure of the system, P_w is the vapour pressure of pure water, R is the gas constant, T is the absolute temperature, σ is the surface tension, V_0 is the liquid molar volume and θ is the wetting angle (Adamson, 1990). $\cos \theta$ equals one for a liquid which perfectly wets the surface (Billings, 2002). Any capillaries smaller than the Kelvin radius will be full of solution. From the Kelvin equation, it can be seen that as the capillary radius increases, the minimum water activity required for condensation to occur also increases. The Kelvin radius is useful because it can be used to show the change in mechanism for adsorption of water and hence determine the water activity at which caking begins.

2.3.5 Size Relationships

There are several possible relationships between moisture content and crystal size. For example, Bressan and Mathlouthi (1994), found that crystalline sugar with an average particle size of 150 μm adsorbs more water than a sample of 360 μm . Similarly, Mathlouthi and Roge (2001) reported that levels of absorbed water were much greater for particles less than 250 μm , than for larger sized crystals, as illustrated in Figure 2.8. It should be noted that the scale of the y-axis is g/kg rather than g/100g, as in Figures 2.6 and 2.7. This isotherm shows an increase in moisture content for the whole range of water activities, which is an effect similar to that seen when amorphous sucrose is present, as shown in Figure 2.6, although it would not be expected that any amorphous sucrose was present at the temperature at which the experiment was carried out (20°C). Also, the increase in moisture uptake does not necessarily explain the caking phenomenon because the asymptotic behaviour that is associated with the onset of caking occurs no earlier.

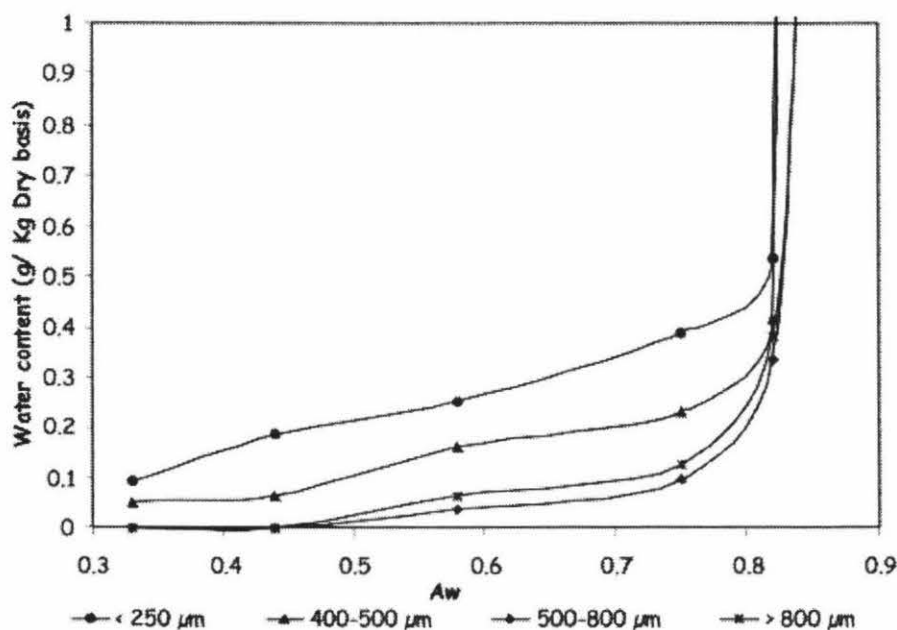


Figure 2.8 Sorption isotherm for different sized crystals (Mathlouthi & Roge, 2003)

If the increase in water activity is due purely to the size of crystals and not the amorphous content of the sample there are numerous possible mechanisms that could be occurring. It could be because small particles dissolve more readily due to their larger surface area, although this would only be expected to be a problem in samples which contain a large number of very small particles. Alternatively, the smaller particles, caused by attrition and crystal breakage are likely to have lost their regular crystalline shape. Irregularities in crystal structure could also increase surface area and cause the crystals to dissolve sooner than the surface of larger crystals.

It is also possible that the onset of caking, where the isotherm becomes exponential, occurs at a lower water activity when small particles are present. If this does occur it is likely to be because smaller particles mean more contact points. As shown in the previous section these will be full of water at a lower water activity, which may mean more liquid bridges form sooner, resulting in an increase in caking.

The amount of bound water is independent of crystal size; however, the amount of free water increases as size decreases (Mathlouthi & Roge, 2001). However, this is

unlikely to be relevant to this study because free water is not associated with caking, whereas bound water is (Bagster, 1970; Ludlow & Aukland, 1990).

No other researchers have published in this area of the relationship between particle size and sorption isotherms for sucrose.

2.4 Caking

Caking is the formation of solid lumps from formerly free-flowing powder. There are a number of factors which may affect the onset of caking, and the degree to which caking is occurring. These can be split into internal factors, ie, the properties of the sugar, and external factors, ie, environmental conditions which sugar is subjected to. Internal factors include shape, particle size, charge, hygroscopic behaviour, moisture content, bulk density and composition (Aguilera *et al.*, 1995). External factors include temperature, relative humidity of the environment, pressure under which the product is being stored, temperature and humidity variations during storage, storage time, applied mechanical stress and the presence of moisture (Aguilera *et al.*, 1995; Mullin, 2001). These factors rarely act in isolation.

Two of the main considerations in previous caking research have been bulk solid consolidation and the formation of solid inter-particle bridges resulting from oscillating moisture migration (Leaper *et al.*, 2002). Under normal atmospheric conditions, whereby the temperature fluctuates dramatically during the course of 24 hours, the effects of bulk solid consolidation - the compression and settling of powder, can be ignored. This is because this effect will be minimal compared to the temperature gradients and the resulting oscillating moisture migration over the studied period.

This study will focus on the relationship between particle size and the relative humidity at which the powder is stored. This means the effect that fine crystals have on the level of caking compared to larger crystals can then be determined.

2.4.1 Humidity Caking

The main cause of caking is temperature gradients, which can exist in the bulk material. These temperature gradients cause fluctuations in interstitial air relative humidity since warm air holds more moisture than cooler air. This results in moisture concentration gradients as moisture migrates to restore equilibrium (Leaper *et al.*, 2002). This means the moisture in a sample is not constant, and will be in greater concentrations in some areas than others. In areas of high relative humidity moisture is adsorbed and condenses onto particle surfaces (Rondeau *et al.*, 2003). This causes the crystal surface to dissolve, which creates a syrupy layer on the surface (Bronlund, 1997). Surface tension effects then cause capillary condensation to occur (Roth, 1976) in the pores of the material. This results in a liquid bridge, consisting of a saturated solution, to be formed between the particles at points of contact (Rondeau *et al.*, 2003; Tselishchev & Val'tsifer, 2003). The adhesive forces of the liquid bridges cause particles to come closer resulting in lumping (Roth, 1976).

When these liquid bridges are exposed to air of a lower relative humidity the solvent evaporates, leaving a supersaturated solution. This solution crystallises forming a solid crystalline bridge between adjacent particles (Roth, 1976; Mullin, 2001). The extent of caking is dependent on how much moisture is adsorbed and desorbed (Bronlund, 1997). This caking process is illustrated in Figure 2.9.

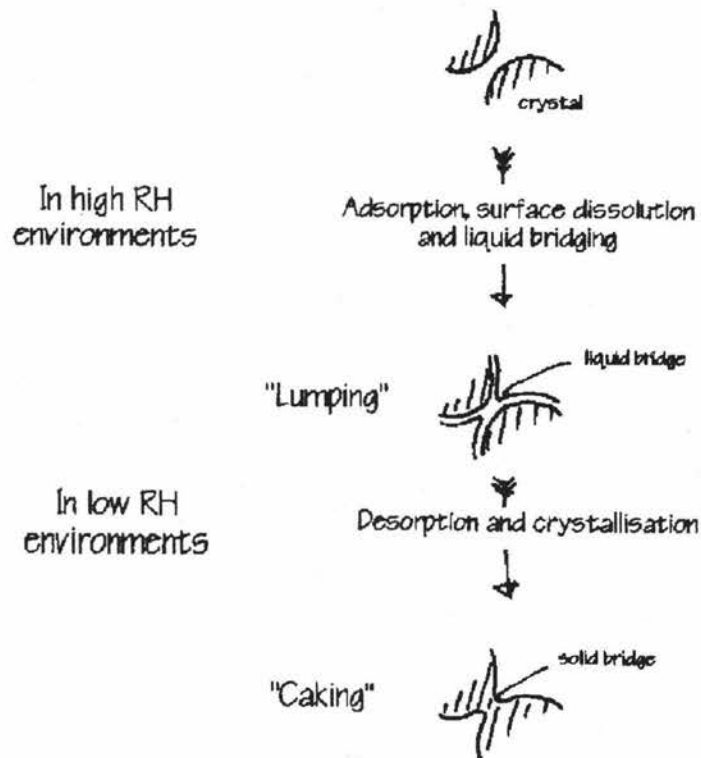


Figure 2.9 Humidity caking mechanism (Bronlund, 1997)

2.4.1.1 Temperature Gradients

Temperature gradients can lead to caking of sucrose powders. A temperature gradient will be set up if either one of the following situations occurs:

- A bin of one temperature is loaded onto a bin of a different temperature (Bagster, 1970).
- The outside of the container is warmer than the sucrose inside, or the outside of the container is cooler than the sucrose inside

These situations often occur during the transportation and storage of sucrose after production.

A temperature gradient causes a change in the relative humidity of the air within the container, since warm air holds more moisture than cold air. This air will no longer be at equilibrium, which results in a concentration gradient. Moisture will then be

absorbed by the solid to reach equilibrium. This causes more moisture to migrate, through diffusion, from the centre or extremities to replace that which has been absorbed. This results in another shift in equilibrium (Leaper *et al.*, 2002).

2.4.2 Caking in Amorphous Sugar

If there is a significant layer of amorphous sugar on the surface of the crystal, amorphous caking is thought to be possible (Billings, 2002). Exceeding the glass transition temperature results in a significant decrease in the viscosity of the amorphous sugar. This decreased viscosity allows the material to flow and form liquid bridges between adjacent particles (cohesion) and between the powder particles and a surface (adhesion). This leads to the formation of a rubber or liquid bridge between particles (Bronlund, 1997). Sugar in this state is described as 'sticky' rather than 'lumped' because of the higher viscosity of the amorphous solution compared to that of the saturated solution. This process is illustrated in Figure 2.10.

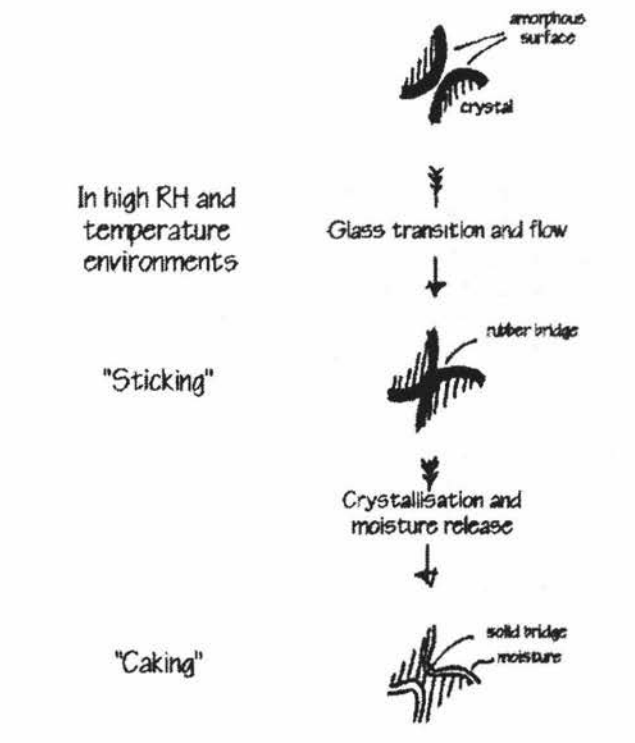


Figure 2.10 Amorphous caking mechanism (Bronlund, 1997)

If the amorphous sugar remains above its glass transition temperature for a sufficient amount of time crystallisation will occur, forming solid inter-particle bridges. This in turn causes the powder to cake.

Billings (2002) found that sugar at NZ Sugar did not contain any amorphous content, therefore, this mechanism is unlikely to be responsible for any caking problems occurring there.

2.4.3 Effect of Fines on Caking

The size of particles is thought to affect caking in a number of ways. The presence of fines in a sample results in an increased specific surface area and particle size distribution (Bagster, 1970). As a result of increased surface area there are more points of contact. A larger particle size distribution is also likely to result in an increase in the number of contact points as smaller crystals can fit into the pores between larger crystals. This can result in an increased tendency for capillary condensation to occur (Billings *et al.*, 2005), and therefore may also increase caking. The size and shape of particles also affect the magnitude of the forces involved in capillary condensation (Tselishchev & Val'tsifer, 2003).

Roge and Mathlouthi (2000; 2003) found that, in a sample containing 5% fines, the flow of the powder was not altered significantly; however, with 10 % fines the sample behaved in the same way as a sample composed solely of fine particles. This can be seen in Figure 2.11, where the friability angle was measured at different relative humidities for samples of standard sugar, standard sugar mixed with 10% fines, and a sample containing only fine crystals. However, contrary to these findings Johanson and Paul (1996) showed that the presence of superfines, crystals the size of powdered sugar, only causes caking when particles have low solubility, and may actually decrease caking strength. If the crystals are highly soluble, such as sucrose, the larger particles start dissolving too quickly for caking to occur. They demonstrated this by calculating the rathole index. This is done by suspending a cylindrical caked sample

on a ledge, then applying a force that shears the cake. The rathole, the empty vertical pipe made from the caked solids, that will cause the sample to collapse as they are removed from the pipe is measured as the caking strength.

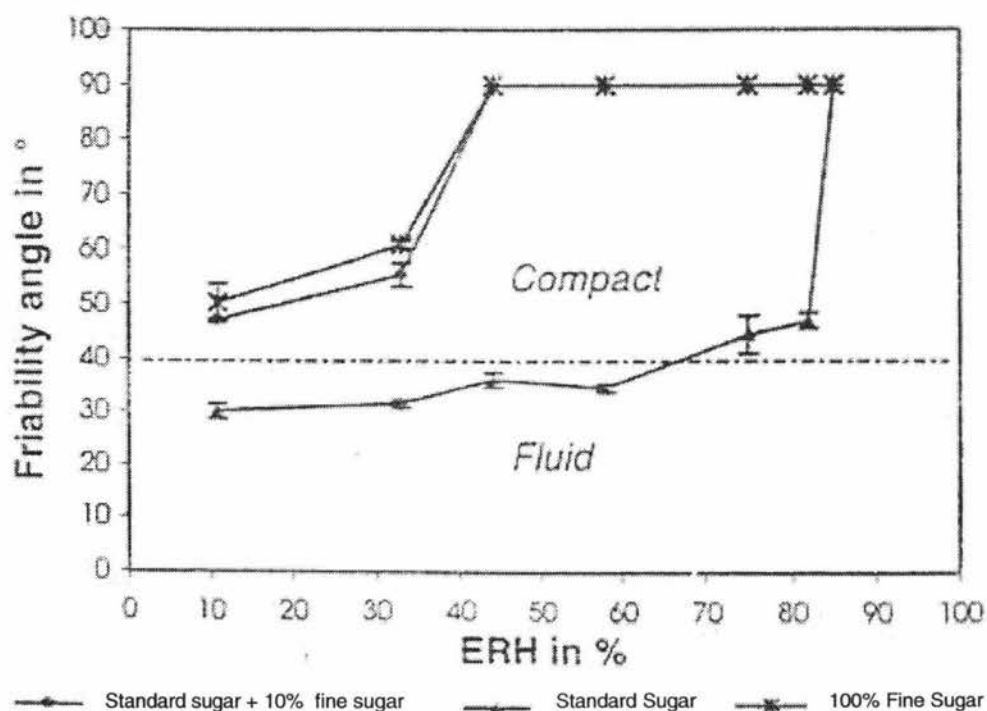


Figure 2.11 Friability angle for samples containing different proportions of fine crystals (Roge & Mathlouthi, 2000)

The altered flow could be caused by a number of factors. For instance, the surface properties of the fines influence the solubility, wettability and sorption isotherms (Provent *et al.*, 1993; Mathlouthi & Roge, 2003). Fines are thought to be far less stable towards increasing relative humidity; Roge and Mathlouthi (2000) found that the onset for caking of fine sugar is 33% relative humidity compared to 80% for larger particles. There are a four mechanisms identified that could be responsible for this, discussed in Section 2.3.5. These were firstly, that the relationship was due purely to an increase in amorphous sucrose on the crystals. This means the amount of amorphous sucrose will need to be measured for all samples used in this work. Secondly, the increase in surface area compared to larger crystals could cause fine

crystals to dissolve more readily. If this is occurring it would be expected that the isotherm will absorb more moisture at every water activity. Thirdly, damage to the crystals, and the loss of smooth surfaces will also increase the surface area, therefore, this study will compare the isotherm and amount of caking for damaged crystals compared to small, undamaged crystals. Lastly, smaller particles mean more points of contact between crystals. This means more capillary condensation could occur at a lower water activity, and the amount of water in capillaries needed for caking would be reached sooner. If this is occurring, more water will be absorbed at lower water activities and the onset of caking will occur at a lower water activity. Also, the critical Kelvin radius will decrease.

2.4.4 Quantification

The extent of caking can be measured in a number of ways. These methods are either associated with the breaking strength of the caked material or the loss of flow. This section will discuss these measurement methods.

One of the most common methods used to measure flowability is a Jenike shear cell or annular cell. The Jenike shear cell measures the yield stress of preconsolidated samples under various normal loads, allowing flow functions to be established and powders to be classified according to their flowability (Mathlouthi & Roge, 2003). In an annular cell the torque is measured as one side of the cell is rotated against the other under normal stress (Sprague & Blumenthal, 1997). Both methods are well documented, however analysis is time consuming. With caking in sucrose also involving a time element with moisture movement through the sample, this method is not seen as being applicable.

Another common measurement is the friability, which involves measuring the minimum angle that a container must be tilted for the sample to flow (Roge & Mathlouthi, 2000). The advantage of this method is that it is simple and fast. However, the disadvantages of this method are that it is not good for samples that are past the 'lumping' phase, and the surface equilibrates first.

The breaking strength of caked particles can be measured with a penetrometer. This instrument consists of pins mounted in a probe that is connected to a counter weight system. Weights are added to the top of the probe until breakthrough is reached (Bronlund, 1997; Billings, 2002). The weight required to break through the caked particles is a measure of the caking strength. This method gives a quantitative result that can be related to caking.

The angle of repose is a measurement of the angle formed between the side of a heap of powder and a horizontal plane. This angle is less than 40° for a free-flowing powder (Aguilera *et al.*, 1995). This method does not require specialised equipment, however, it is not highly sensitive.

Another test related to breaking strength is the blow test. This test involves blowing air through a tube of a fixed diameter onto a flat powder bed. The blow tester is fixed at a set distance above the bed, then the flowrate of the air is increased steadily until a channel forms in the surface of the bed (Brooks, 2000; Paterson *et al.*, 2001; Billings, 2002; Foster *et al.*, 2005). It gives a quantitative result that can be related to the strength of the bridges that form between particles in a packed bed sample. The advantages of this test over other commonly used tests, such as shear cells, is that it can be done in place, it is simple and further tests can then be carried out on the same sample.

In addition to the tests mentioned above, analysis of the microstructure by image analysis may also become an important tool in the characterisation of caking in the future (Aguilera *et al.*, 1995).

From all the methods reviewed, the most appropriate tests to determine the caking strength of sucrose in this study will be the friability and the blowtester. The first of these, friability, has been used in a similar study by Roge and Mathlouthi (2000), so the results obtained can be compared. The latter, the blowtester has been proven to give a quantitative result relating to caking.

2.4.5 Caking at New Zealand Sugar

The penetrometric and blow tester methods were used by Billings (2002) to find the caking point; this corresponds to where the sorption isotherms start to become asymptotic. This was done by allowing samples to equilibrate at different relative humidities. The liquid bridge strength was then measured. This was repeated in order to measure the solid bridge, with the exception that the equilibrated samples were left exposed to ambient conditions for one, two or three days prior to testing. Results for samples equilibrated for two days were similar to those equilibrated for three days, so two days equilibration time was used by Billings. Both the liquid and solid bridge strength measurements were plotted against relative humidity and the intersection of these lines found. This represents where the isotherm becomes asymptotic. For samples taken from New Zealand Sugar this was found to occur at a water activity of 0.77.

Billings also found there was not any amorphous sucrose present, therefore, the mechanism by which caking was occurring was humidity caking rather than amorphous caking.

2.4.6 Prevention of Caking

Several methods have been suggested to minimise the risk of caking. The most common practice in industry is to condition the sugar by blowing dehumidified air through it for long periods of time. Plant trials at New Zealand Sugar have found 18 hours gives reasonable conditioning; but less than eight hours greatly increases the risk of caking. This conditioning removes the bound water associated with caking (Rastikian & Capart, 2000).

In addition to conditioning sugar, several steps can be taken after packing to minimise caking. These include minimising temperature gradients during storage by insulating the wall and allowing sufficient airflow. Also the relative humidity should not exceed

75% (Rastikian & Capart, 2000) and points of contact between crystals should be minimised by producing granular crystals of a more uniform size (Mullin, 2001). In addition, anti-caking agents can be used (Pennington & Baker, 1990), but would result in a product that was not pure.

2.5 Attrition and Particle Size Analysis

Attrition is the unwanted breakage of particles, resulting in a decrease in particle size. It occurs when particles hit each other at high velocity, such as in a pneumatic conveyor, or when particles are subject to shear, such as in a screw conveyor (Neil & Bridgwater, 1999). At New Zealand Sugar fine particles are probably produced both in the crystallisation process and through attrition in conveying lines. This section will discuss the affect of fine particles, the mechanisms of attrition and some of the methods available to quantify this.

2.5.1 Affect of Fines on the Properties of the Sugar

Attrition causes a number of properties of the particle to change such as specific surface area, shape, and lattice structure. It is also possible for phase transitions to occur, adsorption ability and solubility to increase, free radicals to form, and the hygroscopicity to increase (Roth, 1976; Bemrose & Bridgwater, 1987; Ghadiri & Zhang, 2002; Mathlouthi & Roge, 2003). These changes can take place because of the extreme temperatures caused by the friction during the crushing of sucrose. Roth (1976), measured these temperatures to be in excess of 2000 °C. This was done by measuring the luminescence using a spectrophotometer. These changes are detrimental to the quality of the crystals and may lead to increased caking.

When attrition occurs, the properties of the bulk powder also change. These changes include bulk density, internal angle of friction, fluidising velocity, and particle size

distribution. In addition, the powder becomes more tightly packed, with more sites for bonding or bridging (Ludlow & Aukland, 1990), this could also lead to an increase in caking.

Problems are caused by the increase in the number of fine particles. For example, it may mean the bulk material no longer meets the specifications required by the consumer. Crystals that are too small will either be recycled back or will become a waste product (Kalman, 1999). Fine particles can be a hazard to health and safety, through inhalation and because of the increased likelihood of dust explosions. In addition, they are a hazard to the environment through an increase in particulate matter expelled from the plant (Ghadiri & Zhang, 2002). Attrition can also cause wear of containment systems that can, in turn, lead to contamination of the product (Bemrose & Bridgwater, 1987).

As stated in previous sections, there is some evidence to suggest that an increase in the number of fine particles leads to an increase in caking of the powder (Roge & Mathlouthi, 2000, 2003).

2.5.2 Mechanisms of Attrition

Attrition can be caused by abrasion or fracture, as illustrated in Figure 2.12. The first of these, abrasion, is due to the removal of surface layers, edges or corners producing a number of smaller particles plus a slight decrease in the size of the parent particle. Fracture, on the other hand, occurs when the parent particle splits by the propagation of radial or median cracks (Ghadiri & Zhang, 2002). This results in at least two particles that are of a comparable size to that of the parent particle (Neil & Bridgwater, 1994). The mechanisms responsible for attrition are dependant on the mechanical properties of the particle, its shape and the mode of loading (Ghadiri & Zhang, 2002).

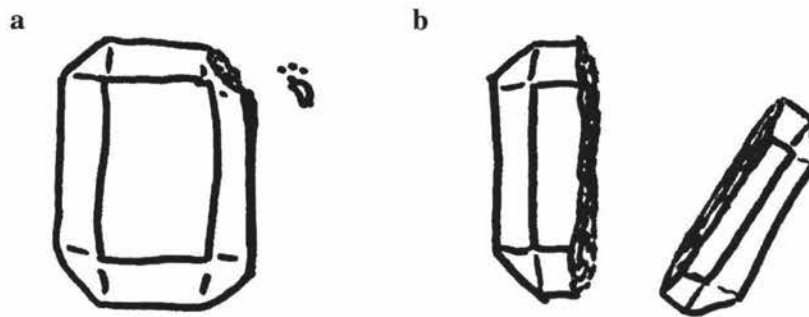
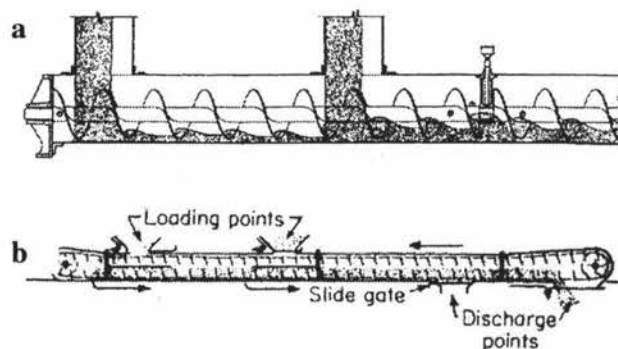


Figure 2.12 a) Abrasion and b) Fracture

One area in which attrition is problematic is during conveying. At New Zealand Sugar both screw conveyors and redler chain conveyors are used to transport sugar through the factory. These are shown schematically below in Figure 2.13. In screw conveyors, attrition is caused mainly by the particles being crushed between the screw blades and casing wall. Redlers, however, use buckets to convey the sugar. Further breakage is caused by interparticle motion, for example one particle rubbing against another (Neil & Bridgwater, 1999). It is proposed that screw conveyors cause significantly more damage to crystals than chain redlers.



**Figure 2.13 a) Screw conveyor b) Redler chain conveyor
(Perry & Green, 1997)**

2.5.3 Measurement/Quantification

Bremrose and Bridgwater (1987) reviewed different techniques for the analysis of attrition. They classified the tests as either single particle tests or multi-particle tests. There are problems associated with both types of tests, irrespective of the particle in question.

Single particle tests usually involve subjecting the particle to either grinding or impact with another particle or a target. These tests allow information to be gathered regarding particle breakage, but it is difficult to relate back to what actually observed in an industrial setting (Bemrose & Bridgwater, 1987).

There is a wide range of multi-particle tests, which rely on many different principles. Most use some mechanically induced motion, either between the particles themselves or between the particles and another larger object. The most common of these tests are fluidised beds, shear cells, rotating drums, grindability tests and the use of vibration (Bemrose & Bridgwater, 1987). They are usually used in conjunction with either sieve analysis or laser diffraction analysis to determine changes in particle size due to attrition. These tests are more closely related to the actual powder use than single particle tests, but are empirical.

The mechanisms of attrition will not be determined in this study, however the differences in particle size caused by attrition will be measured.

2.5.4 Particle Size Analysis

2.5.4.1 Methods

Sieving is suitable for particles in the size range 20 μm to 125 mm (Allen, 1975). A distribution by mass is obtained by shaking powder through a series of woven wire screens with different apertures. The advantages of this method are that it is simple,

cheap and easy (Rhodes, 1998), however the probability that a particle will pass through a sieve is dependent on its dimensions and the angle at which it is presented (Allen, 1975).

Microscopy can be used for particles in the $0.8 - 20 \mu\text{m}$ range, using either an optical or an electronic microscope (Seville *et al.*, 1997). In this method particles are directly observed and measured, therefore a number distribution is obtained. Advantages of this method are that only a small sample is needed, and identification of particles is possible (Seville *et al.*, 1997). However, sample separation and preparation are critical, which means this method is time-consuming.

Laser diffraction is useful over a wide range; from $1 - 1000 \mu\text{m}$ (Kousaka & Okuyama, 1991; Seville *et al.*, 1997). This instrument consists of a laser as a source of coherent light at a fixed wavelength, a suitable detector and some means of passing a sample of particles through the laser beam (Reiser *et al.*, 1995). The diffraction pattern is converted mathematically to give the particle size distribution as a volume fraction (Seville *et al.*, 1997). This method is commonly used in industry. Advantages include the ease of use and repeatability of results. The main disadvantage is the cost of the instrument.

The rate of sedimentation of particles in a liquid can also be used to calculate the particle size distribution for particles in the size range $1 - 1000 \mu\text{m}$ (Seville *et al.*, 1997). The suspension is dilute which means it can be assumed that particles fall at their single particle terminal velocity in the liquid, therefore, Stokes law applies ($Re < 0.3$). The rate of sedimentation of the particles is followed by plotting the suspension density at a certain vertical position against time. This can then be related back to the particle size distribution (Rhodes, 1998).

Electrozone sensing is another commonly used method for small particles,
 $0.3 - 200 \mu\text{m}$

, especially for medical applications (Seville *et al.*, 1997). In this method, particles are dispersed in an electrolyte which is forced to flow through a small orifice, with an immersed electrode on either side. The suspension is sufficiently dilute that only one particle passes through the orifice at a time. As this occurs, the electrical resistance across the orifice changes dependent on the size of the particle. This generates a voltage pulse, the amplitude of which is related to particle volume.

The most useful of the above methods, with respect to this study, will be sieving and laser diffraction. Both these methods are relatively quick and easy. Sugar crystals are a similar length in every dimension, so both sieving and laser diffraction should give accurate representations of the particle size distribution of the sample. Laser diffraction will be the more useful of the two for measuring very fine particles.

2.5.4.2 Sampling

Sampling is the process of selecting a representative part of a population for the purpose of determining parameters of the whole population (*Merriam-Webster's Medical Desk Dictionary*, 2002).

In any analysis, sampling is very important. This is particularly true for particle size analysis where the particle size distribution throughout the sample will not be homogeneous. If a sample is not representative of the bulk powder then findings cannot be generalised to the actual powder. Therefore, the aim when sampling is to obtain a sample that is representative of the bulk powder. To gather this optimum representation Allen (1975) outlines two golden rules of sampling:

- A powder should be sampled when in motion
- The whole stream of powder should be taken for many short increments of time in preference to part of the stream being taken for the whole time.

Any time a powder or particulate matter is handled segregation may take place. The property of the powder that is most involved in segregation is particle size (Allen, 1975). For example, when powder is poured in a heap, the finer particles tend to

collect in the centre of the heap as shown in Figure 2.14. A similar effect occurs in vibrating containers, where a layer of coarser material collects near the surface (Allen, 1975). This means that the surface region has more coarse particles; therefore taking a sample from this area will lead to these coarse particles being over-represented in an analysis.

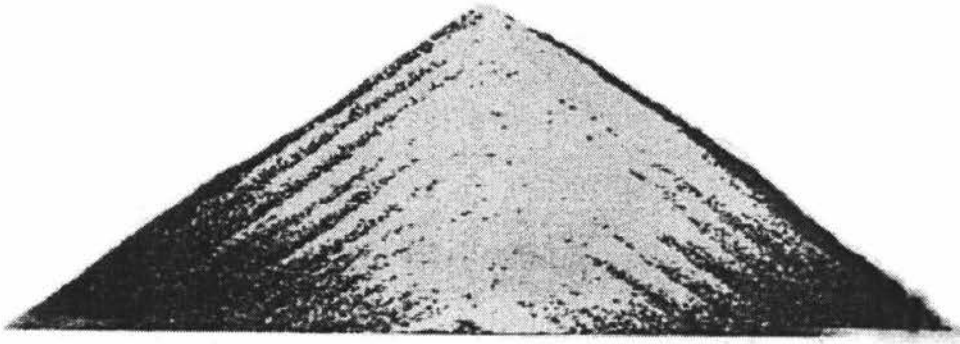


Figure 2.14 Cross section of segregation in a heap (Allen, 1975). The finer particles are shown in grey, and the coarser particles in black

2.5.4.3 Sample Points

The best place to sample from when taking a sample from a conveyor belt or chute is where the powder falls from the end, obeying Allen's first rule. This is because there is less segregation of the powder as it is moving; while the powder is on the conveyor fines are more likely to be concentrated in the centre with coarser particles on the outside.

It is also important the sample is carefully taken. Figure 2.15a shows a bad sampling technique. By passing the sampling container into the stream then back out again the sample is likely to contain a higher proportion of larger particles than the bulk powder. This is not a problem in Figure 2.15b, where the sampler is moved through the powder bed and out the other end. This technique cannot always be used, instead, the sampler can be introduced into the bed upside down, then rotated before passing from the back of the sample to the front. Furthermore the method shown in Figure

2.15a can be used if, and only if, the length of time the scoop is stationary in the stream is significantly longer than the time taken to insert and withdraw the scoop.

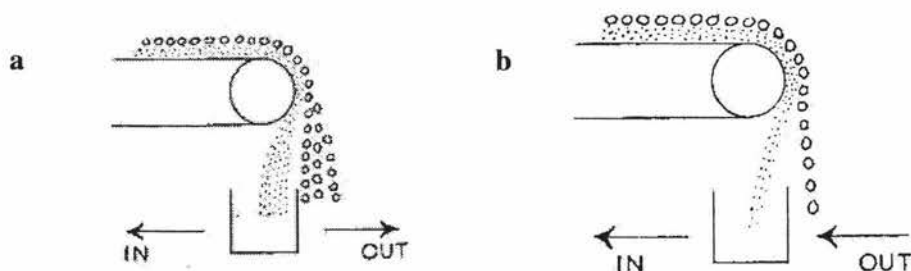


Figure 2.15 a) Bad sampling technique b) Good sampling technique (Allen, 1975)

If it is not possible to sample from the end of the conveyor the whole powder sample on a short length of conveyor should be collected. The easiest method of achieving this is to stop the conveyor and insert a frame consisting of two parallel plates the same size as the belt. All the powder between the frame should then be swept out to give the sample.

Another place it is possible to sample from are from bucket conveyors. In this case, the whole contents of the bucket should be taken. This can then be further divided into smaller samples (Allen, 1975). Segregation would have occurred in the bucket, which means any smaller samples taken will not be representative of the bulk powder.

Sampling from heaps never gives a truly representative sample. As illustrated in Figure 2.14 above, segregation occurs and a representative sample cannot be taken. For the powder to be in a heaped formation it would at some stage have needed to be poured into this heap. It is as the material is poured that a sample should be taken.

2.5.4.4 Subsampling

Quite often the gross sample is too large to be handled easily and smaller sized samples, or 'subsamples' are needed. There are difficulties involved in obtaining these subsamples, and the 'golden rules' outlined above still apply.

The five most commonly used methods are coning and quartering, table sampling, chute splitting, spinning riffling and scoop sampling.

The first of these methods, coning and quartering, involves pouring a sample into a conical heap, then evenly dividing it into four smaller samples. This is illustrated in Figure 2.16. This method assumes the heap is symmetrical about a vertical axis and the cutting line coincides with this axis. In practice the former of these requirements is very unlikely to occur and the latter is difficult to achieve without precision cutting equipment.

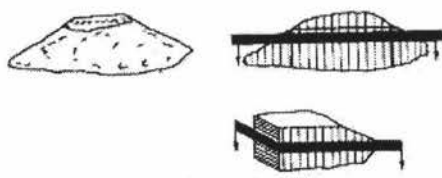


Figure 2.16 Coning and quartering (Allen, 1975)

The scoop sampling method involves plunging a scoop into a sample and withdrawing a sample of the required size. Although this method is very simple, it is particularly prone to error since the whole of the sample does not pass through the scoop and because the sample is taken from the surface which is often not representative of the bulk powder.

In a sampling table, such as that shown in Figure 2.17, the material is fed to the top of an inclined plane which contains prisms to separate the stream and a series of holes, which each remove a section of powder. The powder that reaches the bottom of the table is the sample. The problem with this device is that it depends on the initial feed being uniformly distributed, which is often not the case. Each time part of the sample is removed, the error becomes greater, thus accuracy is low.

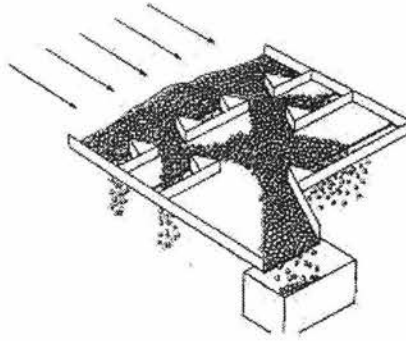


Figure 2.17 Table sampler (Allen, 1975)

A chute sampler is made up of a V-shaped trough at the bottom of which is a series of chutes which feed alternately into two separate trays. This is illustrated in Figure 2.18. The laboratory sample is poured into the top of the trough, collected and repeatedly halved until the desired sample size is obtained. This method can be used to divide samples satisfactory, but relies on correct operation (Allen, 1975).

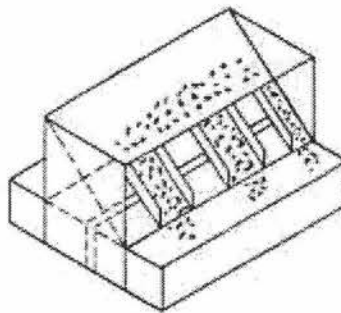


Figure 2.18 Chute riffler sampler (Allen, 1975)

The spinning riffler consists of a series of segmented boxes on a spinning table as illustrated in Figure 2.19. The table is set in motion and the powder fed from the hopper to the boxes. The flow of the powder and the rotational speed of the table should be adjusted so that the table rotates at least 30 times while the powder is flowing. The powder from alternate boxes (for example 2, 4, 6 . . .) is then put together and the remaining powder discarded. This is repeated until the desired sized sample is obtained. Allen (1975) found that this was the most accurate method of sub-sampling.

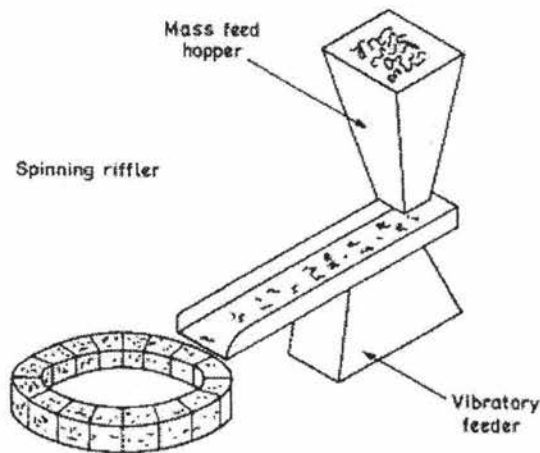


Figure 2.19 Spinning riffler sampler (Allen, 1975)

Allen (1975) evaluated all five methods of subsampling using a sample containing a sugar-sand mixture. The standard deviations and estimated error are shown below in Table 2.1. It can be seen that both the cone quartering and scoop sampling gave unacceptable levels of error. Conversely, the best sample by far was obtained using the spinning riffler. He also found that this method has the least operator bias.

Method	Standard deviation of samples (%)	Estimated maximum sample error (%)
Cone and quartering	6.81	22.7
Scoop Sampling	5.14	17.1
Table Sampling	2.09	7.0
Chute Riffing	1.01	3.4
Spinning Riffing	0.125	0.42
Random Variation	0.076	0.25

Table 2.1 Reliability of selected sampling methods (60:40, coarse:fine, sand mixture; P = 0.60)

In this study a chute riffler will be used. In order to minimise errors the sample will be well shaken prior to being sub-sampled.

2.6 Conclusion

The relationship between fine particles and caking in sucrose is not a new idea; however, most of the current literature in this area has been published by a very small number of researchers, hence should be validated independently. Also there is no definition of the size of 'fine' particles.

The mechanisms involved for caking of both crystalline and amorphous sugar have been well documented; however the effect of particle size on these mechanisms has not been well covered. In fact, given the existing data, it is not clear whether the changes are due to particle size or an increase in the level of amorphous sucrose in smaller particles as a result of attrition. Also contrary findings have been published in this area. In addition, there is very little literature available regarding attrition in screw conveying, such as that used at New Zealand Sugar.

It can be seen that there is a need for further research to be carried out in this area, especially with regards to the effect of very fine crystals.

From the review of current literature, the first logical step in this study would be to determine if the presence of fine crystals does have an effect on caking, and to quantify this. This can be done firstly, by creating a series of sorption isotherms by equilibrating samples over saturated salt solutions, then carrying out caking tests using the friability and blowtest methods. The amorphous content of the crystals used for these isotherms needed to be quantified in order to determine if this was causing changes in the sorption isotherms. The best method for doing this is isothermal microcalorimetry.

The particle size distribution of samples taken at different stages in the process can be measured using sieving and laser diffraction. From the results of these analyses, the amount of fines for each stage during the process is known and the effects of conveying can be determined.

Chapter 3

- Isotherms -

3.1 Introduction

It was identified in Chapter 2 that sorption isotherms contain valuable information about the amount of water contained in a sample at different relative humidities. This means they can be used to give an indication of the onset of caking.

Much research has been published describing the isotherms for crystalline and amorphous sugar (Makower & Dye, 1956; Roth, 1976; Audu *et al.*, 1978; Iglesias *et al.*, 1980; P. Chinachoti & Steinberg, 1984; Roos & Karel, 1991b). However, Mathlouthi and Roge (2001, 2003) are the only papers studying the effect of particle size on the isotherms.

In previous cited work (Johanson & Paul, 1996; Roge & Mathlouthi, 2000, 2003) there have not been consistent definitions of fine crystals. At New Zealand Sugar any crystal less than 300 μm is considered to be “fine”.

It is possible that the presence of fine crystals could affect the isotherm in several ways. The most likely of these is that the onset of caking, when the isotherm becomes exponential, will occur at a lower water activity, as shown in Figure 3.1b. Another possibility is that the fine crystals could absorb more moisture at every water activity, as shown in Figure 3.1a, below. This could be because the amount of adsorption is proportional to the surface area and fines would provide more surface area. However, at very low water activities this effect can also be caused by the presence of amorphous sugar.

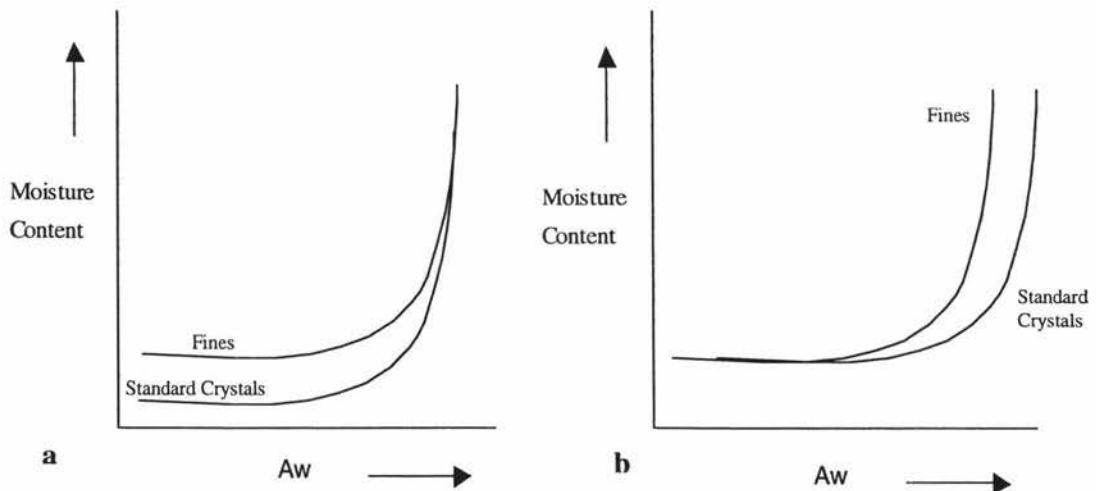


Figure 3.1 Possible effects of fine crystals on the isotherm
a) Fine crystals absorb more moisture at every water activity
b) Isotherm with fines becomes exponential at lower water activity

It is hypothesised that increasing the number of fine crystals in a sample will cause the exponential increase in moisture content to occur at a lower water activity, as shown in Figure 3.1b. It is not expected that the fine crystals will absorb more moisture at every water activity, unless there is amorphous sucrose present. This is because although the fine crystals have a greater surface area, sucrose crystals are very soluble so the bulk crystals will quickly dissolve (Johanson & Paul, 1996).

3.2 Experimental

In this section the isotherms of fines of the following sizes were studied:

- 0-75 μm
- 75-150 μm
- 150-212 μm
- 212-315 μm

This allowed the affect of the size of the fines to be studied.

The effect of the percentage of fines in a sample was also studied. Literature suggests that there is little difference between a sample containing 10% fines and a sample composed completely of fine crystals (Roge & Mathlouthi, 2000). At New Zealand Sugar the level of fines in standard sugar was found to be approximately 0.1%. Given this evidence it was decided that samples containing the following percentages of fines should be tested:

- 100%
- 10%
- 1%
- 0.1%

A series of 16 samples were created, using all possible combinations of the proportion of fines and particle size of the fine crystals. Three repeats were analysed for each of these mixtures, at each water activity tested to generate the isotherm.

Isotherms were also created for samples of sugar taken from around the factory. These samples were from the bottom of the driers, over the electromagnet, as the sugar left the silo after conditioning, standard sugar after it was graded, and standard sugar from the packing line. Sample points are shown in Appendix 1. The purpose of conditioning, or blowing dry air through the silo, is to dry any bound water from the surface of the crystal, as this has been shown to contribute to caking (Rastikian & Capart, 1998). After the sugar is graded it contains a much narrower size range and as the fine crystals are removed. This means it is possible that there are differences in the isotherms depending on where in the process samples are taken.

7g sub-samples of the prepared samples were obtained using a riffle sampler. These sugar samples were then poured into moisture dishes. These were weighed using a Mettler Toledo AB104 (Switzerland), 4 d.p. balance. The differences in the mass of the sample before and after being equilibrated over saturated salt solutions are very small so it was important that all measurements were as accurate as possible. To ensure this was the case, cotton gloves were worn to prevent any moisture being transferred from hands onto the dishes. In addition, the balance was recalibrated each time it was used.

The moisture dishes with the samples of sugar were placed over saturated salt solutions in plastic containers and the containers sealed. Different salts were used to achieve different relative humidities (Greenspan, 1977; Bell & Labuza, 2000). Those that were used in this study are shown below in Table 3.1.

Salt	Formula	RH (%)
Potassium Hydroxide	K(OH)	9
Magnesium Chloride	MgCl	33
Potassium Carbonate	K ₂ CO ₃	43
Sodium Bromide	NaBr	59
Potassium Iodide	KI	69
Sodium Chloride	NaCl	75
Ammonium Sulphate	(NH ₃) ₂ SO ₄	81
Potassium Chloride	KCl	87
Potassium Nitrate	KNO ₃	94

Table 3.1 Relative humidites of different salt solutions at 20 °C (Bell & Labuza, 2000)

It is important that samples are left long enough to equilibrate properly. Crystalline samples need at least 21 days to equilibrate (Bell & Labuza, 2000). In order to determine the required equilibrium time for crystalline sucrose, a series of 12 samples were held at 25 °C over saturated salt solutions for two weeks, then reweighed. The samples were reweighed again after three and four weeks. The initial moisture content was determined by oven drying at 105 °C for three hours in a convection oven.

The results for each salt were averaged then the moisture content and amount of water absorbed by each sample was calculated. When equilibrium is reached the sample mass is constant. The greatest change in moisture content of the samples occurred during the first two weeks, as shown in Table 2 and Figure 3.2. The difference in moisture content between weeks two and three is small, and decreases further between weeks three and four, with the exception of the samples at 87% and 94% relative humidity. The latter sample was liquefied, so was no longer crystalline. The increase in moisture content, then decrease, shown in the samples at 87% relative

humidity, is likely to be caused by a splash of salt on moisture dishes, which is then evaporating. These salts, with either high or low relative humidities take the longest to reach equilibrium. These results show that equilibrium was almost reached after three weeks. Future isotherm samples were left to equilibrate for four weeks to ensure that equilibrium was reached.

Relative Humidity (%)	Moisture Content, (g)				Change in Moisture Content, (g)		
Weeks	Initial	2	3	4	2	3	4
33	0.004106	0.068664	0.055277	0.05823	0.06	-0.01	0.00
59	0.004245	0.067993	0.051046	0.064285	0.06	-0.02	0.01
69	0.003584	0.073834	0.087414	0.085064	0.07	0.01	0.00
75	0.003647	0.087862	0.069516	0.082046	0.08	-0.02	0.01
81	0.004061	0.154257	0.129394	0.126793	0.15	-0.02	0.00
87	0.00423	1.20624	0.967628	0.744046	1.20	-0.24	-0.22
94	0.004022	8.134258	12.03205	16.01793	8.13	3.90	3.99

Table 3.2 Change in moisture content in desiccators over time

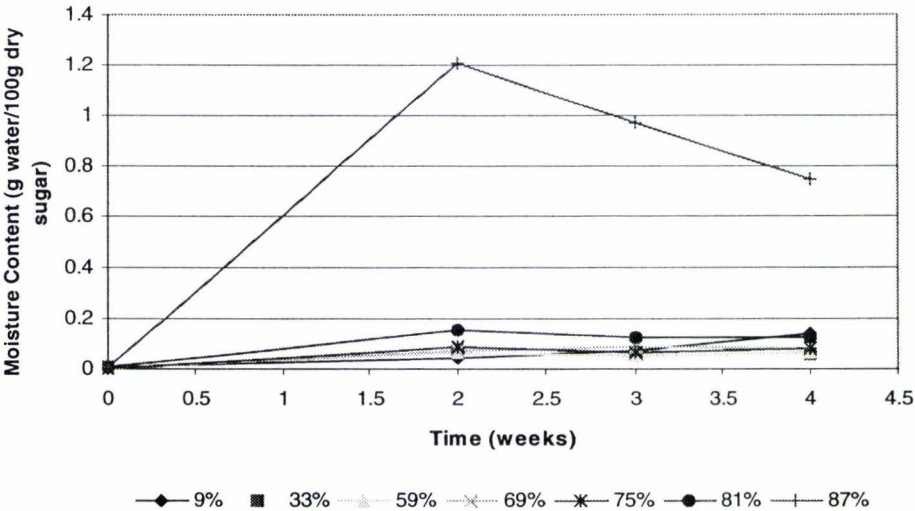


Figure 3.2 Time taken for samples to reach equilibrium

After four weeks, samples were reweighed and the difference in the amount of moisture was calculated. As soon as the samples are exposed to the atmosphere they begin to absorb or desorb moisture, so it is important their lids were put on as quickly

as possible, to seal the sample from the ambient air. They were then weighed in a random order. Ambient temperature and relative humidity were also measured, using a 0-50 °C alcohol thermometer and 0-100 % relative humidity Honeywell probes (Model IH-3610-1). These probes were calibrated over saturated salt solutions of potassium hydroxide, sodium bromide, sodium chloride and potassium nitrate.

The sorption isotherms that developed were working isotherms. This means desorption occurred in samples in which the desiccators equilibrium water activity was below the starting water activity of the sugar, and likewise adsorption occurred in the samples in which the equilibrium water activity was above. To get a sorption isotherm the resultant change in mass was adjusted for the initial moisture content of the sample. This was measured by weighing the change in mass after drying for three hours at 105 °C in a convection oven, then cooling over P_2O_5 . Sorption isotherms could then be drawn.

3.3 Results and Discussion

Isotherms were measured for samples taken from different parts of the plant. This is shown in Figure 3.3. No differences were found in the isotherms for these process samples.

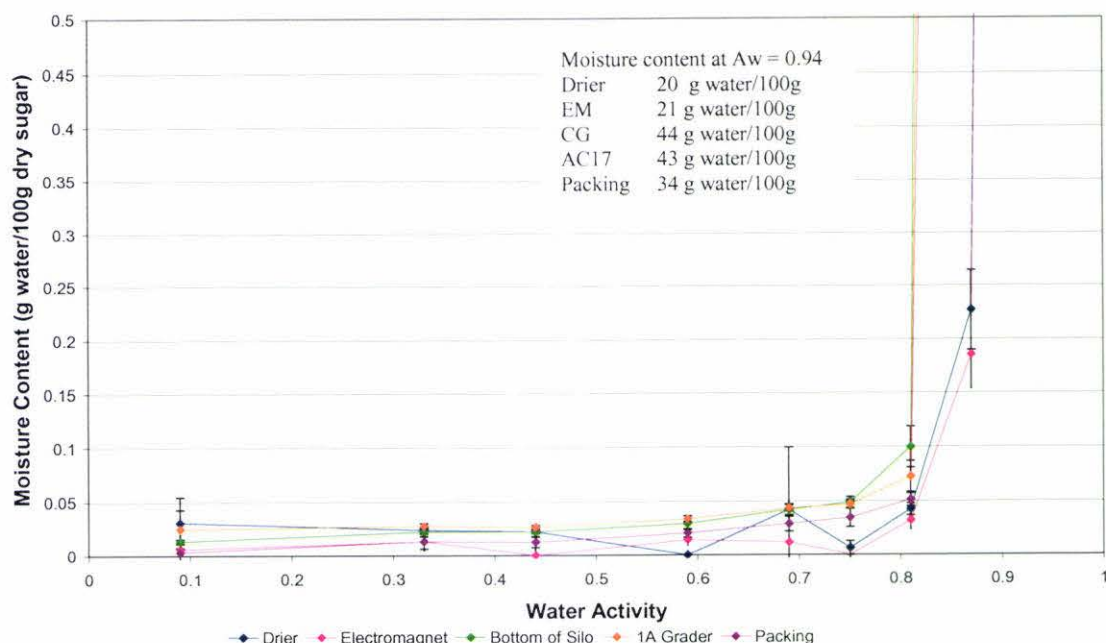


Figure 3.3 Working isotherms for samples taken from around the factory.

In order to quantify the effect of fine crystals on the isotherm it is important to know what the isotherm looks like for sucrose samples which do not contain any fine crystals. Therefore, an isotherm was measured using only standard sugar in the 600 – 850 μm range. A GAB isotherm was drawn for all the literature values (Roth, 1976; Franks, 1982; Iglesias & Chirife, 1982; Bakhit & Schmidt, 1993). When the isotherm from this study was compared to this GAB isotherm, it was found to be marginally lower. The differences could be due to different methods used to create the isotherms. For example, Roth used saturated salt solutions in vacuum desiccators. Laaksonen, *et al* (2001), found that these desiccators absorbed less moisture at lower water activities, and more at higher water activities, than when vacuum was not used.

The data presented by Roge and Mathlouthi (2000; 2003) in Figure 3.4, is lower than all other reported data. This could be because although they used saturated salt solutions and did not keep them under vacuum, the length of time they left samples to equilibrate was seven days rather than four weeks. It was found in this study, that there was still some change in moisture content after samples had been left over saturated salt solutions for three weeks.

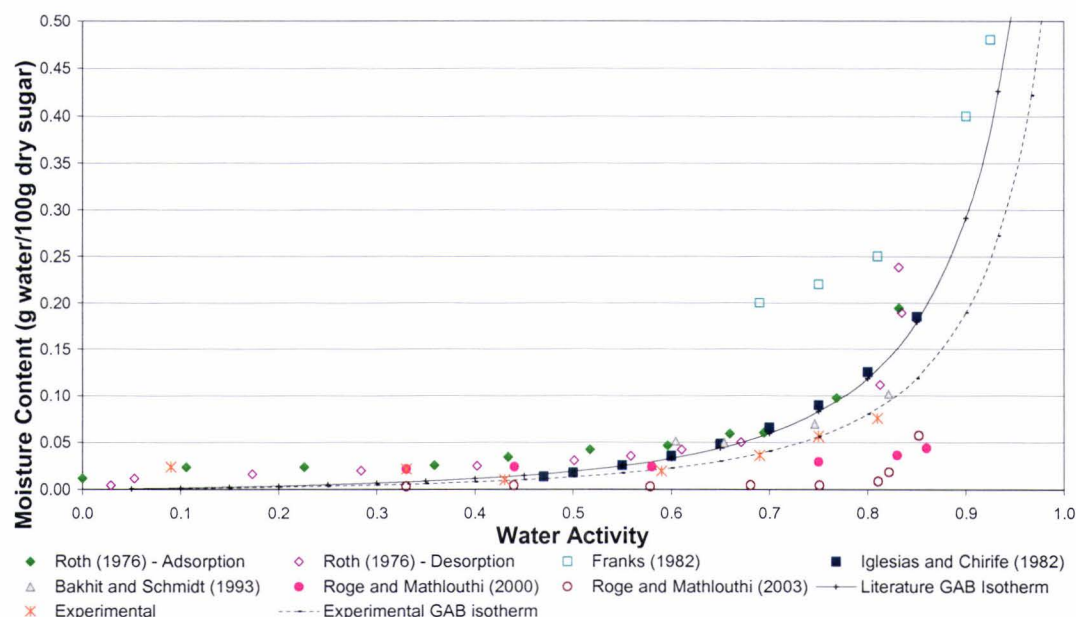


Figure 3.4 Comparison of results to published data

3.3.1 Effect of Crystal Size

No significant effect of particle size on the isotherms was recorded. There may be a small increase in moisture uptake by very fine samples, 0-75 μm and 75-150 μm , but only for samples composed solely of fine crystals, however this is not within the error limits of the moisture content. This is shown in Figure 3.5. In samples composed of both standard sugar crystals and fine crystals, such as the 10% sample shown in Figure 3.6, the fine crystals had no effect. There is some fluctuation between samples at different water activities. This is likely to be due to the limitations of the experimental methodology.

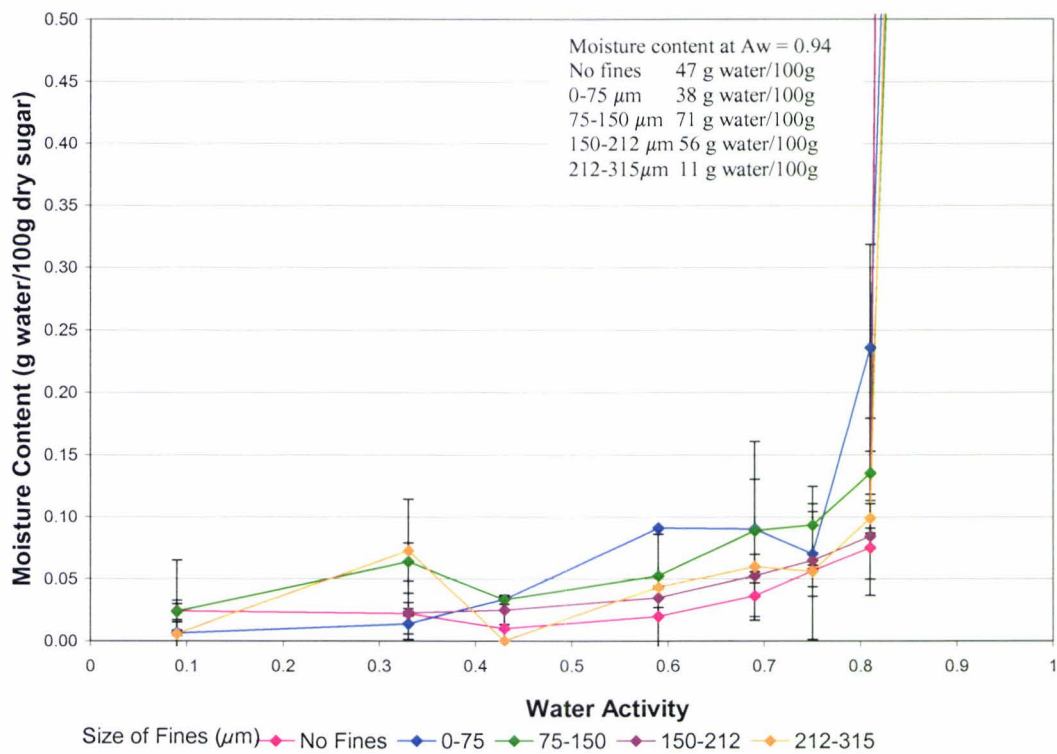


Figure 3.5 Working isotherms for samples composed of 100% fine crystals

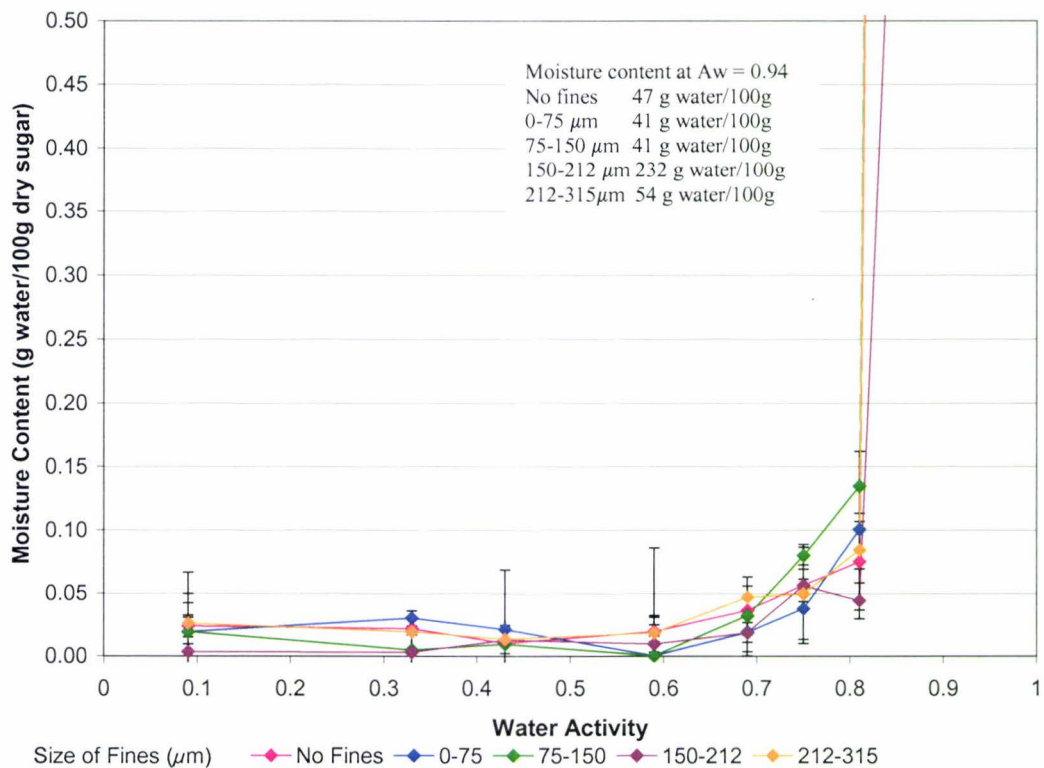


Figure 3.6 Working isotherms for samples composed of 10% fine crystals, mixed with 600-850 μm crystals

3.3.2 Effect of Proportion of Fine Crystals

No significant effect of the proportion of fine crystals was found. There may be a small effect in particle size for very small sucrose samples, 0-75, Figure 3.7, and 75-150, Figure 3.8, containing only fine crystals, however the errors in the method are greater than the difference. No effect on the isotherm was found for samples containing larger fines, between 150 and 315 μm , as shown in Figures 3.9 and 3.10.

The increase then subsequent decrease at a water activity of 0.69, for the sample containing 0.1% fine crystals, in Figure 3.9 is likely to be caused by either salt solution splashing onto the moisture dishes.

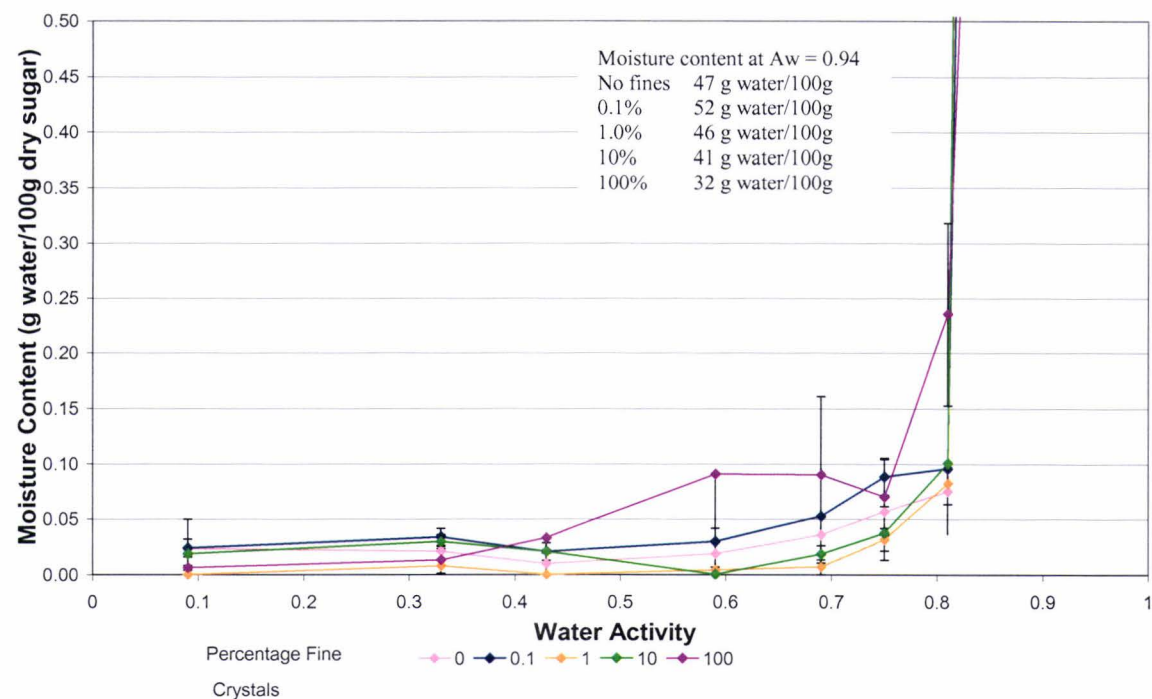


Figure 3.7 Working isotherms for samples composed of varying proportions of 0-75 μm crystals, mixed with 600-850 μm crystals

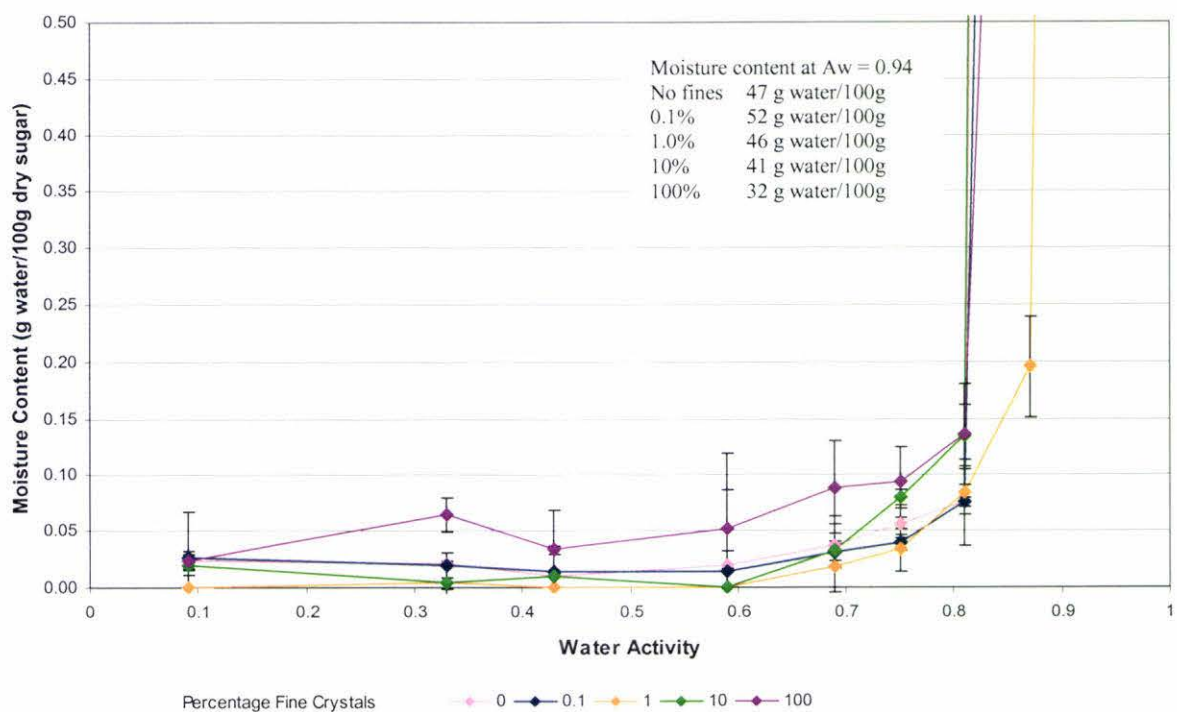


Figure 3.8 Working isotherms for samples composed of varying proportions of 75-150 μm crystals, mixed with 600-850 μm crystals

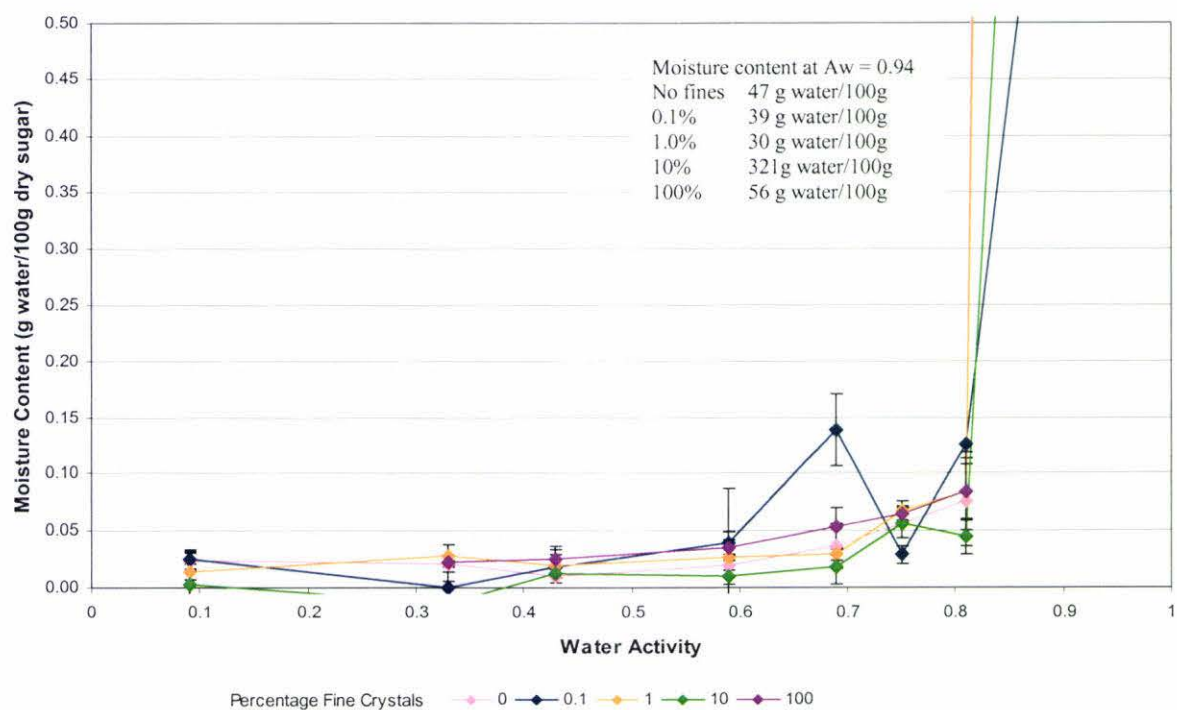


Figure 3.9 Working isotherms for samples composed of varying proportions of 150-212 μm crystals, mixed with 600-850 μm crystals

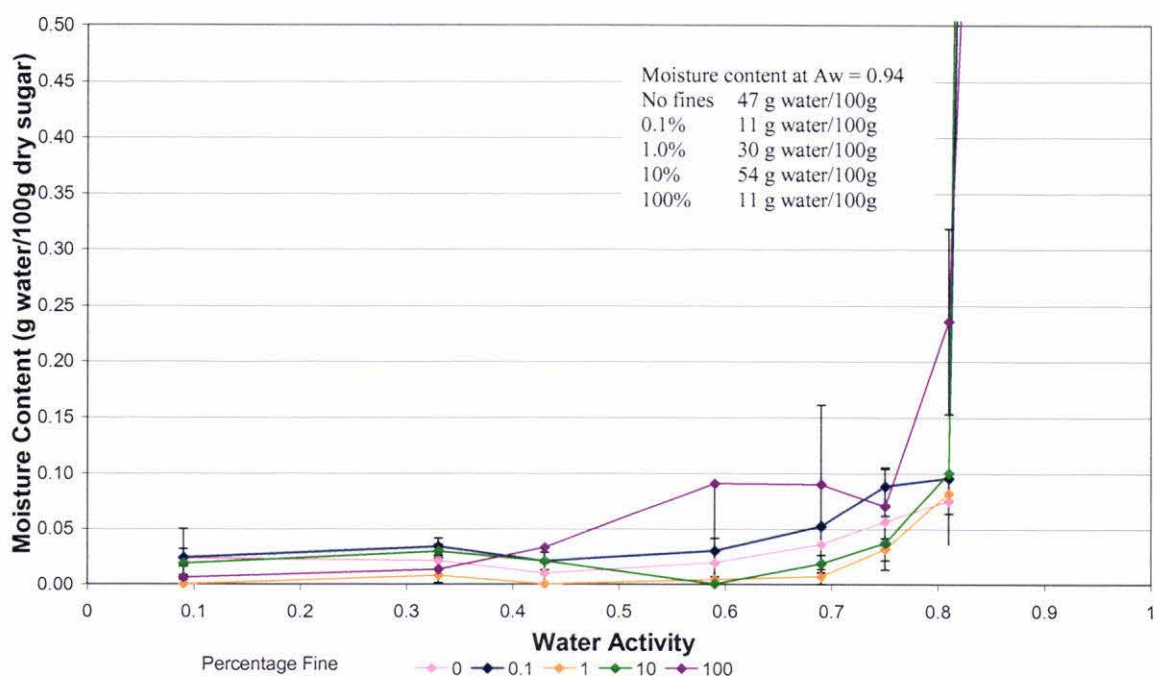


Figure 3.10 Working isotherms for samples composed of varying proportions of 212-315 μm crystals, mixed with 600-850 μm crystals

3.3.3 Comparison to Literature

The only other literature relating particle size of sucrose to the isotherm was published by Mathlouthi and Roge (2000, 2001, 2003). They used samples of less than 250 μm , 400-500 μm , 500-800 μm and greater than 800 μm . Only the first of these samples is considered as fines in this report. Their isotherms are lower than all those in this report, for fines of the same size, as shown in Figure 3.11, and also lower than other isotherms reported in literature. Possible reasons for this were discussed earlier in Section 3.3.

The smallest size fraction used by Mathlouthi and Roge was <250 μm , which will have a similar particle size distribution to the 150-212 μm sample used in this study. This isotherm for this size fraction in this study was found to be the same as that of larger crystals. Isotherms became exponential at the same point for smaller crystals as larger crystals in the study by Mathlouthi and Roge, however, they found that the 0-250 μm crystals absorbed more moisture at every relative humidity. This is characteristic of amorphous sucrose, however it is unlikely that there is any amorphous sucrose present at the temperature and relative humidities used in these

experiments. An alternative explanation is that the small crystals might have come closer to equilibrium as it can be seen in Figure 3.11 that their data is close to the data from this work, remembering that they only stored their samples for seven days.

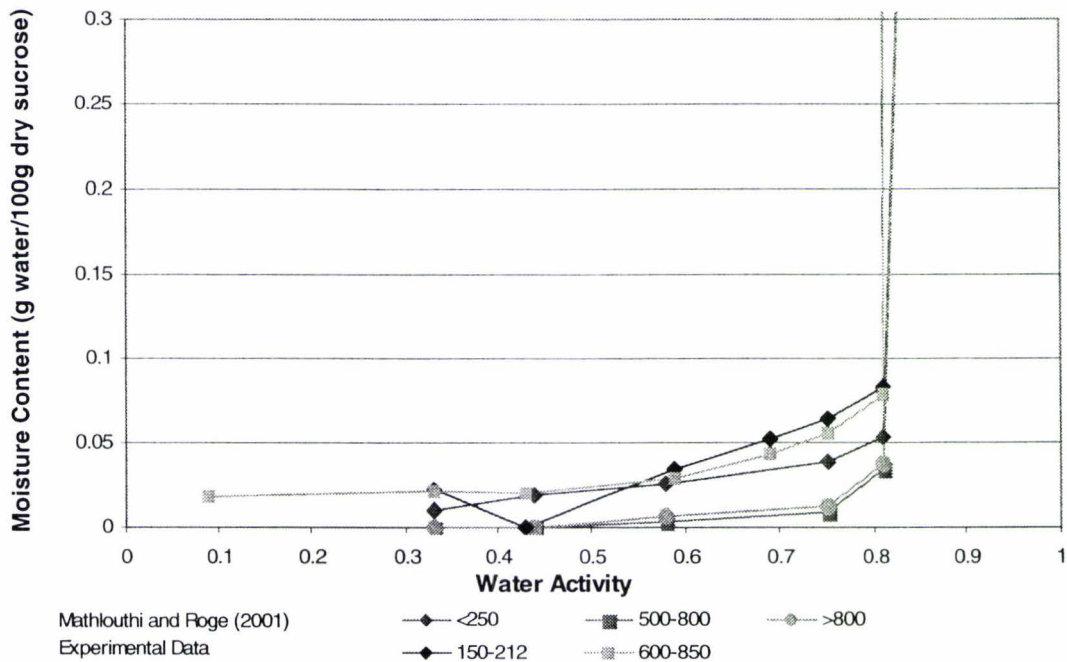


Figure 3.11 Comparison of particle size isotherms with those published by Mathlouthi and Roge (2001)

When their data is compared using the percentage of fine crystals present there are again differences. For example, when the results from this study were compared to those reported by Mathlouthi and Roge (2001), in Figure 3.12, for crystals of a similar size (150 – 212 μm) the same trends are not shown, but there are some similarities between their sample and the current samples when compared with smaller crystals, 75-150 μm . Both these isotherm series show little difference between standard crystals, and samples containing 10% fine crystals, but a greater difference between the 10% fine sample, and 100% fine sample. However, the errors in the isotherms generated in this study are greater than the difference between samples. The data generated by Mathlouthi and Roge shows a lot less scatter, which means there method of measurement is probably more sensitive than that used in this study.

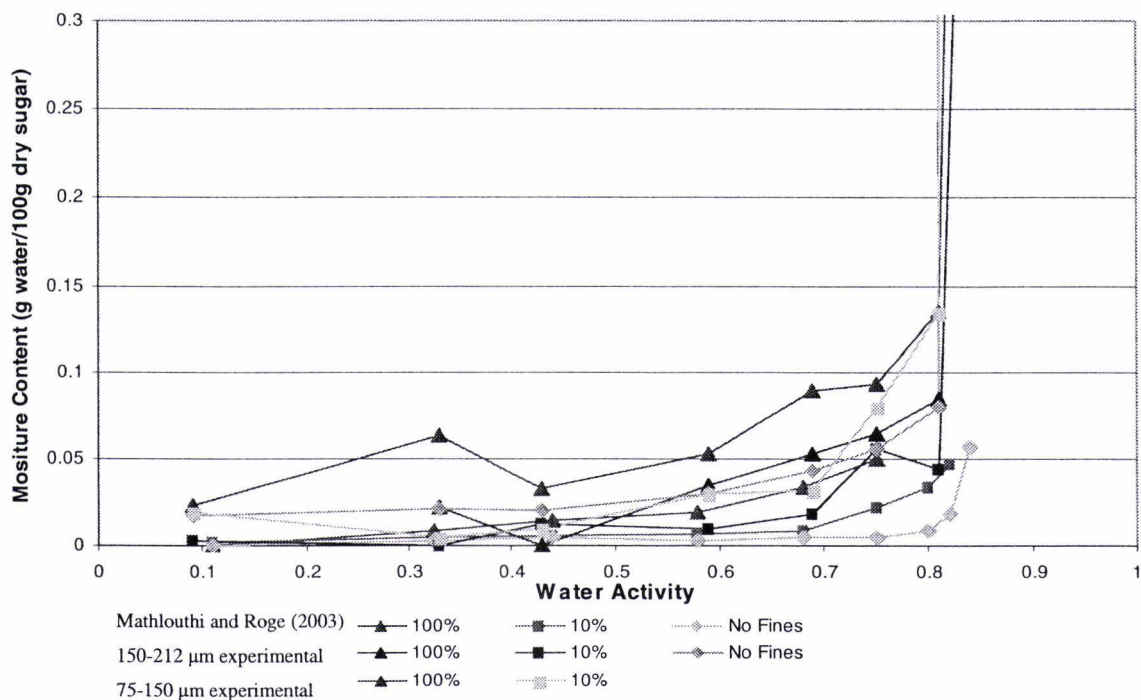


Figure 3.12 Comparison of isotherms with varying percentages of fines with those published by Mathlouthi and Roge (2001)

Mathlouthi and Roge’s data for samples containing different proportions of fines were very similar to their data for different sized crystals. Also, again there is much less scatter in their data than the data points from this study, suggesting a more accurate measurement method.

Another possible cause of the difference in results is the level of compression and tapping the sample receives. Both these factors would cause the particles to pack together more closely. This closer packing is likely to result in more points of contact, and would also decrease the angle at these points. This would also decrease the size of the capillaries, or gaps, between crystals. It is likely this has more of an effect than particle size.

In order to keep the packing the same, while not causing segregation of different sized particles, the samples used to measure the isotherms were gently shaken to ensure a flat surface, and tapped only once. Care was then taken to ensure they were not tapped or bumped again.

3.4 Conclusions and Recommendations

Neither crystal size, nor the proportion of fine crystals, was found to have any significant effect on the moisture sorption isotherms for sucrose. There may be a small effect with very small crystals – those 0-75 μm , and to a lesser extent 75-150 μm , but only when they were present in large quantities. In addition, the effect of relative humidity is still much greater than any possible effects of particle size.

It is recommended that the sorption isotherms be repeated using Dynamic Vapour Sorption, because this is expected to be a more accurate method and might eliminate a lot of the errors and uncertainties associated with the saturated salt method used in this study. This will help determine if any possible caking effect seen with the very small crystals is real, or due to errors in the method.

There is quite a lot of variation in the crystalline sucrose isotherms published by different researchers. A lot of this variation is likely to be due to different methods, and different residence times allowed for samples to come to equilibrium. In addition, some researchers have shown an effect of particle size on their isotherms, which was not seen in this study. This effect is likely to be caused by a small amount of amorphous sucrose in their samples. In the next chapter the amount of amorphous sucrose present in samples used to generate the isotherms in this study will be determined.

Chapter 4

- Determination of Amorphous Sucrose

Content -

4.1 Introduction

The isotherms for amorphous and crystalline sugar are vastly different, as shown in Chapter 2, which means any amorphous sucrose present in samples, even at very low concentrations, will affect the isotherm, and may mask any effect of particle size. Since the isotherm influences caking, any amorphous sucrose will also affect the level of caking that is occurring in the isotherm samples. Therefore, it is important to determine if any effect on the isotherm and caking is related purely to size, or if it is caused by amorphous sugar. To do this the amorphous sugar in all the samples used to measure the isotherms will be determined using a thermal activity monitor.

Amorphous material recrystallises when the amount of moisture held by the amorphous material reaches a concentration at which the glass transition temperature is lower than the ambient temperature. The energy released by the recrystallisation reaction is termed the heat of crystallisation. For sucrose this is 10.5 kJ/mol at 30 °C and 33 kJ/mol at 60 °C (Pennington and Baker (1990); converted from imperial units using Perry and Green (1997)). This heat of recrystallisation can be measured and used to determine the amorphous content in the sample.

4.1.1 Thermal Activity Monitor

The Thermal Activity Monitor (TAM) was used in this research to determine the amorphous content of different sucrose samples. It is a heat conduction microcalorimeter, which is based on the theory that all chemical, and biological processes result in the generation or consumption of heat. The instrument is capable of detecting very small heat flows (± 50 nW) (Bergqvist & Soderqvist, 1999) produced or absorbed.

The TAM, Figure 4.1, consists of a temperature controlled waterbath ($\pm 0.0001^\circ\text{C}$). Inside this are four independent calorimeter units, as shown in Figure 4.2, each of which contains two ampoule holders. These holders are surrounded by a pair of thermopile heat sensors, in contact with a metal sink.

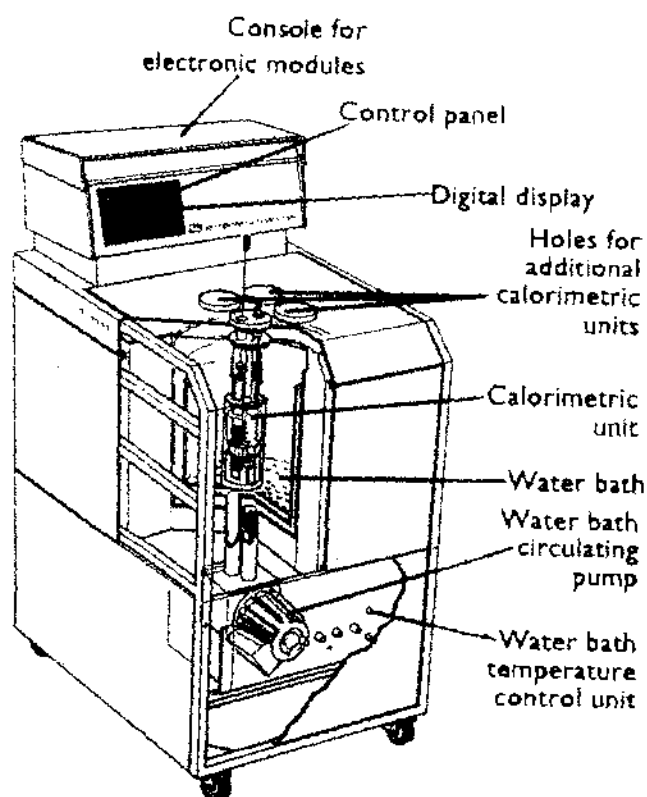


Figure 4.1 The thermal activity monitor (Thermometric brochure)

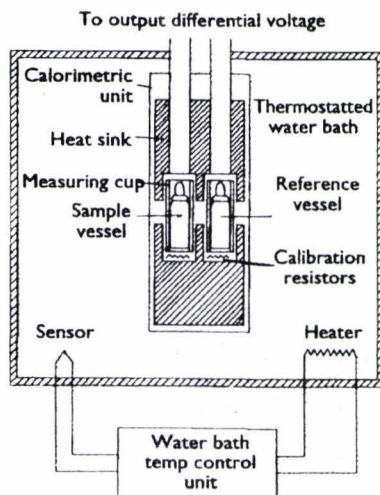


Figure 4.2 Inside a calorimetric unit (Thermometric brochure)

As a reaction proceeds, the change in heat causes a temperature differential across the thermopiles, which is registered as a voltage difference. This can be directly related to the heat flow from the sample. This principle is shown in Figure 4.3.

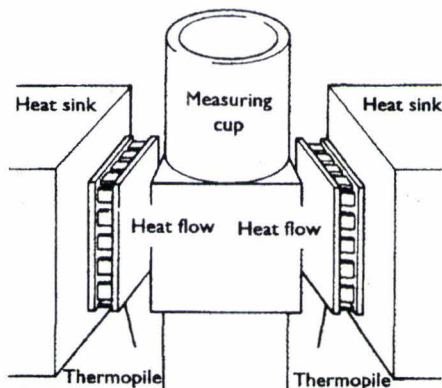


Figure 4.3 Heat flow in the calorimeter (Thermometric brochure)

The closed ampoule method is based on the principle that all processes occur and are measured in a closed system. This means it provides a very controlled environment. A small glass vial is used, inside which, is placed the sample and small tube containing a saturated salt solution as shown below in Figure 4.4. The salt solution absorbs or desorbs water until the equilibrium relative humidity for that salt is reached. A second ampoule is used as a reference cell.



**Figure 4.4 Glass ampoule and sample
(Thermometric brochure)**

Due to the sensitivity of the instrument it will pick up all other mechanisms and reactions occurring as well as those being targeted. For example, the evaporation of fingerprints on the side of the vial or the adsorption of atmospheric humidity onto previously dry powder caught in the screw thread of the lid (Buckton & Beezer, 1991). Therefore, it is necessary to be vigilant when preparing the samples.

4.2 Experimental Methodology

In order to preserve any amorphous content that may be present in samples, a small sub-sample was taken of each sugar sample used to measure the isotherms in Chapter 3. Each of these sub-samples was placed in a sealed bag with as much air removed as possible. These bags were stored over P_2O_5 , a strong desiccant, until the amorphous content could be measured. This was to ensure no moist air entered the sample, and to fully dry the samples.

For each size fraction of sugar, including standard sugar (600-850 μm), a sample composed entirely of that size fraction was analysed using the TAM. From these results the amorphous content of all other samples used in the isotherm section could

be calculated, if any amorphous content was found. The amorphous content of a sample of milled sugar, which had been left at 87 % relative humidity for a week to recrystallise, was also measured. This sample was recrystallised in order to try to eliminate the effect of amorphous sucrose on the isotherm so only the effect of fines will be seen. Therefore it is not expected that there would be any amorphous sucrose still present in this sample. It should also be noted that this sample was a lot stickier than the other samples tested.

In addition, the amorphous content of the samples used to test the effect of crystal damage, in Chapter 7, was also measured. The samples in this section that were most likely to contain an amorphous component were the clamgates sample in which recrystallised milled sugar had been added, and the sample taken from the clamgates then recombined to mirror the particle size distribution of the electromagnet sample.

The samples were analysed using the Thermal Activity Monitor 2227 (Thermomatic AB Sweden) at Fonterra, Kapuni. The method used was that developed by Billings, (2002), using 87 % relative humidity. At this humidity any amorphous content will recrystallise, even if there is only a very small amount present (Sebhatu *et al.*, 1994). It will also occur relatively quickly. Some samples were also repeated at 53% relative humidity to ensure that there was not a crystallisation peak that was being missed because it was occurring before the samples were thermally equilibrated.

0.2 g of sample was weighed into a 4 mL glass ampoule. A Durham tube was three-quarters filled with a saturated solution of potassium chloride, to give a relative humidity of 87 % (Bell & Labuza, 2000), and placed inside the ampoule. The ampoule was tightly sealed with a Teflon covered rubber disc.

While the sample was being prepared, the TAM was turned on to obtain a baseline. The sample and reference cell were then held in position for 20 minutes to thermally equilibrate before being lowered into the calorimetric unit. Samples were left in the TAM for at least four hours and up to twenty hours, to make sure all the amorphous content had been recrystallised.

All heat flows generated during the experiment were recorded by the Digtam software, and the reaction peaks were then integrated to give the total energy for the reaction. The following integral peak curve, Figure 4.5, and Equation 4.1, developed by Billings (2002), was then used to determine the amorphous content in each sample.

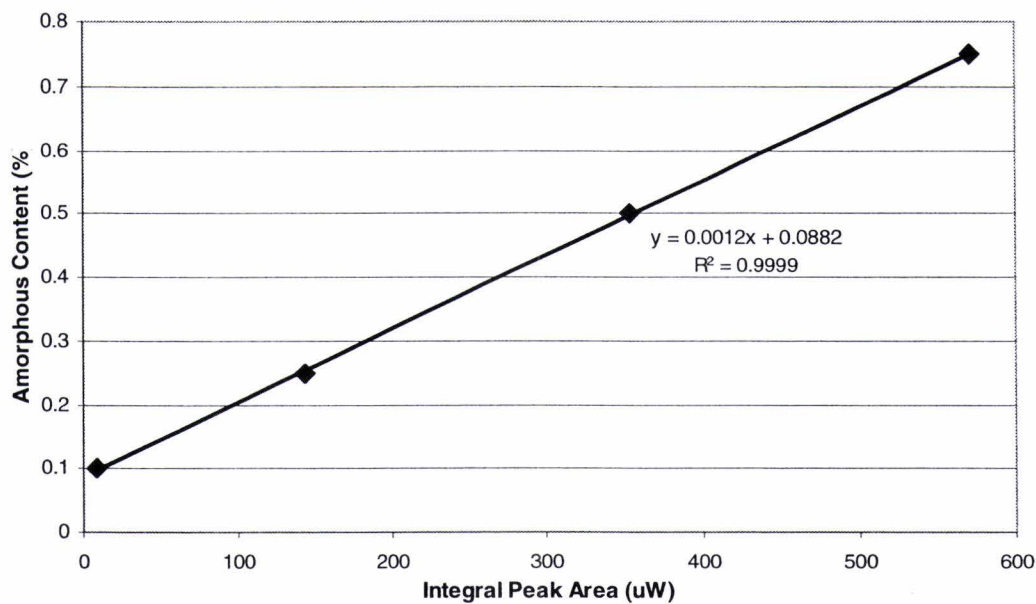


Figure 4.5 Amorphous content vs integral peak curve (Billings, 2002)

$$X_{\text{amorphous}} = \text{Integral Peak Area} * 0.0012 + 0.0882$$

Equation 4.1

4.3 Results

The amorphous content of the samples were found using the integration peak curve, given above. Samples were first normalised for mass. This value was then multiplied by the result of Equation 4.1. The results are shown below in Table 4.1.

Sample	RH	Sample Size	Integrated Peak Area (mJ)	Amorphous content (%)
Standard	87	0.244	-49.560	0
212-315 μm	87	0.192	-26.305	0
150-212 μm	87	0.210	-43.380	0
75-150 μm	87	0.196	0.896	0.08749
0-75 μm	87	0.221	0.957	0.09873
0-38 μm	87	0.208	0	0
Recrystallised				
Recombined	87	0.211	0	0
Clamgates				
Clamgates + Fines	87	0.222	0	0

Table 4.1 Amorphous contents of different samples

The TAM printout for standard sugar (600-850 μm) with no amorphous component is shown in Figure 4.6. The first section of this graph, before the first peak, is the baseline measurement. The first peak, after approximately seven minutes, is due to the sample being placed into the TAM. The second peak, twenty minutes later occurs when the sample was lowered into position. This was seen in most of the samples that were analysed, and was approximately the same size in all samples. It would not usually be expected that this peak would be negative. A negative peak could mean desorption of water from the sample, heat transfer from the TAM to the sample or dissolution of sample. In addition, the baseline of most of the samples moved by approximately $-3 \mu\text{W}$. This probably means the TAM needed longer to measure the baseline before the sample was placed in the TAM.

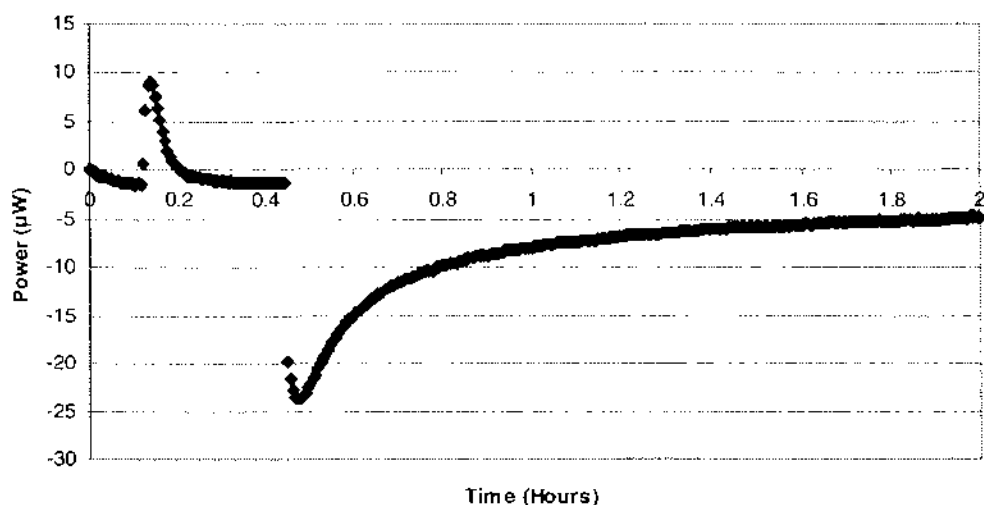


Figure 4.6 TAM curve for standard sugar sample, containing no amorphous content

Desorption of water is endothermic, which means it uses heat, and therefore would generate a negative peak. It is very unlikely that the peak that is seen in Figure 4.6 is due to desorption of water from the crystals because the samples have been dried over P_2O_5 , which is a very strong desiccant. For water to desorb when the samples are exposed to a relative humidity of 87%, the samples would need to be at an equilibrium relative humidity greater than 87%. Even if the samples were exposed to the air in the laboratory the humidity would only be approximately 50%.

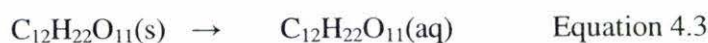
One likely explanation for the negative peak, is that the sample was not properly thermally equilibrated before being lowered into measurement position. The temperature difference required to heat the sugar by this much was calculated using Equation 4.2 (Terrill, 2003).

$$q = -mC_p\Delta T \quad \text{Equation 4.2}$$

where q is the heat energy (J), m is the mass of the sample (kg), C_p is the heat capacity of sugar (1.8643 kJ/kgK (Bubnik *et al.*, 1995)) and ΔT is the change in temperature (K).

It was found that the temperature difference for the standard sample would be 0.1089 °C. This calculation assumes the glass vial and saturated salt solution are at thermal equilibrium, and only the sugar is being heated, whereas in reality it is likely these are also being heated. If this were the case the temperature difference would be less than 0.1089 °C. This is realistic.

Another possibility is that the sugar crystals are starting to dissolve, as was seen in the higher relative humidity solutions during the isotherm experiments in Chapter 3. This follows the endothermic reaction given in Equation 4.3.



To determine if this was a feasible explanation the number of moles of sucrose in the standard sample was calculated. In 0.244g of sucrose there are 7.13×10^{-4} moles. This was then multiplied by the heat of solution of sucrose (-5526×10^9 J/mol (Perry & Green, 1997)) to give a change in energy of -3.94×10^9 J if all the sugar dissolved. This is several magnitudes higher than the differences that were seen in any of the samples analysed in the TAM; therefore it is unlikely the crystals are dissolving. In addition, when samples were removed from the TAM after the measurement there was no sign of dissolution.

The most likely explanation is that the sample is slightly cooler than the TAM before it is lowered into the measurement position.

Some of the samples also had a positive peak preceding the negative peak, as shown below in Figure 4.7.

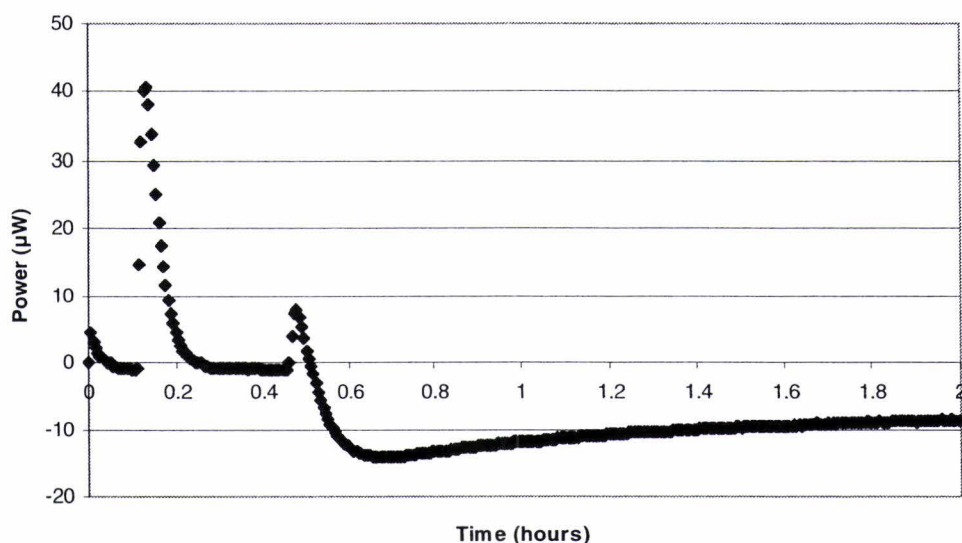


Figure 4.7 TAM curve for 75-150 μm sample which may contain some amorphous sucrose

This positive peak could either be due to heat from friction as the samples are lowered, or it could be from recrystallisation. If it is due to the latter, it is possible that the negative section is disguising some of the recrystallisation that is occurring. Also, recrystallisation could have occurred before the sample was lowered, however, the samples would not be expected to recrystallise until later as shown by other researchers (Angberg, 1995; Billings, 2002). In order to make sure samples were not recrystallising before they were lowered into position, some samples were repeated using a relative humidity of 53 %, achieved by using a saturated solution of calcium chloride in place of potassium chloride. The results are shown below in Table 4.2. There were no significant differences from running the samples at a relative humidity of 87 %.

Sample	RH	Sample Size	Integrated Peak Area (mJ)	Amorphous content (%)
75-150	53	0.181	2.6381	0.082686
0-38	53	0.187	0.0557	0.000063

Table 4.2 TAM samples repeated at 53% RH

In addition, if there was a significant proportion of amorphous sucrose in these samples it would be seen in the isotherm. The theoretical differences in isotherms for samples containing 0.1% and 1.0% amorphous sucrose, compared to the GAB isotherm for standard sugar are shown below in Figure 4.8. These differences were not seen in the isotherms.

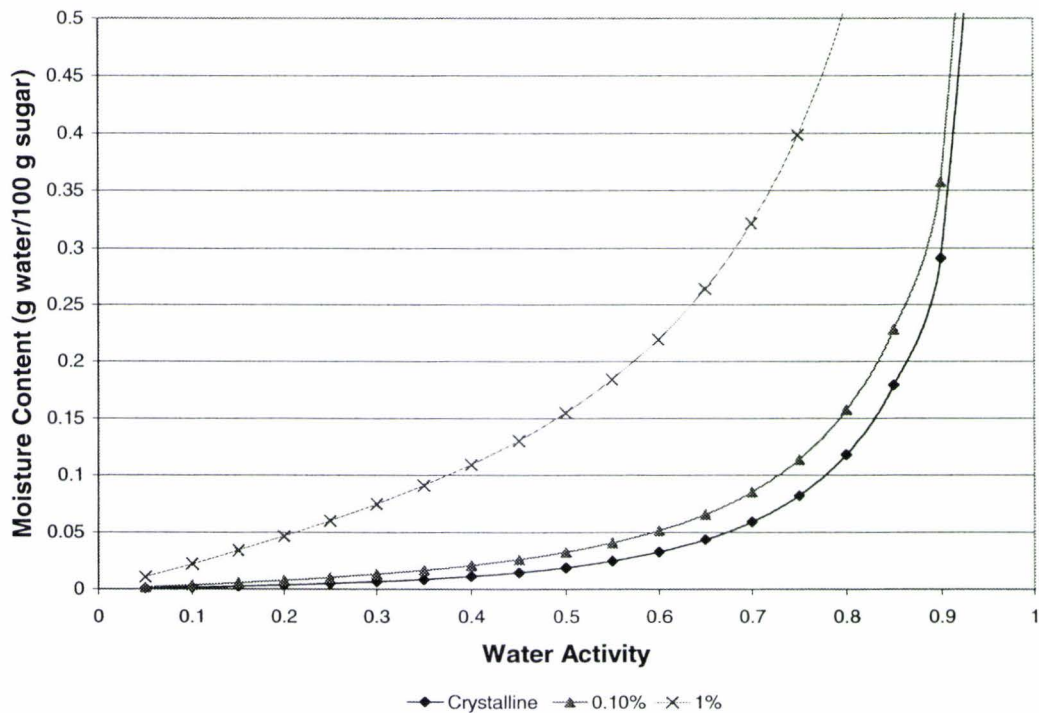


Figure 4.8 Effect of amorphous sucrose on the isotherm

These results were compared to those by Billings (2002). The only differences for the samples containing no amorphous component, was that the second peaks were positive in the study by Billings. This is probably because the samples were slightly warmer than the TAM, so heat flowed from the samples to the TAM. When there was a small amount of amorphous sucrose found in the study by Billings, there was a secondary peak due to recrystallisation. This can be seen in Figure 4.9, for a sample which was found to have 0.16% amorphous sucrose. This peak occurred after approximately 2400 seconds (40 minutes).

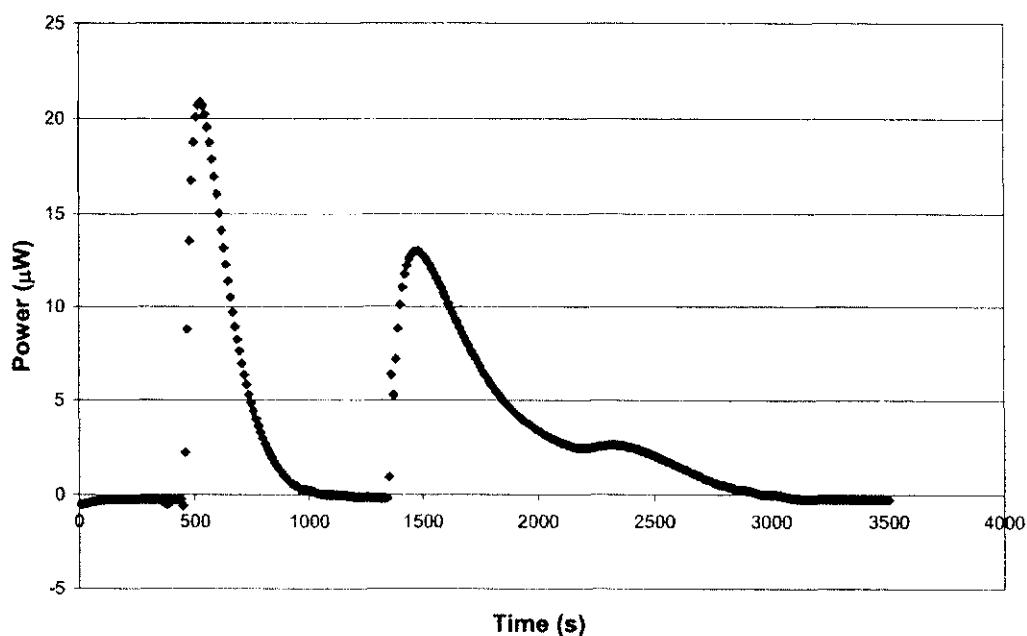


Figure 4.9 TAM curve for sample containing 0.16% amorphous sucrose (Billings, 2002)

No peaks were found in this region during this work. It can therefore be concluded that there is no amorphous sugar in the samples used in the isotherms and caking tests, in Chapters 3, 5 and 7. Also, because of the extremely low amorphous contents found in the samples that were tested, it was not necessary to test samples containing lower proportions of fine crystals.

4.4 Conclusion

No significant amorphous content was found using the TAM method. There may be a very small amorphous component in the sucrose crystals smaller 150 μm, but this is below the detectable limit, of 0.1%, of the instrument used. In addition, the exothermic peaks shown by these samples may be due to friction as the samples were lowered into the measurement position.

The differences that would be seen in isotherms if 0.1% or 1.0% amorphous sucrose was present, were plotted. These differences were not seen in the isotherm experiments in this work (see Chapter 3), which confirms the level of amorphous sucrose present is below 0.1%.

This means the possible differences seen in the isotherms measured and caking tests carried out in this study were not caused by amorphous sucrose.

The next chapter will identify the effect of particle size on caking in sucrose, using both the friability and blowtest methods.

Chapter 5

- Caking -

5.1 Introduction

Caking is the formation of solid lumps of powder, resulting in the loss of free flowability. There are two stages of caking – liquid bridging, followed by solid bridging (Roth, 1976; Mullin, 2001).

Liquid bridging is the formation of a liquid solution between crystals. It is caused by capillary condensation within pores, which causes the crystal surface to dissolve. In a packed bed contact points between crystals cause pores, or capillaries, to be formed. Surface tension effects allow the pressure in these capillaries to be lower than the atmospheric pressure (Bronlund, 1997; Billings, 2002). This means that inside these capillaries the saturated vapour pressure above the liquid surface is lower than that of the bulk air, at the same temperature. Condensation will occur within the capillaries if the vapour pressure is lowered enough to be greater than the saturated partial pressure above the capillary surface (Billings *et al.*, 2005).

Solid bridging occurs as liquid bridges crystallise. This usually happens as sugar crystals that have been exposed to a high relative humidity, and have formed liquid bridges, are exposed to a lower relative humidity causing the liquid bridges to dry out, nucleation to occur and crystallisation to proceed. As the solution in the liquid bridges dries out it leaves a solid bridge between particles (Bronlund, 1997).

The Kelvin radius is a measure of the size of the capillaries that are full of water-sugar solution at any given water activity (Billings *et al.*, 2005). This can be calculated using the rearranged Kelvin equation, Equation 5.1 (Adamson, 1990). It can be seen

from this equation, as the surrounding water activity increases the number and size of the capillaries that are full also increases. The critical Kelvin radius is the radius of the largest pores that are full of water when caking occurs.

$$r_k = \frac{-2.\sigma.\cos\theta.V_0}{\ln a_w.R.T} \quad \text{Equation 5.1}$$

where r_k is the Kelvin radius (m). σ is the surface tension of the solution; this was calculated by Billings *et al* (2005) to be 80.2 N/m for sucrose at 20°C. θ is the wetting angle; it is assumed that the liquid perfectly wets the surface, therefore, θ equals zero and $\cos \theta$ equals one. V_0 is the liquid molar volume; for a saturated solution of sucrose this is $6.13 * 10^{-5} \text{ m}^3/\text{mol}$ (Billings *et al*, 2005). a_w is the water activity of the sample. R is the gas constant, 8.314 J/molK. T is the absolute temperature (K).

In this section of work, sucrose samples were left in different relative humidity conditions to induce caking. Then the caking strength was measured and critical Kelvin radius calculated.

5.2 Experimental

Any sugar crystals below approximately 300 μm are considered as fines at New Zealand Sugar. To determine whether all particles in this range were causing caking problems, or only the smaller particles, the sugar crystals were further sieved into 0-75 μm , 75-150 μm , 150-212 μm and 212-315 μm fractions. For each fraction a series of samples were prepared containing the following proportion of fine particles: 0, 0.1, 1, 10 and 100 %, mixed with standard sugar (600-850 μm). Caking tests were carried out on all these mixtures.

5.2.1 Liquid Bridging

In order to create liquid bridges between samples, they were held over saturated salt solutions for four weeks, until equilibrium was reached. The salt solutions that were used were the same as those used in the isotherm section, with the addition of magnesium nitrate and cobalt chloride. These salts give a relative humidity of 54 % and 65 % respectively. Aluminium moisture dishes were used for the friability samples, and plastic petri dishes for the blowtest samples.

5.2.1.1 Friability

Friability is a measure of the flowability of a powder. As a powder is tilted it will reach a certain angle whereby bonds between the crystals break and the powder will flow (Roge & Mathlouthi, 2000). The more caked a sample is, the greater this angle will be.

The friability angle is measured using a tilting platform as shown in Figure 5.1. The moisture dish is mounted onto the platform, which is then mechanically tilted at a speed of 0.299 revs/min until the powder begins to flow. At this stage the liquid bridges are broken. The distance, y , as shown in Figure 5.1, is then measured. Using the height of the platform, x , the friability angle can be accurately calculated.

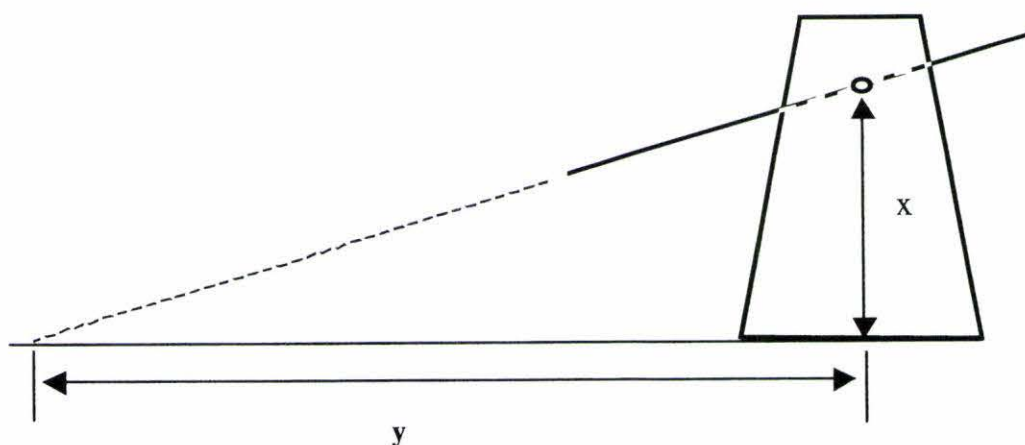


Figure 5.1 Rotating platform

5.2.1.2 Blowtester

The blowtest measures the airflow required to break the bridges that are formed between particles. The blowtest consists of a 1 mm tube, placed 3mm above the flat powder bed at an angle of 45° to the horizontal. It is fixed at a set distance above the flat powder bed, then air is blown through the tube and onto the powder bed. The flowrate of air is increased steadily until sugar particles are first dislodged from the surface of the samples (Brooks, 2000; Billings, 2002; Billings *et al.*, 2005). The flow at which this occurs is recorded. The test was repeated up to three times on different parts of the bed.

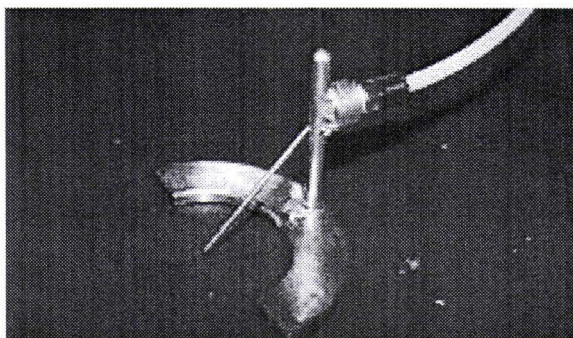


Figure 5.2 Blowtester

5.2.2 Solid Bridging

To cause the liquid bridges to crystallise, samples were left over P_2O_5 , under vacuum, for seven days. The friability and blowtest measurements were then carried out as above.

5.3 Results and Discussion

In some samples it was found that instead of being either free flowing or caked, there were areas of localised caking. These lumps, in some instances, made measurement

by friability or blowtest difficult. They could have been due to the sample not being mixing well enough, or settling of the sample. In order to try to overcome this samples were shaken well, before sub-samples were taken. They were then put through the riffle sampler, which would further mix the samples. Once they were in dishes care was taken not to bump or tap the samples.

5.3.1 Liquid Bridging

5.3.1.1 Friability

The friability angle was plotted against the equilibrium relative humidity, for each different size fraction of fine crystals, and for each different proportion of fine crystals. The only sample that showed any significant difference, as the amount of fine crystals increased, was the sample containing 0-75 μm fines, as shown in Figure 5.3, below. This shows for samples composed completely of fine crystals, the angle needed for the powder to flow increased at water activities higher than 0.33, until a water activity of 0.70 where the powder did not flow. When a lower proportion of fine crystals were present, ie, 10%, 1%, 0.1% or 0%, the friability angle was found to be no different from standard sugar, and the samples became too caked to flow at a water activity between 0.59 and 0.69.

There may also be a similar effect in samples containing 75-150 μm fines shown in Figure 5.4. It can be seen for the 100% sample that an increase in the angle needed for flow, occurred after a water activity of 0.44, oppose to 0.33 for the sample of smaller crystals shown in Figure 5.3. However, the friability angle error bar for the point at a water activity of 0.59 is so large that it is difficult to tell if this effect is real.

All other plots are shown in the Appendix A2.

These results show that the friability test is more useful as a qualitative measure to tell if a sample is caked or not, rather than being quantitative. When a sample is not caked, it flows easily, at approximately 45° , whereas once the sample becomes caked it does not flow, and the friability angle is greater than 90° .

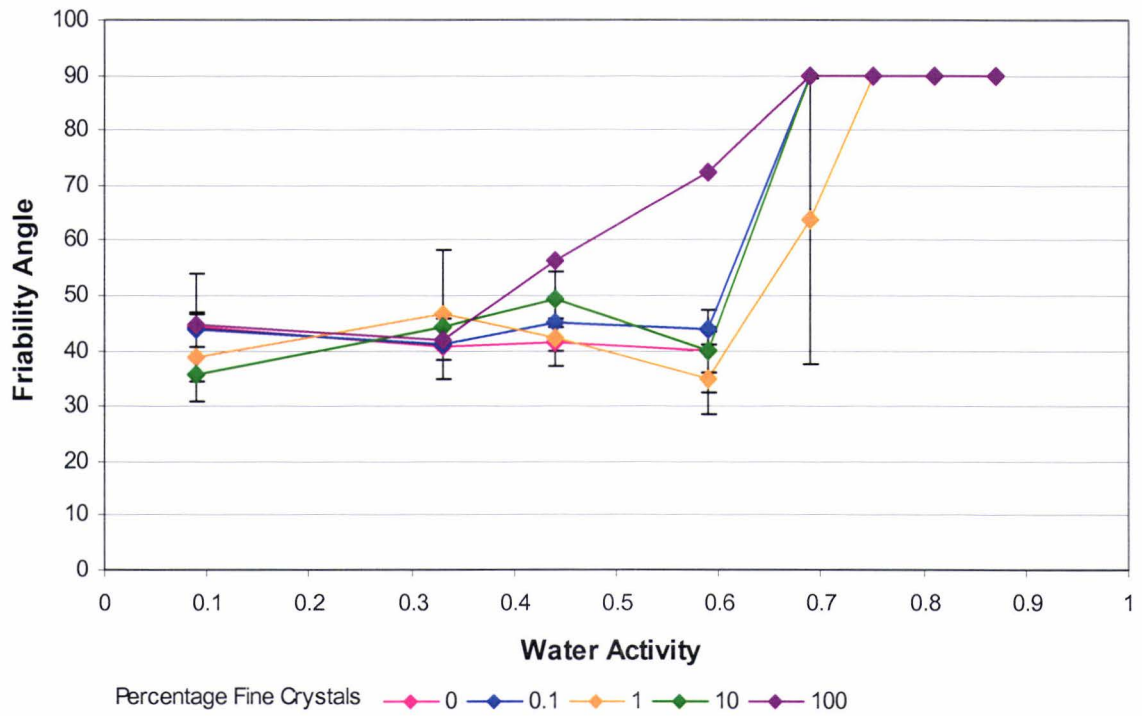


Figure 5.3 Angle required to break liquid bridges in samples containing varying proportions of 0-75µm crystals, mixed with 600-850µm crystals

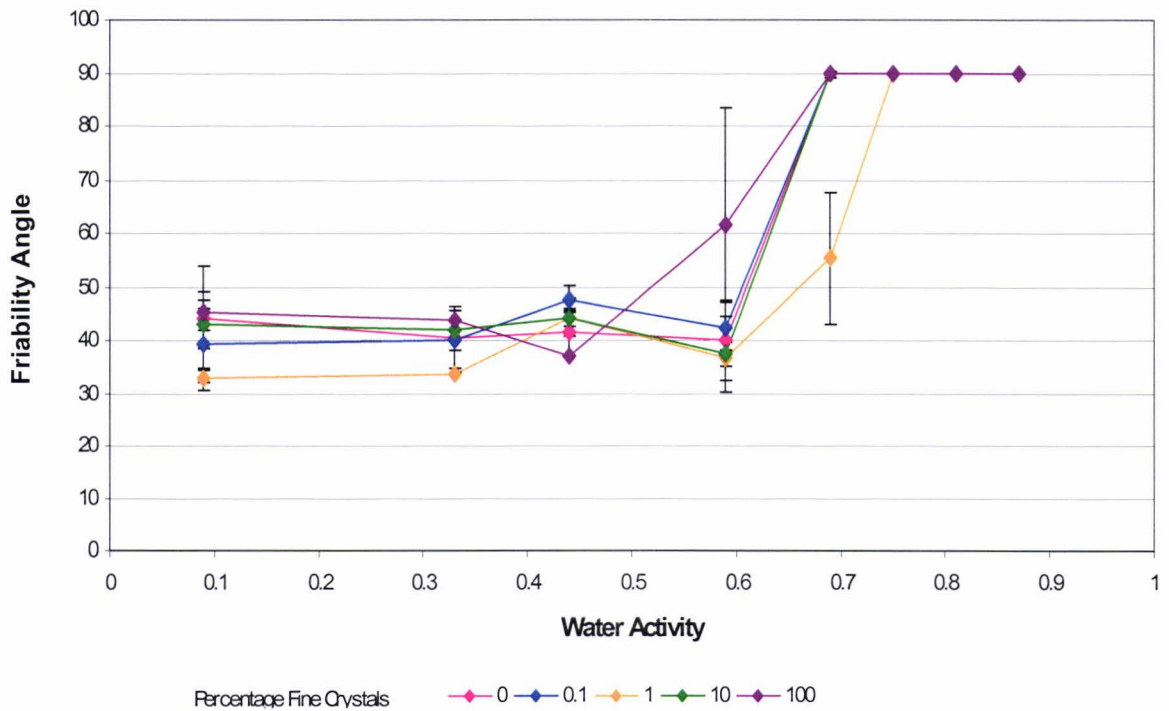


Figure 5.4 Angle required to break liquid bridges in samples containing varying proportions of 75 - 150µm crystals, mixed with 600-850µm crystals

5.3.1.1.1 Comparison of Friability Measurements and Isotherms

There are some minor differences between the results from the isotherms and the friability tests, however the same conclusions can be drawn. For example, the isotherms became exponential at a water activity between 0.8 and 0.9, whereas the friability angle increased at a water activity of between 0.59 and 0.69. Also, the sample containing 100% 0-75 μm crystals starts to increase at approximately the same water activity, but the increase is very gradual for the isotherm; a water activity of 0.59 is needed before there is a definite increase in water absorption, whereas for the friability test caking starts at a water activity of 0.44. These differences are probably due to differences in what is being measured – the isotherm measures the amount of water absorbed by the sample, whereas the friability test measures the caking that is a result of this increase in water. Therefore, a loss of flow can be seen when samples first start to absorb water, rather than when the increase in moisture becomes exponential. However, despite these differences the trends that are shown are the same, with the 100% 0-75 μm sample displaying signs of caking earlier than other samples, and to a lesser extent the 100% 75-150 μm .

5.3.1.1.2 Comparison of Results in This Study to Literature

These results are different from those obtained by Roge and Mathlouthi (2000), Figure 2.9. They reported a significant difference at lower humidities, in the flowability of samples containing 100% fines, compared to standard sugar. The results of this study, however, show no difference at lower humidities. It was also found in this study, samples containing 10% fines acted in a way similar to standard sugar containing no fine crystals, rather than acting in the same way as a sample containing 100% fines. In addition, the onset of caking occurred much earlier in their data, and is increasing from the first measured point. In comparison, where an effect of fines was seen in this study it started at a higher water activity and was more gradual. These differences could be due to amorphous sucrose in their samples. To determine if this was a feasible explanation, the glass transition temperature, T_g , at the onset of caking was found, using Billings (2002). At a water activity of 0.33 the T_g is approximately -58°C , which is far below 20°C , the temperature these tests were carried out. Therefore, sucrose is very unlikely to exist in its amorphous form. In addition, the water activity required to exceed the T_g was also found to be 0.07.

This means the differences that are seen are likely to be because Mathlouthi and Roge (2000) used a more sensitive measure of friability.

5.3.1.2 Blowtester

In contrast to the friability and isotherm experiments, the blowtester shows a definite effect of fine crystals, especially in the 0-75 μm range. It was found that both the proportion of fines present, and the size of these fine crystals had an effect.

5.3.1.2.1 Effect of Proportion of Fines

The strongest effect of the proportion of fine crystals occurred with fine crystals in the size range 0-75 μm (Figure 5.5). This figure shows that the onset of caking occurs much earlier for samples containing higher proportions of fine crystals. In the sample containing no fine crystals the onset of caking is not reached until a water activity of 0.65. In contrast, in the sample containing 100% fine crystals caking had started at a water activity of 0.43. Additionally, the sample containing 10% fine crystals acts more like the sample composed solely of fines than the standard sample.

In the sample containing slightly larger crystals, 75-150 μm , the effect of having 100% fines is the same. This is shown in Figure 5.6. The onset of caking for this sample is once again a water activity of 0.43, however, the curve does not increase as quickly, indicating the liquid bridge strength at each water activity is not as strong. Caking in the 10% sample may start slightly earlier than in samples containing less fines, however the difference is not significant enough to be conclusive. There is very little difference in the amount of caking occurring in samples containing 10, 1, 0.1 or 0 % fines.

There is less difference between the samples with larger 'fine' crystals, 150-212 and 212-315 μm fines, shown in Figures 5.7 and 5.8 respectively. Both these graphs show a small effect of particle size; the onset of caking in the 100% sample occurs at a water activity of 0.59, compared to 0.65 for all other samples. In addition, the differences between different mixtures in these two figures are not as obvious as those shown by the very small crystals in Figure 5.5.

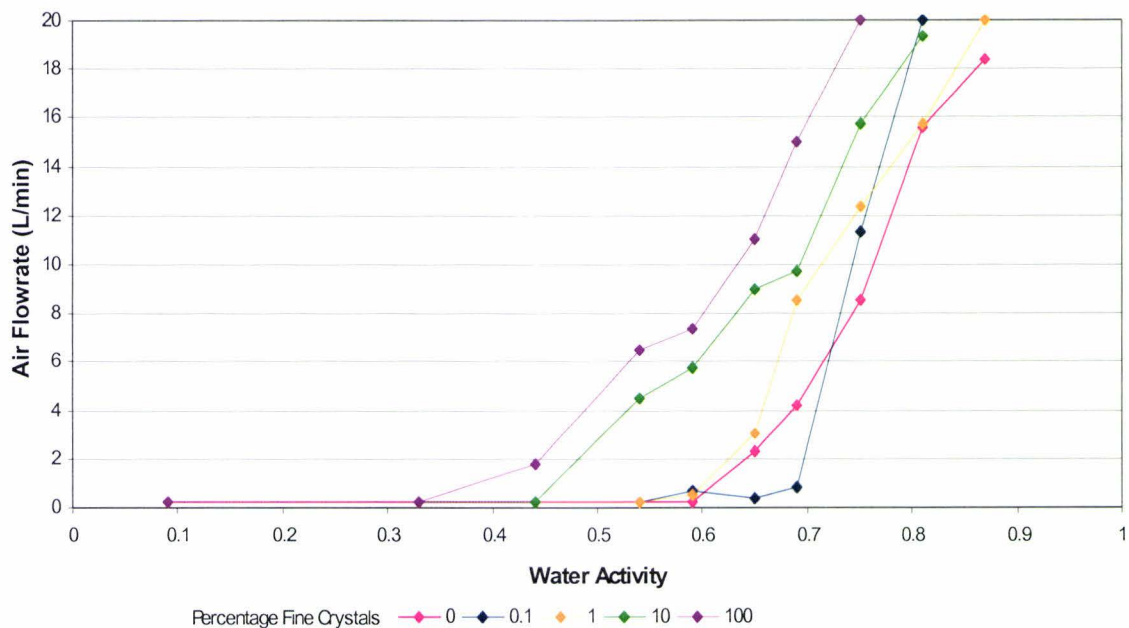


Figure 5.5 Airflow required to break liquid bridges in samples containing varying proportions of 0-75 μm crystals, mixed with 600-850 μm crystals

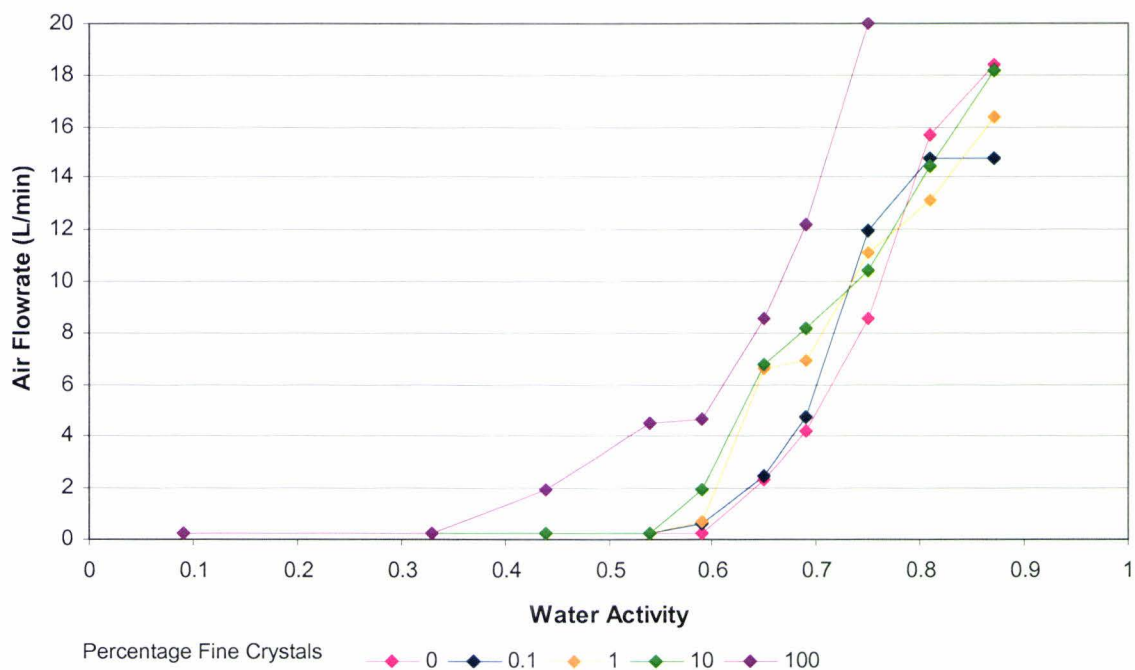


Figure 5.6 Airflow required to break liquid bridges in samples containing varying proportions of 75-150 μm crystals, mixed with 600-850 μm crystals

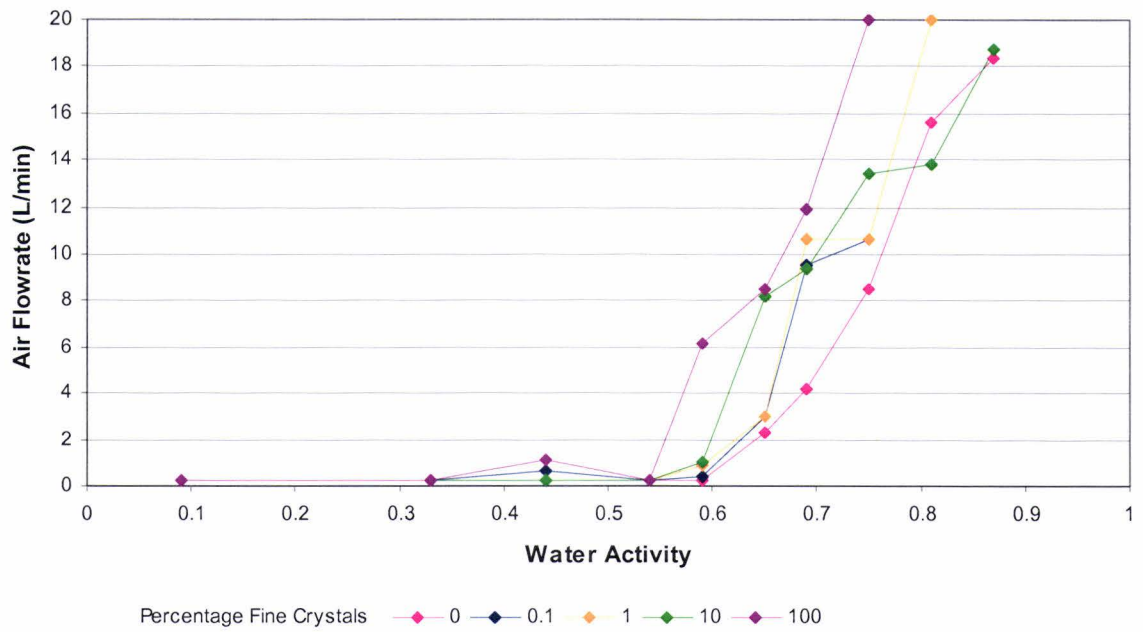


Figure 5.7 Airflow required to break liquid bridges in samples containing varying proportions of 150-212 μm crystals, mixed with 600-850 μm crystals

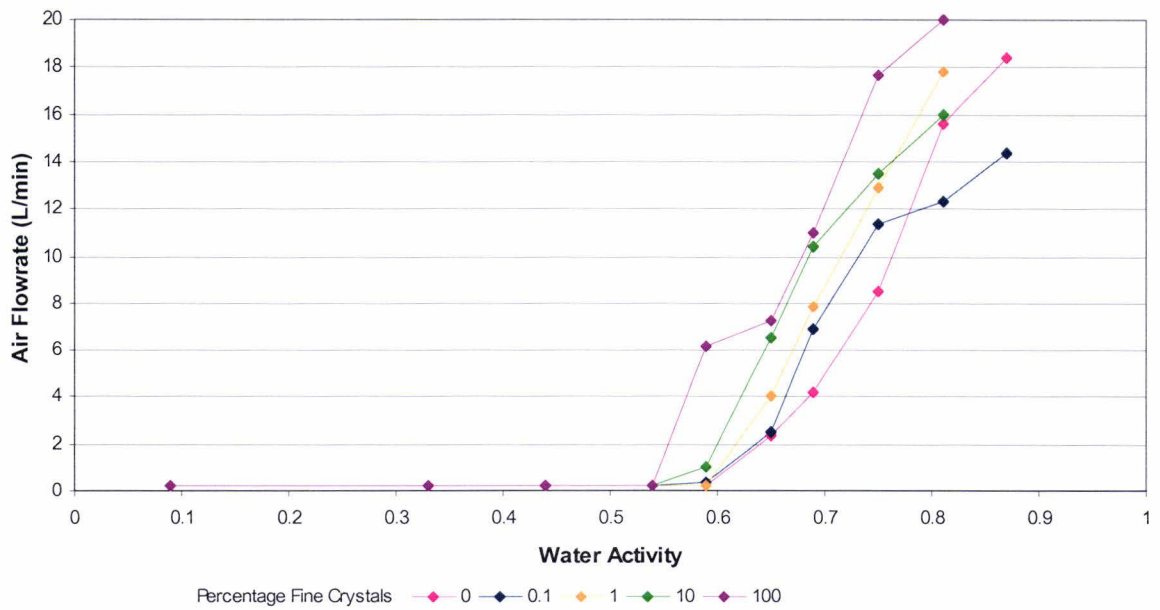


Figure 5.8 Airflow required to break liquid bridges in samples containing varying proportions of 212-315 μm crystals, mixed with 600-850 μm crystals

From these results it can be concluded that the proportion of fines does have an affect on caking, but this is also dependent on crystal size. This effect is very prominent in samples containing very small crystals, but there is less of an effect as the size of the 'fine' crystals increases.

All other plots are given in Appendix A2.

5.3.1.2.2 Effect of Size of Fine Particles

When the effect of particle size on the isotherm was measured it was found that there was an effect, however this was not as strong as the effect shown by the proportion of fines in the sample. In the sample containing only fines, shown in Figure 5.9, the biggest difference is seen between the fine particles and the standard sugar. There is a noticeable difference in the curve for 0-75 μm crystals compared to the larger crystals, however the difference between the three samples in the 75-315 μm range was insignificant.

The graph of the 10% sample, Figure 5.10, is similar, but the curves are shifted to the right, ie, caking does not occur until a higher water activity. There was less difference between the standard sized sugar and the samples mixed with 10% fines, than appears in samples containing 100% fines.

There is no effect found for samples containing less than 10% fine crystals.

All other plots are given in Appendix A2.

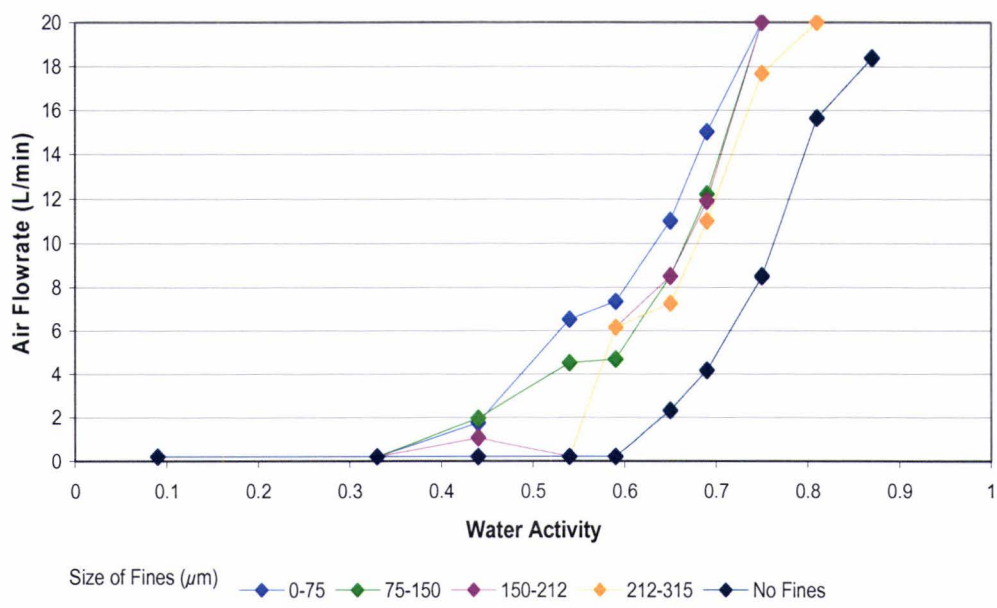


Figure 5.9 Airflow required to break liquid bridges in samples containing 100% fine crystals

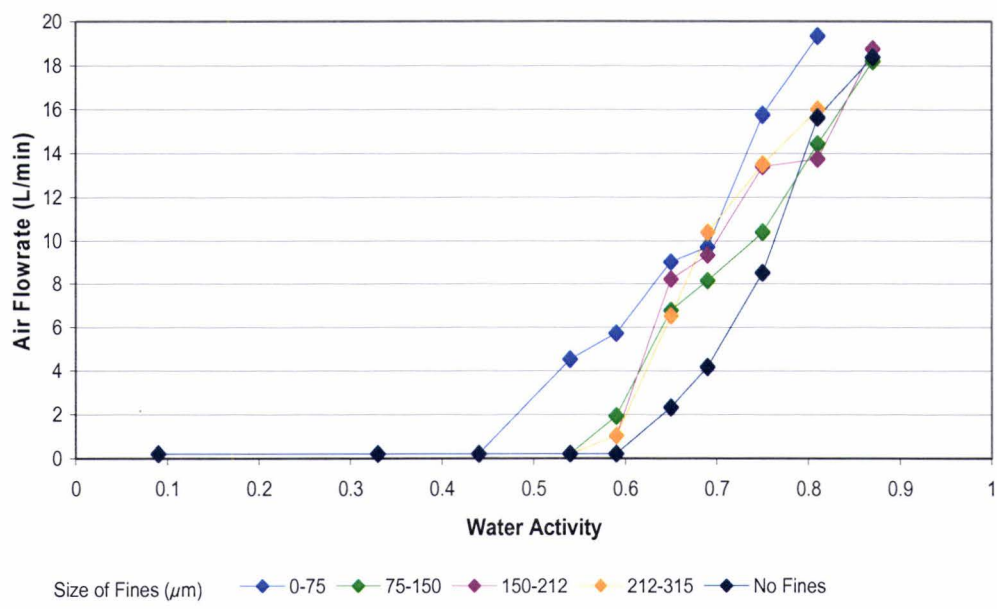


Figure 5.10 Airflow required to break liquid bridges in samples containing 10% fine crystals, mixed with 600-850 μm crystals

From these results it can be concluded that particle size does have an effect on caking but only for very small particles, below 150 μm , and when they are present in a high proportion.

It was also found that the blowtester is more sensitive to changes in caking than the friability test, and can be used to give a quantitative result, rather than just being qualitative.

With more samples smoother curves would be obtained and localised caking would have less of an effect on the results.

5.3.1.2.3 Comparison to Literature

Billings (2002) has also reported using the blowtest to measure caking in sucrose.

There is not a lot of difference between the standard sample in this test, and the results published by Billings, except the onset of caking occurred at a lower relative humidity in this study. This study found caking occurred at water activities between 0.65 and 0.75, compared to water activities of between 0.75 and 0.85 in the study by Billings. Samples at the higher water activities in this study had liquefied so bridging strength could not be measured. These differences are likely to be because samples were left longer to equilibrate in this study, so the whole bed was equilibrated, rather than just the top surface. This could mean the crystals below the surface are also bonding to the surface layers, which could mean a greater airflow would be needed to break the surface. Also in this study it was not possible to measure above 20 L/min due to the limits of the compressed air being used and the limits of the flowmeter. If higher flowrates could have been achieved, it might have been possible to get measurements for the samples that required an air flowrate greater at 20 L/min to break the powder surface.

5.3.1.2.4 Relationship Between Blowtester and Isotherm Measurements

It can be seen that the blowtester measurements are much more sensitive to particle size than the moisture content results in the isotherms. At a water activity of

approximately 0.81 the isotherm becomes exponential. The blowtester results however, show liquid bridging had started in the standard sample at a water activity between 0.59 and 0.70, becoming fully caked at a water activity of approximately 0.87. For fine sugar, 0-75 μm , caking starts at a water activity between 0.33 and 0.43 becoming fully lumped at a water activity of 0.75. These differences are probably due to the increased sensitivity and accuracy of the blowtest method. This measurement is a different type of force measurement – it measures the force required to dislodge a liquid or solid bridged particle from the surface. It has been seen that the blowtester showed differences in the caking strength in relation to the size and proportion of fines in a sample, but no significant differences in the moisture content were seen in the isotherms. This means that the increases in moisture content required for significant bridging to occur are virtually undetectable, and a very accurate method of measuring isotherms would be necessary to detect these changes.

5.3.2 Solid Bridging

5.3.2.1 Friability

The friability test was repeated for samples after solid bridges were formed by leaving the samples over P_2O_5 , under vacuum for seven days. It was found that the results were very similar to those obtained in the liquid bridging experiments, however there were some minor differences. Firstly, the 100% 0-75 μm sample became fully caked at a lower water activity. Also, the onset for caking of the 100% 75-150 μm sample occurred at a lower water activity, but this sample still became fully caked at the same point.

Plots are given in Appendix A2.

5.3.2.2 Blowtester

The results of the solid bridging experiment for the blowtest are similar to those found in the liquid bridging section. However, there are some differences including that the airflow required to break the solid bridges at the same water activity is greater than

that required to break liquid bridges. This is to be expected and confirm the work of Billings (2002) who found the same trend. For example, in the 0-75 μm sample, shown in Figure 5.11, caking has already begun at a water activity of 0.33 and the sample reached the limit of the blowtester at a water activity of 0.69. Conversely in the liquid bridging section caking wasn't detectable until a water activity of 0.45, and the limit was reached at a water activity of 0.75. Other samples reached the limit at a water activity between 0.7 and 0.8. This compares to a water activity between 0.8 and 0.9 found in the liquid bridging experiments.

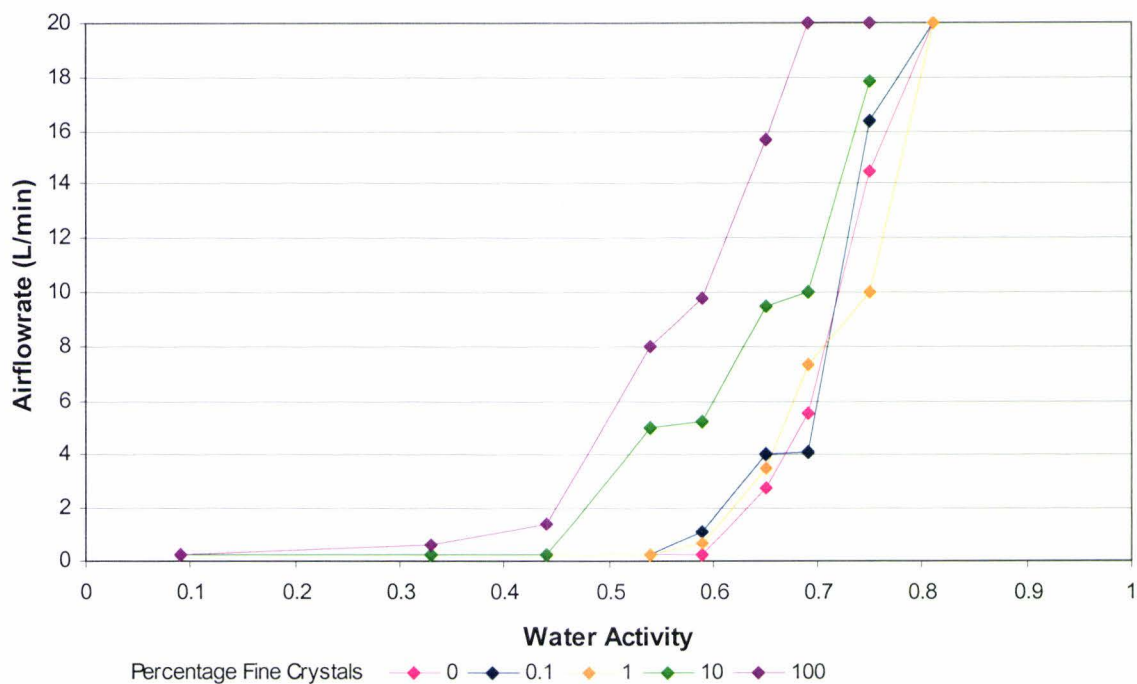


Figure 5.11 Airflow required to break solid bridges in samples containing varying proportions of 0-75 μm crystals, mixed with 600-850 μm crystals

In addition, the solid and liquid bridge strengths are related to each other by a straight line as shown in Figure 5.12. This also shows that the solid bridges are stronger than liquid bridges.

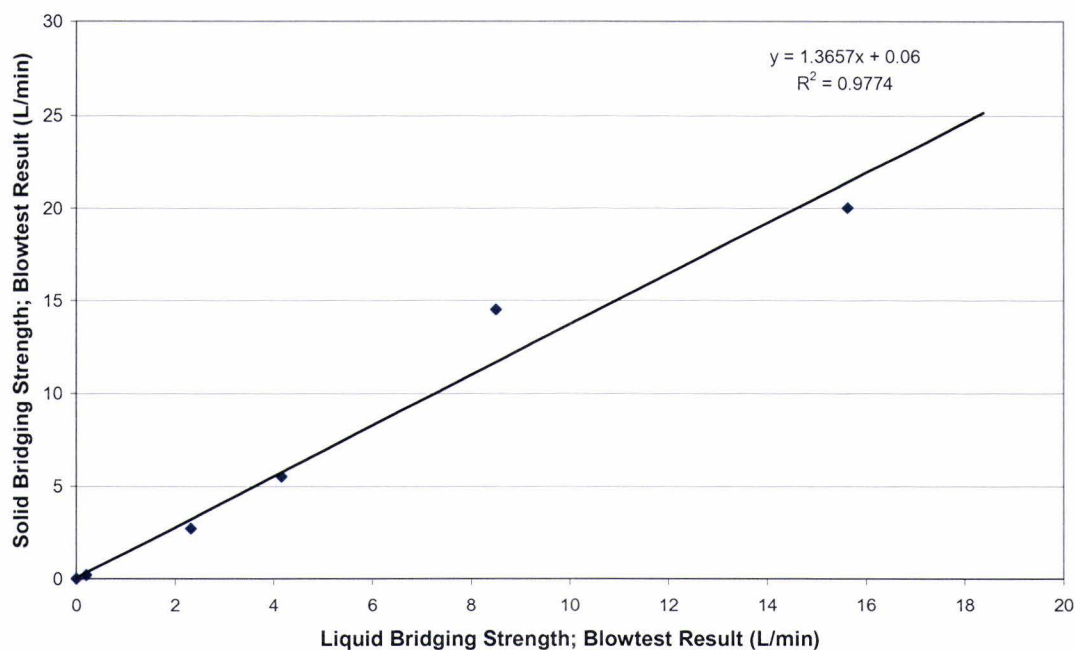


Figure 5.12 The relationship between the solid and liquid bridges for standard sugar

5.3.3 Kelvin Radius

The relationship between the Kelvin radius and water activity is given by equation 5.1 (page 5-2), and is also shown below in Figure 5.13.

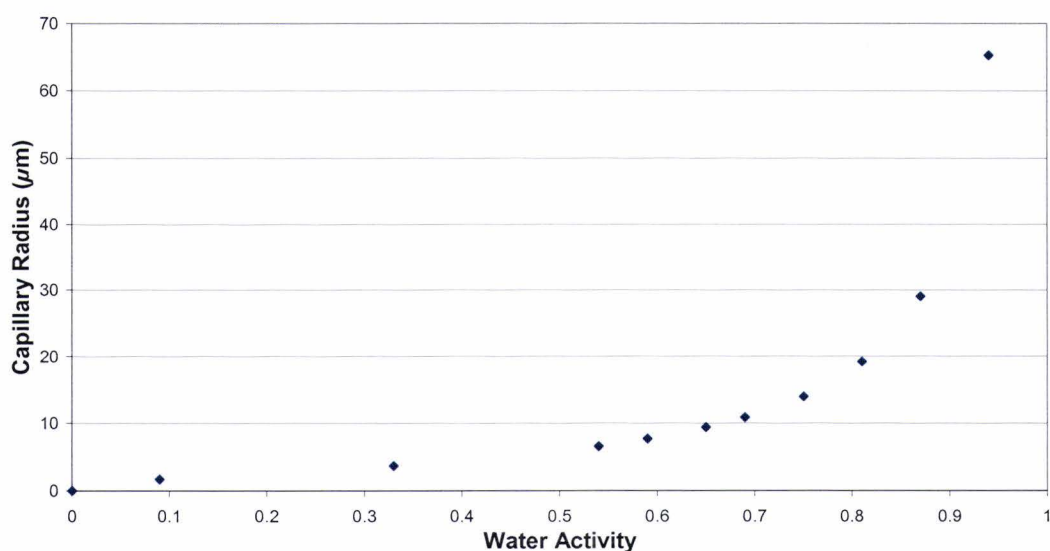


Figure 5.13 Capillary radius vs water activity at 20 °C

The critical Kelvin radius at which caking would occur, can be determined for different samples by plotting the airflow required to break bridges using the blow test, against the capillary radius (see Figure 5.14). The graph can be split into two distinct linear sections, in the first flat section, the crystals are absorbing water, then capillary condensation starts to occur, and the slope of the graph increases dramatically. Two trendlines were applied to this data, as shown in Figure 5.14, and the intercept found by solving the equations simultaneously. This is the critical Kelvin radius. The Kelvin equation can then be applied to find the water activity this is equivalent to.

Due to the nature of the data obtained in the liquid and solid bridging experiments it is only possible to find the Kelvin radius using the results from the blowtest, but not the friability test. For many of the friability samples there are no data points for friabilities between approximately 45° and 90°, which is where capillary condensation is occurring. This means the two trendlines are almost parallel, as shown in Figure 5.15, and therefore not useful. The samples that do have data points in the capillary condensation range have only one, or occasionally two, points in this range, which means any results that are obtained are not likely to be accurate.

The capillary radius verses airflow needed to break the liquid bridges formed in a sample of standard sugar is shown below in Figure 5.14. The critical Kelvin radius for this sample was found to be 8.3 μm, which is equivalent to a water activity of 0.61.

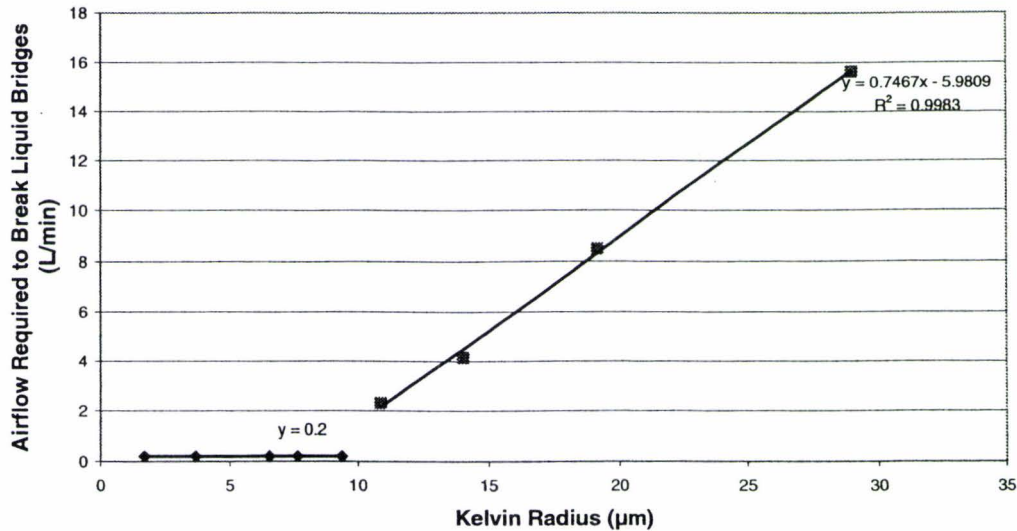


Figure 5.14 Kelvin radius vs airflow required to break liquid bridges in standard sugar

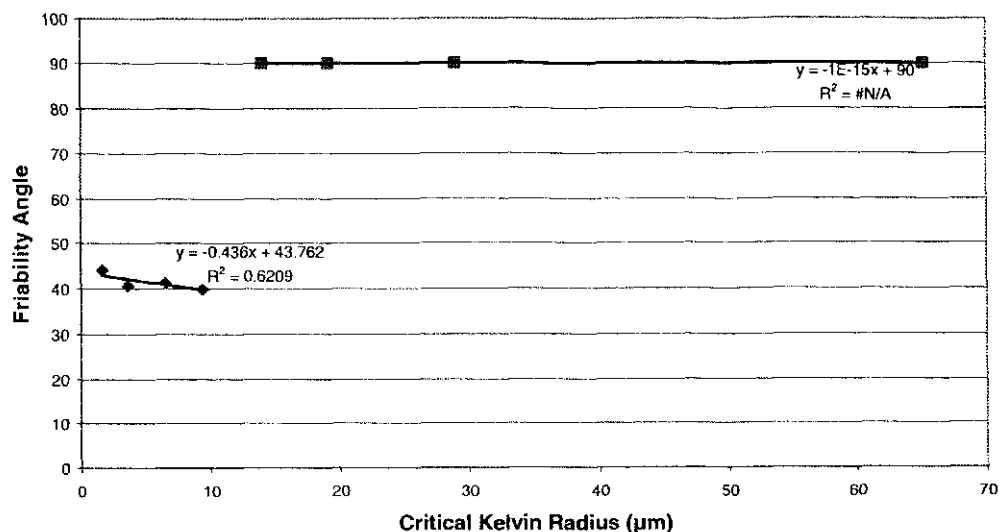


Figure 5.15 Kelvin radius vs friability angle required to break liquid bridges in standard sugar

The critical Kelvin radius and water activity are dependent on both particle size, and proportion of fine crystals in the sample. Figure 5.16 shows the capillary radius verses the airflow required to break the liquid bridges in a sample of 75-150 μm sugar. The critical Kelvin radius for this sample was found to be 3.9 μm , which is equivalent to a water activity of 0.36. This Kelvin radius is less than half that of standard sugar.

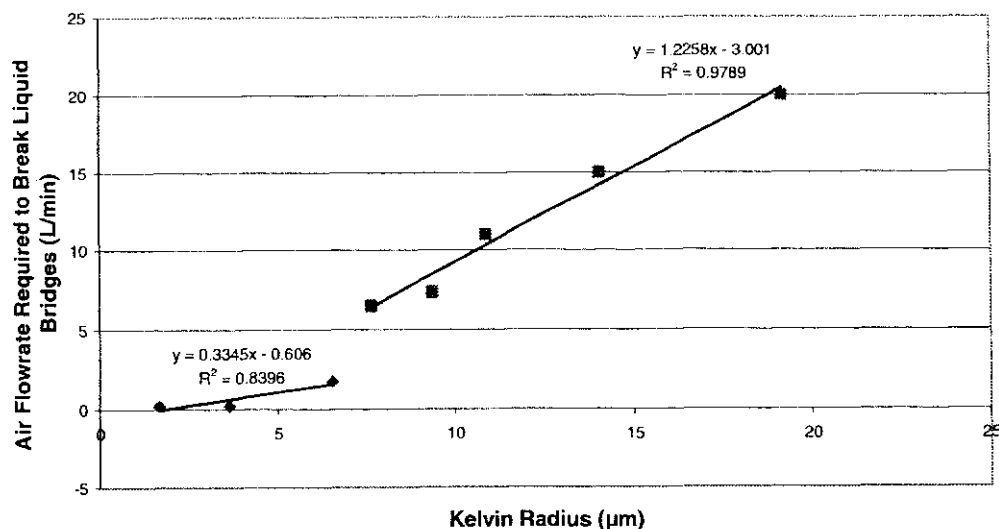


Figure 5.16 Kelvin radius vs airflow required to break liquid bridges in 100% 0-75 μm sample

This analysis was repeated for the solid bridging samples. A summary of the results is shown below in Table 5.1. It can be seen that the critical Kelvin radius is similar for both the liquid and solid bridging experiments. The differences between liquid and solid bridging for most of the samples was less than 1 μm , however, there were two samples that where the differences were significantly more than this – the 0.1% 0-75 μm liquid bridging sample was 12.4 μm , compared to 7.4 μm for the solid bridging, and the 0.1% 150-212 μm was 4.5 μm compared to 8.6 μm for the liquid bridging. These unexpected differences are probably due to localised caking in samples, and the actual critical Kelvin radius is expected to be approximately to 8 μm , similar to the standard sugar sample, since tests have shown there was no effect when only 0.1% fine particles were present. It is expected that the critical Kelvin radius for both liquid and solid bridging would be the same because it is a measure of where caking starts, rather than how strongly caked the samples are.

Percentage of Fine Crystals (%)	Size Range of Fine Crystals (μm)	Liquid Bridging		Solid Bridging	
		Kelvin Radius (μm)	Water Activity	Kelvin Radius (μm)	Water Activity
100	600-850	8.3	0.61	7.5	0.58
	0-75	3.9	0.36	5.5	0.48
	75-150	5.3	0.47	5.0	0.44
	150-212	5.4	0.47	5.4	0.48
	212-315	6.7	0.55	6.3	0.53
10	0-75	3.0	0.26	3.8	0.35
	75-150	6.0	0.51	4.6	0.42
	150-212	6.0	0.51	5.1	0.45
	212-315	6.7	0.55	5.9	0.51
	0-75	8.5	0.62	7.7	0.59
1	75-150	6.5	0.54	6.5	0.54
	150-212	6.8	0.55	6.1	0.52
	212-315	4.2	0.38	3.9	0.36
	0-75	12.4	0.72	7.6	0.59

75-150	7.4	0.58	8.7	0.63
150-212	8.6	0.63	4.6	0.41
212-315	11.0	0.69	8.4	0.62

Table 5.1 Critical Kelvin radiuses and water activities for different samples

These values for the critical capillary radius are less than those found by Billings (2002). This is because of differences in the results obtained for the blowtest. These differences could have been caused by the different equilibrium times which samples were subjected to in order to form liquid and solid bridges, Billings left samples one, two and three days to equilibrate and form liquid bridges, then exposed these samples to ambient conditions to overnight in order to form solid bridges. In comparison, in this test samples were left four weeks to equilibrate and form liquid bridges, then were left for one week over P_2O_5 , under vacuum, to ensure liquid bridges dried out. The ambient air at New Zealand Sugar was measured to be between 40 and 60 % relative humidity most days, which is too high to dry samples. Alternately, these differences could be because it was not possible to measure airflow above 20 L/min in this study, meaning the solid bridging curves are possibly not as steep as they would be if this data were obtained. This in turn, means the intercept of the solid and liquid bridging lines may seem to occur at a lower Kelvin radius than it would have otherwise.

These differences show that the size of crystals in the sample does have an effect on caking. In order to determine how strong this correlation was a graph was drawn of the critical Kelvin radius vs the average particle size of the fines, where the average particle size was calculated by using laser diffraction particle size analysis (described in detail in Section 6.2.3) on the fine crystals in the samples. The methodology for this calculation is given in Appendix A4, page A-13. This graph is shown in Figure 5.17 for liquid bridging and Figure 5.18 for solid bridging.

A trend line was then fitted to each set of data. The formula of this line, and R^2 are given in Table 5.2. It can be seen that there is a strong correlation between the particle size and critical Kelvin radius for samples containing both 100% and 10% fines, but not for samples with a lower proportion of fines than this. This again shows

there is a definite effect of particle size on caking. The increase in the critical Kelvin radius with increasing particle size indicates that when there are a greater proportion of smaller particles present capillary condensation starts to occur at a lower water activity. This is probably because of the increased number of contact points. It is recommended these tests be repeated with crystals approximately the same size as the Kelvin radius to confirm this theory. This means all the pores will be full of water when the critical Kelvin radius is reached. In addition, there is also an effect of the proportion of fine crystals. From the results shown in Figures 5.17 and 5.18, the minimum proportion of fine crystals required to affect caking will be between 1 and 10%. In both figures the first four data points for the 1% samples appear to decrease; however, this is unlikely to be a real effect. The tests that have been carried out in earlier sections showed there was very little difference between the bridge strength of samples containing 1% fines and samples containing no fine particles. The apparent downward trend of these samples is probably due to experimental error.

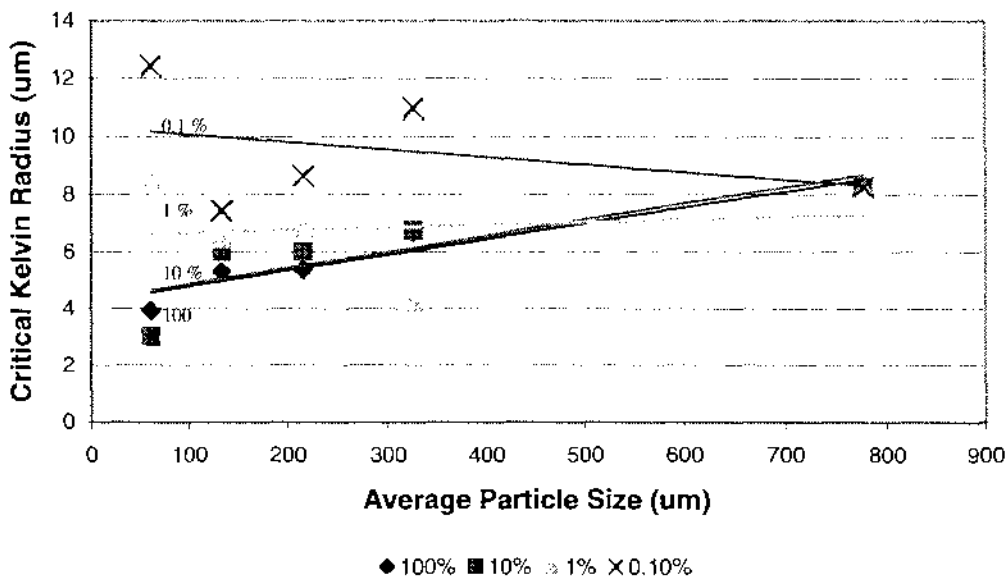


Figure 5.17 Kelvin radius, calculated from liquid bridging data, vs average particle size of fine crystals for samples with varying proportions of fine crystals

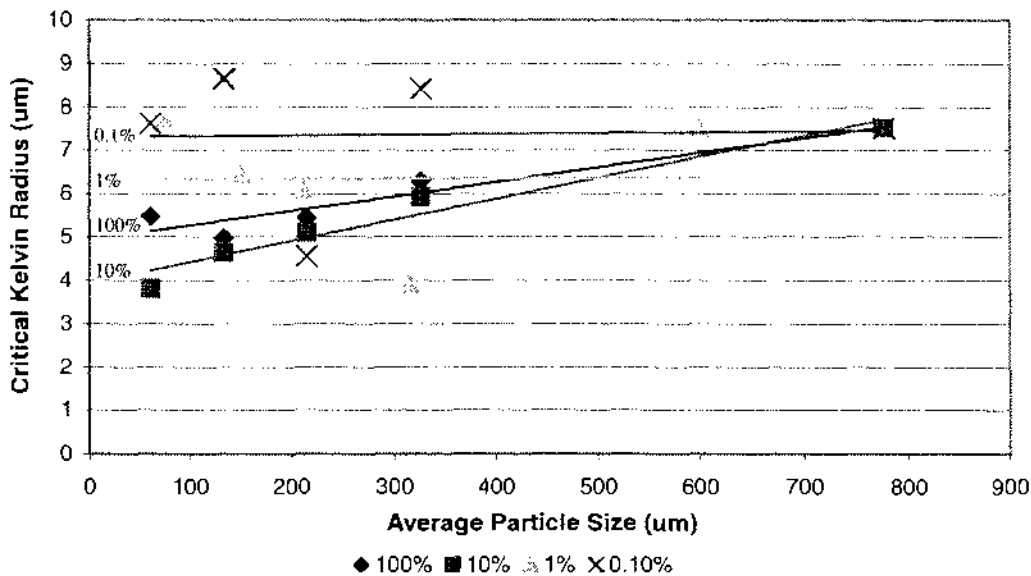


Figure 5.18 Kelvin radius, calculated from solid bridging data, vs average particle size of fine crystals for samples with varying proportions of fine crystals

	Percentage Fine Crystals (%)	Formula	R ²
Liquid Bridging	100%	$y = 0.0056x + 4.2264$	0.9065
	10%	$y = 0.0057x + 4.2946$	0.7055
	1%	$y = 0.0009x + 6.5834$	0.0213
	0.1%	$y = -0.0026x + 10.336$	0.1237
Solid Bridging	100%	$y = 0.0034x + 4.9187$	0.9026
	10%	$y = 0.0049x + 3.929$	0.9517
	1%	$y = 5 * 10^{-5}x + 6.3392$	0.0001
	0.1%	$y = 0.0002x + 7.303$	0.0010

Table 5.2 Correlation between size of ‘fines’ and critical Kelvin radius

5.4 Conclusion and Recommendations

In this study both the friability and the blowtest were used to measure caking strength. It was found that the blowtest was a lot more sensitive than the friability test, and is therefore more useful in this work. It could be used to give a quantitative result for the onset of caking, which could then be used to relate to the Kelvin radius.

The friability test showed a small difference in flowability for the samples containing 100% 0-75 and 75-150 µm crystals, but no effect by any other sample. The blowtest, however, showed a definite effect of both particle size and proportion of fine crystals. This was strongest in the 100% and 10% 0-75 µm samples, and 100% 75-150 µm samples, but there was also a small effect of the proportion of fine crystals shown for sample containing larger ‘fines’. This means fine crystals do affect caking.

The Kelvin radius is a useful parameter because it can be used to determine the exact water activity at which caking occurs. It was found that the critical Kelvin radius, the radius of the capillary that would be fill of water at the onset of caking, decreased with decreasing particle size. This indicates the likely mechanism for caking is the

capillary condensation theory, and the Kelvin radius decreases because there are more contact points between particles.

It is recommended that these tests be repeated with crystals of approximately the same size as the critical Kelvin radius, up to 10 μm in radius. This means at the onset of caking all pores will be full of water due to capillary condensation; therefore, a stronger effect on both the isotherms and caking tests should be seen. It is also recommended that more data is generated in 1% to 10% fines range, using the blowtest and Kelvin radius calculation. This will allow the determination of the level of fines critical for caking.

Compaction and settling of the bulk sugar will lead to an increased number of contact points, which will theoretically lead to increased caking. It is therefore recommended the effect of compaction and settling on caking be studied.

The next chapter will identify where fine crystals are being formed in the manufacturing process.

Chapter 6

- Size Analysis -

6.1 Introduction

Although a lot of research has been carried out to determine the extent to which attrition is occurring in pneumatic transportation of solid state powders (Kalman, 1999; McLeod, 2002), there has been very little published relating to solid phase transport.

The New Zealand Sugar Company uses both screw conveyors, and redler chain conveyors to move crystalline sugar through the factory. It is thought that screw conveyors cause more crystal damage, but to date no studies have been conducted to test this theory.

The purpose of the size analysis is to determine where in the process fines are created and to form a definition for both 'fines' and 'normal' crystal size. This chapter will also compare conveying systems and determine if significant damage is occurring.

6.1.1 Different Methods for Describing Particle Size

Particle size is one of the most important physical properties used to describe a powder. However, there are many different ways of estimating particle size. This is because the only shape that can be uniquely defined by its diameter is a sphere, whereas in practice most particles are irregularly shaped. One of the most common

methods of describing particle size is to derive the diameter of a sphere with an equivalent volume. However, there are still many different properties that can be measured, for example Feret's diameter, Figure 6.1a, the length of the particle measured at random along a given line, or Martin's diameter, Figure 6.1b, the length of a theoretical horizontal line splitting the particle into two equal areas. Another way to report the diameter is to calculate the diameter of a circle containing the same area, as shown in Figure 6.1c, or to calculate the diameter of a sphere with the same volume (Kousaka & Okuyama, 1991; Perry & Green, 1997). For this reason it is only possible to compare powder measurements taken using the same method.

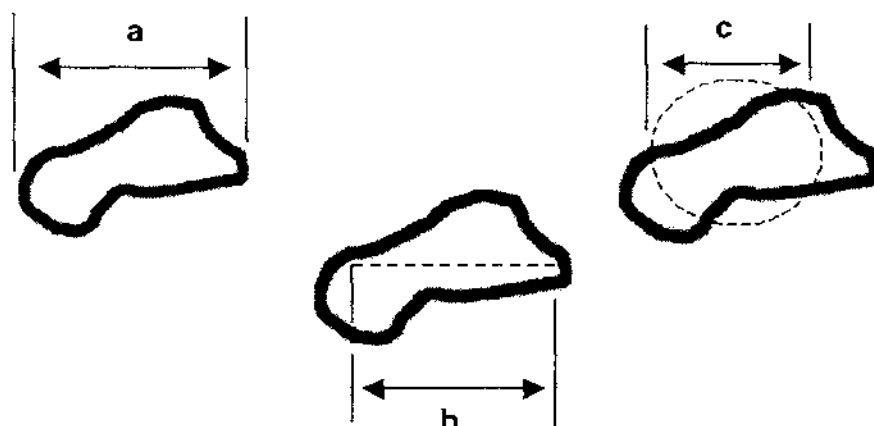


Figure 6.1 Different methods of reporting the diameter of a particle

a) Ferret's diameter b) Martin's diameter c) Diameter of an equivalent sphere

6.1.2 Different Parameters Used to Estimate Average Particle Size

There are also a number of different calculations used to measure the average particle size. The most common estimations are the mean, median and mode of the data. The first of these, the mean particle size, is the arithmetic average of all the data. There are a number of different means, some of which are discussed below. The median is the value at which 50% of particles are larger and 50% smaller. The mode is the value that occurs most commonly.

If data has a perfect normal or gaussian distribution these parameters will all be exactly the same, as shown in Figure 6.2a. However, if the distribution is bimodal, such as that shown in Figure 6.2b, this is not the case. As the figure shows, the mean is between the distributions, even though there are no particles of this size. The median is in the higher of the two distributions, dividing the whole data set exactly in two. The mode is at the top of the higher curve.

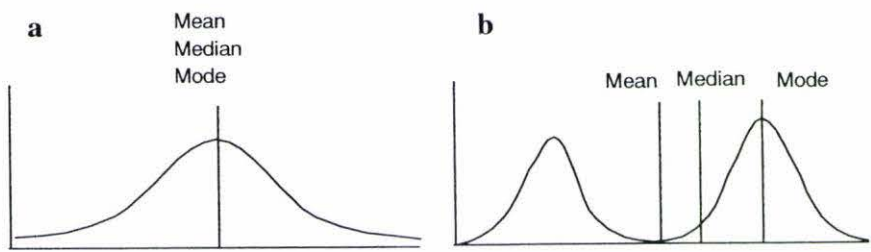


Figure 6.2 a) Normal distribution b) Bimodal distribution

6.1.2.1 Mean Particle Size

There are many different methods for calculating the mean particle size. For example, to calculate the mean size of three spheres with diameters 1, 2 and 3 units, the number-length mean particle size, $D[1,0]$ could be calculated using equation 6.1:

$$D[1,0] = \frac{\sum d}{n} = \frac{1+2+3}{3} = 2.0 \qquad \text{Equation 6.1}$$

where d is the diameter and n is the number of particles. However, this requires knowledge of the number of particles present, which is not always possible.

In industry the most widely used definitions are the equivalent volume mean diameter, $D[4,3]$, equation 6.2, and the equivalent surface area mean diameter, $D[3,2]$, equation 6.3, which is also known as the Sauter mean diameter (Kousaka & Okuyama, 1991). Both these mean diameters are determined by a laser diffraction analysis. They are calculated as follows:

$$D[4,3] = \frac{\sum d^4}{\sum d^3} = \frac{1^4 + 2^4 + 3^4}{1^3 + 2^3 + 3^3} = 2.72 \quad \text{Equation 6.2}$$

$$D[3,2] = \frac{\sum d^3}{\sum d^2} = \frac{1^3 + 2^3 + 3^3}{1^2 + 2^2 + 3^2} = 2.57 \quad \text{Equation 6.3}$$

The following formula is used to calculate the mean particle size in a sieve analysis:

$$X_p = \frac{1}{\sum \frac{M_i}{X_i}} \quad \text{Equation 6.4}$$

where M_i is the mass of powder caught by sieve i , and x_i is the geometric mean of sieves i and $i-1$, the larger sieve through which the powder passed.

There are also many other techniques which are equally accurate in estimating particle size, for example the number-surface area mean particle size, or the number-volume mean particle size (Kousaka & Okuyama, 1991; Perry & Green, 1997).

6.1.3 Sieve Analysis

Sieving involves shaking a powder through a series of sieves with different sized apertures. The smaller the particles, the more sieves it passes through. This method measures the Sauter mean diameter of the particles. The size of powders which can be analysed using this method, range from 2000 μm down to 50 μm ((Gee & Bauder, 1986), cited in Eshel *et al.* (2004)). Furthermore, wet sieving in water or alcohol can be used for particles smaller than this and is useful down to 10 μm (Allen, 1975).

Sieving is one of the oldest methods of analysing particle size, yet is still one of the most commonly used. Products in which sieving is regularly used include cereals such as malt (Schwarz *et al.*, 2002) or oats (Doehlert *et al.*, 2004), soils ((Gee & Bauder, 1986), cited in Eshel *et al.* (2004)), pharmaceutical powders (Abou-Chakra *et al.*, 2003) and sugar, for example for in-process tests at New Zealand Sugar.

The main advantages which make sieving an attractive option include that it is fast, simple and relatively inexpensive (Rhodes, 1998).

There are also many disadvantages to this method. Fortunately, some of them, such as the large sample size required and not being able to measure sprays or emulsions (Seville *et al.*, 1997) are not relevant to this project. However other factors are, for example, dry powders under 38 μm are very difficult to analyse by sieving (Allen, 1975) because of static electricity effects. Also, a time weight distribution is not produced, because sieving measures the second largest dimension (Allen, 1975) and furthermore, errors can be caused by material cohesiveness (Laitinen *et al.*, 2002). Despite all these disadvantages sieving is a useful method of analysis in this project.

6.1.4 Laser Diffraction

Laser diffraction offers a volume-based distribution. For instance, if 12% of the distribution is in the size category 6.97 – 7.75 microns, this means the total volume of all particles with diameters in this range represents 12% of the total.

Laser diffraction works by measuring the forward diffraction of a laser beam to estimate the particle size. This works because the angle of diffraction is inversely proportional to particle size. Furthermore the intensity of the diffracted laser beam at any angle is a measure of the number of particles with a specific cross-sectional area in the beams length (Eshel *et al.*, 2004). This scattering pattern is captured using an optical unit made up of many individual detectors (Seville *et al.*, 1997).

In order to transform this data from a diffraction pattern into particle-size data, several assumptions are made (Perry & Green, 1997), in the form of either the Fraunhofer or Mie Theories. The first of these assumes that the laser beam is parallel and the detector is at a distance far greater than the size of the diffracting particle. It also assumes that there is only forward scattering, ie, light is not deflected by more than one particle. Furthermore, all interference is assumed to be smaller particles, leading

to additional peaks (*Malvern Website*, 2005). The latter theory, the Mie Theory, is a solution of Maxwell's equations, a set of four fundamental equations describing the behaviour of electric and magnetic fields (Eshel *et al.*, 2004). The Mie Theory provides a solution for the case of a plane wave on a homogeneous sphere of any size. It also takes into account transmission through the particle; therefore, the refractive index needs to be known (Eshel *et al.*, 2004).

These assumptions mean the Fraunhofer theory is simple and easy to calculate, but not as accurate as the Mie theory. It is a good approximation for particles greater than 50 μm . In comparison, the Mie Theory offers an exact solution to scattering of light from a homogeneous sphere, but not from an irregularly shaped particle (*Malvern Website*, 2005). A combination of these two theories is used by the Malvern Mastersizer 2000, the laser diffraction analyser used in this study.

Laser diffraction is capable of measuring particles down to a size of approximately 1 μm (Kousaka & Okuyama, 1991). This means it has applications in many industries including the sugar industry.

Many advantages of laser diffraction have been reported. Firstly the ease of operation (Perry & Green, 1997; Laitinen *et al.*, 2002) and short time needed for analysis, each sample takes only a few minutes to analyse (Eshel *et al.*, 2004), therefore, this method is useful for in-process testing. Also, only a small sample is needed, $\leq 1\text{g}$ (Eshel *et al.*, 2004), allowing this method to be used for valuable powders. In addition, the reproducibility of results (Perry & Green, 1997; Laitinen *et al.*, 2002; Eshel *et al.*, 2004) and the wide range of size fractions into which the entire range of particle sizes can be divided (Eshel *et al.*, 2004), mean this method is valuable in research.

The main disadvantage of laser diffraction is the high cost of the instrument (Eshel *et al.*, 2004). Another disadvantage is that it is important to know other properties of the powder such as the density and refractive index.

6.1.5 Comparison of Sieving and Laser Diffraction

Sieving and laser diffraction are both useful methods for describing particle size, however it is important to note that they are not measuring the same dimensions. Sieving measures the second largest dimension of the particle and gives a mass percentage, whereas laser diffraction measures the volume of the particle and thus gives a volume percentage.

Abou-Chakra *et al.*, (2003) compared sieving to laser diffraction for the same samples and found that the methods were sufficiently different to give two different conclusions. They found sieving resulted in a coarser particle size distribution than laser diffraction analysis. This demonstrates that it is important to know the method that is being used, and the limitations of that method.

Of these two methods, sieving is the most useful for samples that contain a wide particle size distribution; firstly, because a large sample is used, so it is easier to get representative results, and secondly because samples are split into their different size fractions, which could then be used in further experiments. However, for samples containing only fine particles, laser diffraction is more appropriate because the instrument is capable of splitting these samples into a lot more different size fractions.

6.2 Experimental

6.2.1 Materials

Samples of dry sugar crystals were taken from around the plant. These sample points are shown in Appendix A3 (page A-8). Where possible samples were taken before and after every screw conveyor, redler and bucket conveyor. In order to get representative samples, sugar was taken as it fell from the end of the conveyor if this was feasible, as recommended by Allan (1975). In situations where this was not possible the equipment was stopped and a grab sample was taken. These samples

were then analysed by sieve analysis. This allowed the level of fines in the plant to be accessed.

There are many variables because sugar refining and drying is an industrial process. One of the main reasons for differences in particle size between samples is due to the crystallisation process, which is a batch process. This means no two batches will have identical particle size distributions. These batches are mixed together as the sugar crystals are dried, then left to condition for up to 18 hours in the silo. Therefore, it is impossible to get an entire series of samples from the same batch.

After sugar crystals are dried and conditioned they are graded into different products dependent on the crystal size. The approximate size distributions of these products are:

- Manufacturers >850 μm
- Standard 1A sugar 300 – 850 μm
- Caster <600 μm
- Fines Free Caster 180-600 μm

It should be noted the product packaged as ‘standard white sugar’ is known as 1A sugar at New Zealand Sugar. In this study it will be referred to as ‘standard 1A sugar’ to avoid confusion with the ‘standard’ sugar (600-850 μm) used in previous chapters.

To determine if the attrition occurring was greater for a screw conveyor or redler, a series of samples were taken before and after a standard sugar redler and standard sugar screw. These two conveyors contain the same size sugar, but are different lengths. In order to compare two screws of equal lengths, the analysis was repeated using the caster screw and standard 1A sugar redler, after the sugar crystals are graded. The approximate time the sugar spent in each conveyor was calculated (given in Appendix A4, page A-9), to eliminate batch variations. It was not possible to do this for the packing screw because of the time taken to walk from one end to the other was much greater than the time the sugar spent in the screw, but the time between samples was kept to a minimum. These sample points are shown in the Appendix A3 (page A-8).

To determine if the loading of the conveyor had an effect on attrition, additional samples were taken with less sugar running through the conveyor. During processing this would occur only for a few seconds during start-up and shut-down, or if the graders were run slower. In order to take these samples the vibrational amplitude of the grader feeders was decreased. This meant less sugar was going through the graders and therefore less through the conveyors that follow.

6.2.2 Sieving

Sieving has been used as a method for determination of particle size distribution for many years. It has a low initial capital cost and is easy to carry out, however it is important that parameters such as shaking time and force are standardised. In order to achieve this, a mechanical shaker was used.

Samples were taken before and after every unit operation under normal operating conditions and sieved to develop a picture of the size of particles present at different stages in the process.

The standard sieve series increases by the fourth root of two for each sieve. For the experimental part of this work every second sieve in the series was used. These sieves were:

- Caster and Fines Free Caster 600, 425, 300, 215, 106, 75, 53 μm
- Standard 1A 850, 600, 425, 300, 215 μm
- Manufacturers 1700, 1180, 850, 600, 425 μm

The samples obtained from around the factory contained approximately 200g of sucrose. These samples were halved using a riffle sampler then one of these 100g samples was poured into the top sieve. The sieves were then placed on the shaker and shaken for exactly ten minutes. Each sieve was re-weighed and the amount of sugar determined. The particle size distribution was then calculated.

6.2.3 Laser Diffraction

Laser diffraction allows a more detailed, and highly accurate analysis of particle size to be obtained. The objective of doing this is to get a more complete picture of the particle size changes around the plant and to compare the differences in results obtained from sieving and laser diffraction. Laser diffraction was also used to determine the actual distribution of the crystals used in the caking tests and isotherms in the previous chapters.

Samples of the white crystalline sugar products produced at the New Zealand Sugar Company, and the samples used in the isotherm and caking experiments were analysed using laser diffraction. The sugar products analysed were manufacturers sugar, standard sugar, caster sugar and fines free caster sugar. The samples used in the isotherm and caking experiments were samples of 0-75 μm , 75-150 μm , 150-212 μm , 212-315 μm , and 600-850 μm sugar obtained by sieving.

Analysis was carried out at the Fonterra Research Centre in Palmerston North using a Malvern 2000 Longbed particle size analyser and free-fall feeder.

6.2.4 Bulk Density

Bulk density is a measure of how tightly a material packs together. It can be defined as the mass divided by the volume occupied by the material.

The purpose of measuring the bulk density is to determine how the sucrose particles pack together, and to determine the effect this has on the isotherm. It is expected that the bulk density of smaller particles will be less than that of larger particles, while the bulk density of samples with a large size distribution will be greater than samples composed of particles of a similar size.

The bulk density can be measured as poured bulk density or tapped bulk density. The first of these, poured bulk density, is determined by allowing the powder to settle in a container under gravity, whereas the latter, tapped bulk density, is determined by tapping the container holding the sample, which results in improved packing conditions (Abdullah & Geldart, 1999). The latter is a better simulation of what condition the sugar is in after packaging.

The exact volume of the container needs to be known. This was determined by weighing the dry container, filling with water and reweighing. The temperature was measured and density tables used to calculate the volume.

6.2.4.1 Poured Bulk Density

To determine the poured bulk density, sugar was very gently poured into a container with a measured volume of 74.20 cm^3 . The top was levelled using a ruler and the sample weighed. This was repeated until three measurements agreed, then the average of these measurements was determined.

6.2.4.2 Tapped Bulk Density

The same container that was used to determine poured bulk density was also used to find the tapped bulk density. This container was filled to approximately the one-third mark, then tapped 100 times to settle the sugar. More sugar was poured in; up to the two-thirds mark, then the whole sample tapped again. This was repeated until the container was full. The top was levelled using a ruler and the sample weighed. This was repeated until three measurements agreed, then the average of these three measurements was found.

6.3 Results and Discussion

The samples taken from the plant were analysed using a sieve analysis. It was found that the variation between batches in the plant was much greater than the differences caused by conveying, so the results from this could not be used to quantify the effects of different types of conveying systems. The results could, however, be used to give an idea of the amount of fine crystals present at different stages in the plant.

The results from this analysis are given in the Appendix.

6.3.1 Size of Different Products

Figure 6.3 below shows the particle size distributions for the different products produced at NZ Sugar, analysed by sieve analysis. It can be seen that manufacturers sugar has the largest crystal size, followed by standard 1A sugar with caster being the smallest. Fines free caster is very similar in shape to caster sugar, but has a slightly larger average particle size because the fine crystals have been removed.

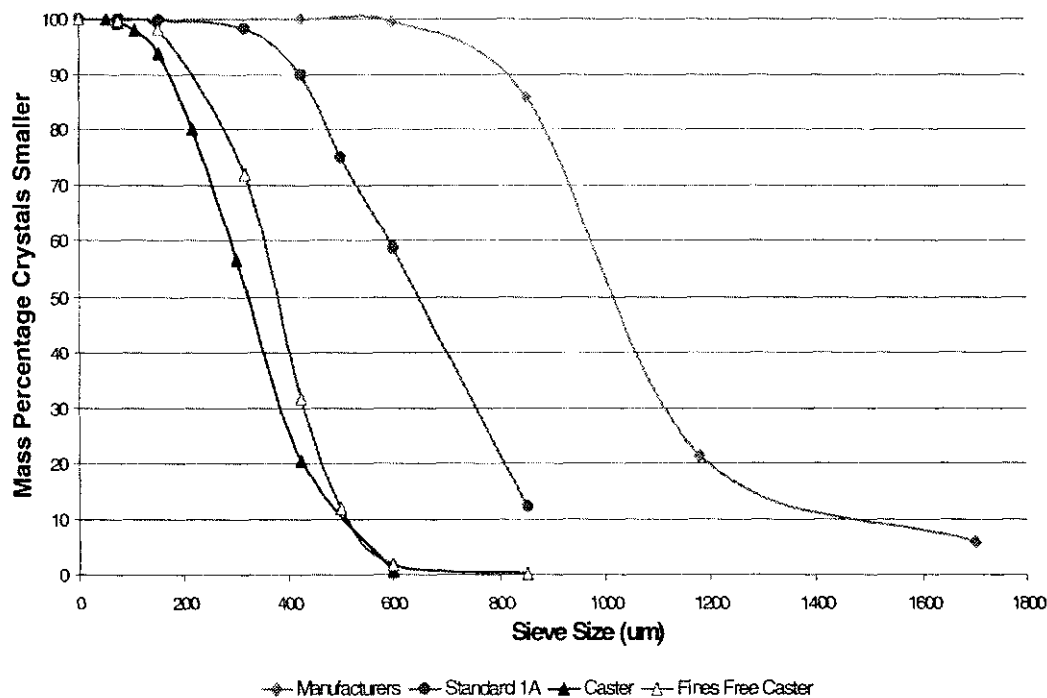


Figure 6.3 Sieve analysis for different products

The mean crystal size for standard 1A sugar is between 600 and 850 μm . This same size fraction was defined as ‘standard sugar’ in the isotherm and caking experiments. These particle size distribution curves were compared to those obtained using laser diffraction. It can be seen in Figure 6.4, that the trends shown are the same for both methods of analysis. However, there are some small differences between individual samples, especially in the 0-200 μm range. There are a few reasons for this. Firstly, laser diffraction divides the sample into a lot more fractions, especially in the region containing very small particles. It also has a much greater capability in this region than sieving, and is able to accurately measure particles as small as 1 μm . Sieves are not only unable to measure particles this small, but these particles can adhere to other larger particles as the sieves are being shaken.

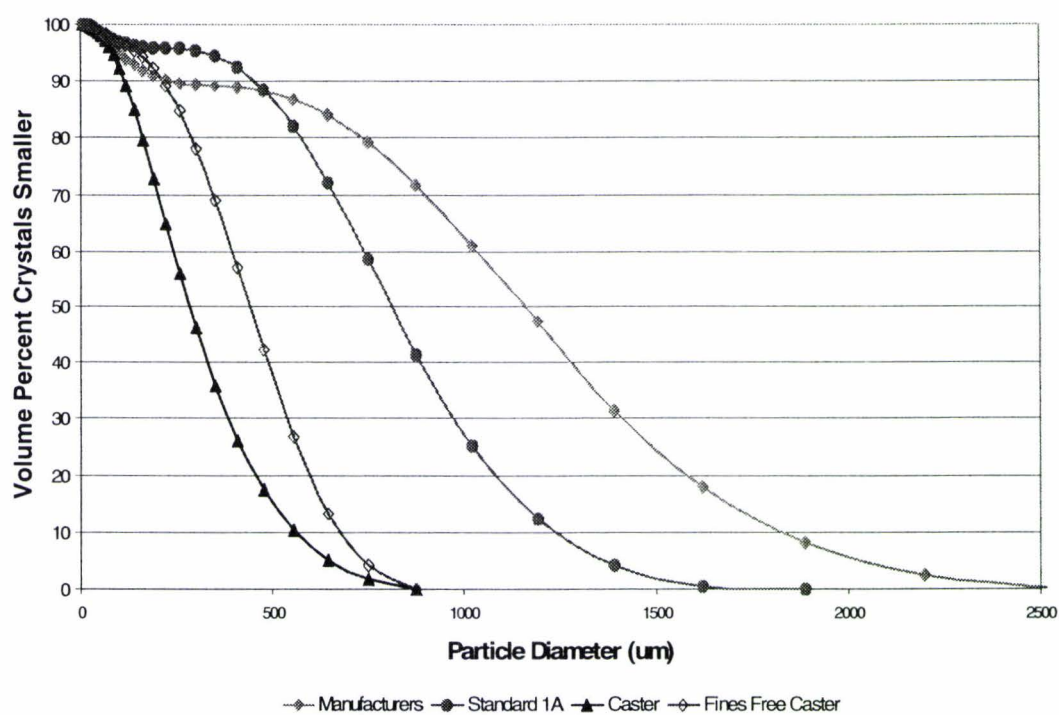


Figure 6.4 Laser diffraction analysis for different products

The unexpected increase in very small particles seen in the manufacturers sample is likely to be caused by one of two factors. Either this increase is caused by light scattering off multiple large crystals, and therefore is not a real effect, or else dust crystals which were previously stuck to larger particles have been measured separately in the Malvern Mastersizer.

6.3.2 Fines in the Plant at New Zealand Sugar

Fines are usually considered as any crystals below approximately 300 μm in size. It can be seen from Table 6.1 below that there is a significant amount of fines in the 150-315 μm range in the sugar as it is dried and conditioned. Fines smaller than this are minimal. There are very few fine crystals which remain in the manufacturers or standard 1A sugar samples after grading, however more than quarter of the caster sample can be considered fine. There are not enough fines in these product samples to affect caking, as shown in Chapters 3 and 5.

It should be noted that these results are specific to when the samples were taken, and the proportion of fines in samples taken at a different time will vary.

Sample	0-75	75-150	150-315
Preconditioning	0.1	1.5	23.4
After Conditioning	0.4	2.5	17.1
Manufacturers	0	0	0.1
Standard 1A Sugar	0	0.1	2
Caster	1.2	6.3	31.8
Fines-free Caster	0.2	1.6	26.5

Table 6.1 Percentage of fine crystals in samples taken before and after conditioning, and product samples

6.3.3 Redler vs Screw

In order to determine if there was a difference between the samples taken before conveying and those taken after, the data was graphed and a statistical analysis carried out. The purpose of graphing the data is to be able to visually examine the results to see if there were any major differences. These differences are potentially very small so a statistical analysis is needed to confirm if they are significant.

The graphical analysis showed that there was very little difference in the size distribution of samples taken at the start and the end of the standard sugar redler. This

is shown in Figure 6.5. Differences could, however, be seen in the distributions before and after this same sugar went through the packing screws. This is shown in Figure 6.6.

It can be seen from the shorter caster screw in Figure 6.7, that this screw follows the same trend as the packing screw. Again, there are some differences in the particle size before and after, which means attrition is occurring.

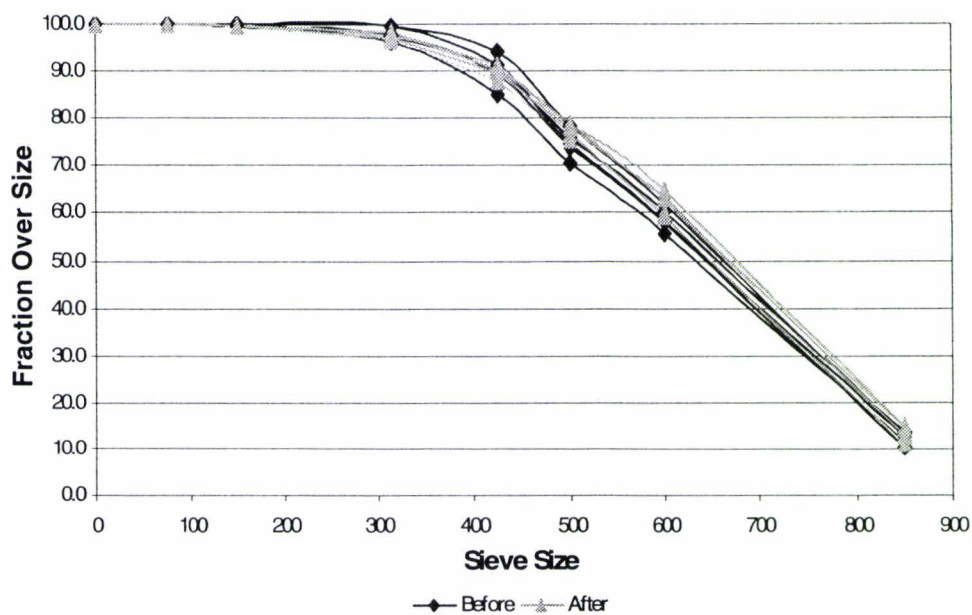


Figure 6.5 Particle size distribution before and after standard 1A crystals were conveyed in a chain redler post-graders

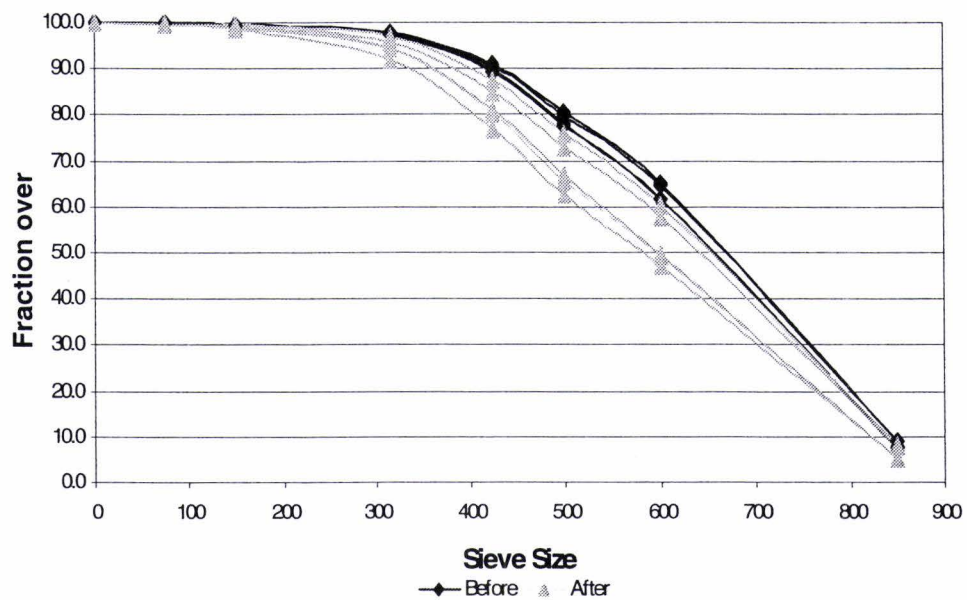


Figure 6.6 Particle size distributions before and after standard 1A crystals were conveyed in a screw conveyor to be packed

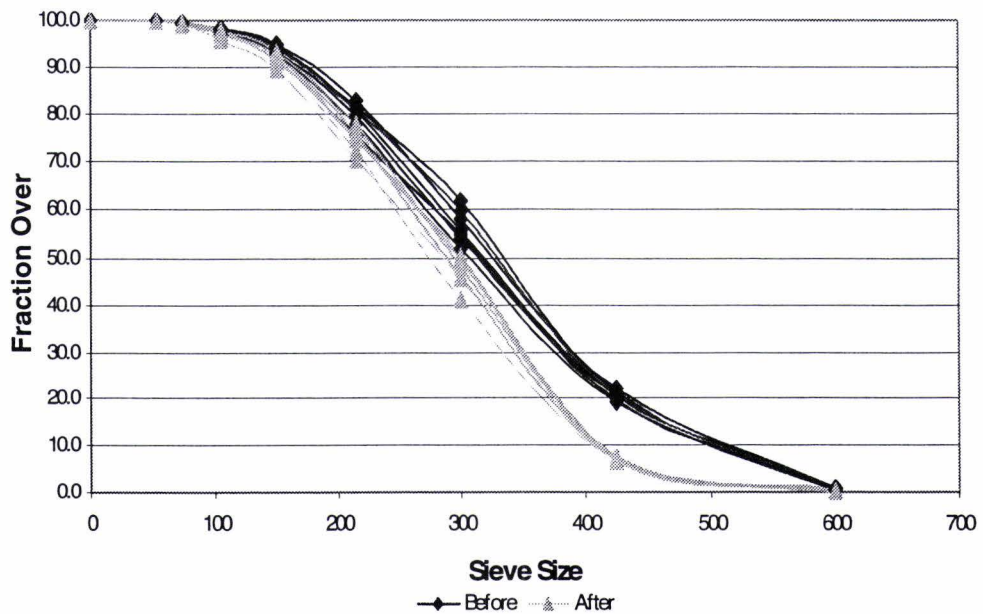


Figure 6.7 Particle size distributions before and after caster crystals were conveyed in a screw conveyor post-graders

The statistical analysis carried out was the students t-test. Both the mean and median of each data set was compared. To calculate the mean particle size, Equation 5.4 was used. A smooth curve was drawn and the median point found using TechDig (version 2.0, Ronald B. Jones), a computer program which allows the exact value of a point on a curve to be determined.

The null hypothesis in the statistical analysis is that there is no difference between samples, ie, the mean and medians are the same before going into the conveyor as leaving. The t-statistic was calculated for each set of data and the critical t value determined. If the value of the t-statistic was less than the critical value, samples can be said to be 'not significantly different', however, if the t-statistic does exceed the critical value, samples are said to be significantly different at the $p < 0.05$ level (95% confidence level). This means if the t-statistic is greater than the critical t-statistic it can be concluded that the samples taken before the conveyors are different from the samples taken after. In addition the p-values, the probability of the t-statistic exceeding the critical t value was also calculated for each set of samples. If p is very small the t-statistic is unlikely to exceed the critical t value and the assumption that the samples are equal can be rejected. Again this means the samples are significantly different, and attrition is occurring. A one-sided test was used, because any damage to the crystals will cause a decrease in size.

It can be seen from Table 6.2 that the calculated p-values for the redler are significant at the 95% confidence level. This means that the null hypothesis, that there is no difference in between samples, cannot be rejected. Therefore, it can be concluded that the redler is not causing any damage to the crystals.

Conversely, it was found that the screw conveyors were causing significant damage. The p-values that were calculated are zero at the 95% confidence level for both screws. This means it is safe to reject the null hypothesis and conclude that there is some damage to the crystals being caused by the screw conveyors.

	Standard 1A Sugar Redler		Standard 1A Sugar Packing Screw		Caster Sugar Screw	
	Mean	Median	Mean	Median	Mean	Median
Mean 1	593.0	652.7	584.7	661.5	274.4	321.2
Mean 2	593.7	662.9	512.3	612.5	249.0	290.3
t-stat	-0.055	-1.541	4.654	3.430	6.123	6.340
P(T<=t) one-tail	0.48	0.08	0.00	0.00	0.00	0.00
t Critical one-tail	1.86	1.89	1.86	1.86	1.78	1.78

Table 6.2 Results of one tailed t-test for different conveyers

The difference in the amount of damage to the crystals is due to the mechanism of conveying. Redlers use buckets, in which the sugar is poured in and conveyed with minimal rubbing. Screw conveyors meanwhile, have a turning screw that conveys the sugar, and which can cause grinding of the crystals between the blades and walls of the conveyor.

6.3.3.1 Loading

At lower loading, the particle size distribution through a redler, as shown in Figure 6.8, is very similar to that at a higher loading, shown in Figure 6.5 above. Again, it can be seen that there is no difference in size before and after conveying using a redler chain conveyor.

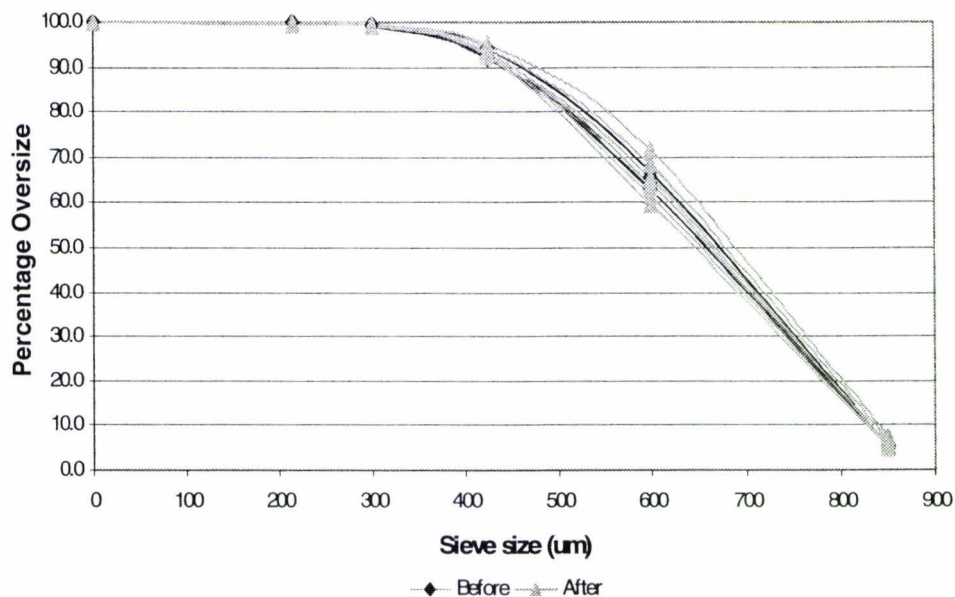


Figure 6.8 Particle size distribution before and after standard 1A crystals were conveyed in a chain redler conveyor at low levels

The particle size distribution over the caster screw at low loading is also the same as at high loading. It can be seen again in Figure 6.9 that some damage is occurring in this screw conveyor.

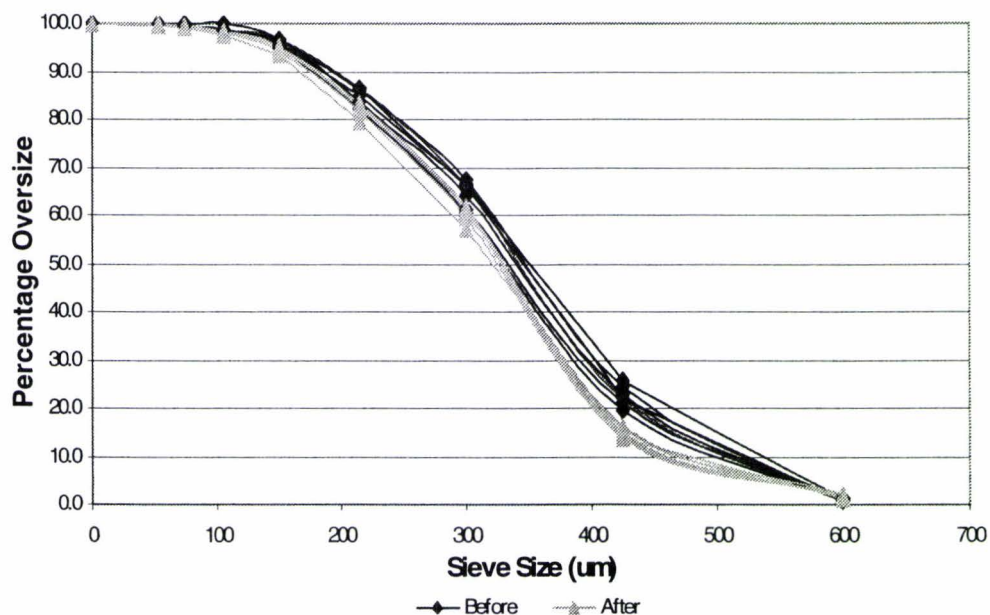


Figure 6.9 Particle size distribution before and after caster crystals were conveyed in a screw conveyor at low levels

When these samples were compared statistically in Table 6.3, no significant difference was found between the samples taken before and after the chain redler. This can be seen from the high p-value for both the mean and median of the samples. There was still damage occurring, however, in the screw conveyor. The p-values are again zero, which means the difference between samples is significant. The t-statistics are similar to the analysis carried out earlier, with a higher conveying throughput. This means there is no less damage occurring when the conveyors are run at less than their full load.

	Standard 1A Sugar Redler		Caster Sugar Screw	
	Mean	Median	Mean	Median
Mean 1	437.1	666.4	296.5	343.2
Mean 2	439.8	664.9	275.2	327.5
T-statistic	-0.696	0.245	6.595	6.044
P(T<=t) one-tail	0.250	0.405	0.000	0.000
T Critical one-tail	1.782	1.782	1.782	1.782

Table 6.3 Results of one tailed t-test for different conveyors at low loading

The absolute values for the means and medians at high loading and low loading are different. This is because the samples were taken at different times so are susceptible to random variations due to this being an industrial process. However, when the differences in means, medians and t-statistics are compared it was found that they were very similar. The biggest difference was between the median values for the caster screw; the absolute values changed by 30.9 at high loading, and 15.7 at low loading. Since the differences in means are similar, this is probably not significant, and is likely due to sampling errors. Therefore, it can be concluded that differences in the amount of damaged being caused by conveying systems at a lower loading is not different from the damage being caused at higher loading. Also, it is unlikely conveying systems would run at a low loading for a significant length of time while the plant is operating. In addition, the level of fines produced in the screw conveyors are so small that they are unlikely to have an effect of the critical water activity where the sugar begins to cake, as shown in Section 5.

6.3.4 Size in Relation to Isotherm

The particle size distribution of each sieved fraction used to mix samples for the isotherms and caking strength tests, have been further analysed using laser diffraction. These fractions are between sieve series so cannot be sieved further. The results of this are given in Appendix A5, page A-14.

6.3.5 Bulk Density

The poured and tapped bulk density for the samples used in the isotherm and caking experiments are shown below in Table 6.4.

	Percentage of Fine Crystals (%)	Crystal Size (µm)				
		0-75	75-150	150-212	212-315	600-850
Poured (kg/m ³)	0.1	830	833	830	833	
	1.0	838	836	843	852	
	10	836	865	864	857	
	100	720	756	796	824	831
Tapped (kg/m ³)	0.1	933	927	932	929	
	1.0	949	946	939	946	
	10	1002	971	967	965	
	100	703	908	918	945	936

Table 6.4 Poured and tapped bulk densities for isotherm and caking samples

It can be seen from these results that the bulk densities of the samples composed completely of smaller particles are less than that of the mixtures of small and large crystals. Also, the tapped bulk density is noticeably more than the poured bulk density, because as the crystals are tapped they move to fill the gaps between larger crystals. The relationships between these densities and the isotherm and caking data are discussed below.

6.3.6 Packing

It was found in Chapter 5 that caking occurred at a lower water activity for samples of smaller crystals and samples containing more fine crystals.

An attempt was made to establish a relationship between the blowtester results and number of contact points per unit volume. In order to do this, the number of contact points within the different samples needed to be calculated. This would be dependent on the packing mechanisms present in these samples.

Three possible packing conformations were identified. Either the small crystals all fitted in between the larger crystals, or the small crystals formed a layer around the larger crystals by static forces, or both small and large crystals are randomly mixed. These are shown schematically in Figure 6.10. In order to determine which effect is predominant the bulk densities were used.

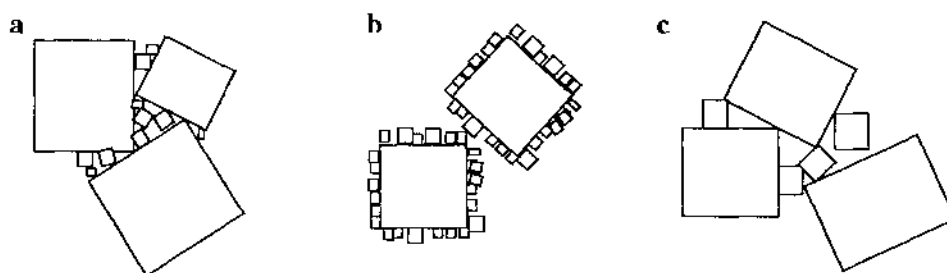


Figure 6.10 Different packing conformations: a) Small particles fit between large particles
b) Small particles form a layer around large particles
c) Random mixing of both large and small particles

The theoretical bulk density if all small particles fitted between the large was calculated. Calculation methodology is given in Appendix A4, page A-11. The results of this are shown below in Table 6.5. It can be seen that if particles were packing in this manner, the bulk density of the samples would increase more than what has actually been shown. This means some smaller particles are holding larger particles apart.

The bulk density was then found for the case of small crystals forming a layer around the larger crystals. Calculation methodology is given in Appendix A4, page A-12. The resultant bulk densities for samples containing 1% and 10% fines are shown in Table 6.5. These are less than the actual bulk density values; therefore some fine crystals are filling the gaps between the larger particles.

Sample	Bulk density (kg/m ³)		
	Actual bulk density	Conformation (a)	Conformation (b)
1% 0-75	838	846	821
1% 75-150	836	846	821
1% 150-212	843	846	823
1% 212-315	852	846	823
10% 0-75	836	988	750
10% 75-150	865	983	755
10% 150-212	864	983	762
10% 212-315	857	985	766

Table 6.5 Actual and theoretical bulk densities for different packing conformations

It can be seen from Table 6.4 and 6.5 that the bulk densities for the mixtures were greater than the bulk densities of the particles that made up these samples. Therefore, it can be concluded that the packing mechanism present will be a combination of the first and third suggested, ie, randomly packed, with some small crystals fitting between larger crystals.

A search of the literature was conducted with regard to the coordination number (number of contact points) of mixtures of cubic particles, as these were likely to closely approximate the shape of a sugar crystal. Traditionally research has been focussed on the different possible packing arrangements of equivalent sized spheres (Linoya *et al.*, 1991), however there is little published regarding the packing of multi-component mixtures of non-spherical particles. In addition, most of these articles focus on computer-simulated models to calculate the void space or packing density

(Suzuki & Oshima, 1983; Nolan & Kavanagh, 1995; Zou & Yu, 1996; Gan *et al.*, 2004).

In order to determine if contact points did affect caking it was assumed the number of crystals will be approximately proportional to the number of contact points, therefore, this property was used instead. The calculation methodology is given in Appendix.

The blowtester result verses the number of crystals is shown for water activities of 0.59, 0.65, 0.69, 0.75, 0.81 and 0.87 in Figures 6.11 – 6.16 respectively. The formulas for the trendlines of these samples are given in Table 6.6.

a_w	Formula	R^2
0.59	$Y = 1.0017 \ln(x) - 14.802$	0.7369
0.65	$Y = 1.1404 \ln(x) - 13.929$	0.6750
0.69	$Y = 1.0103 \ln(x) - 8.5006$	0.4375
0.75	$Y = 1.4229 \ln(x) - 10.7800$	0.6560
0.81	$Y = 0.1265 \ln(x) + 14.643$	0.0046
0.87	$Y = 0.6419 \ln(x) + 7.33$	0.2198

Table 6.6 Formulae for correlations between number of crystals and blowtest result at different water activities

This shows a correlation between the number of crystals and the blowtester result for water activities of 0.59, 0.65, 0.69 and 0.75, although the correlation at a water activity of 0.69 is weaker other three. This is due in part to one point that is much lower than the others. If this point were removed, the r^2 increases 0.52, however it is not far enough out to be considered as an outlier. At water activities above this, samples became fully lumped and it was not possible to measure the liquid bridge strength using the blowtester due to the limits of the air and flowmeter being used.

In order to make this property more useful in industry, it is recommended further research be conducted to more accurately model the number of contact points present in different mixtures. If this can be done, it can be related to the level of caking that could be expected to occur in any sample at any given water activity.

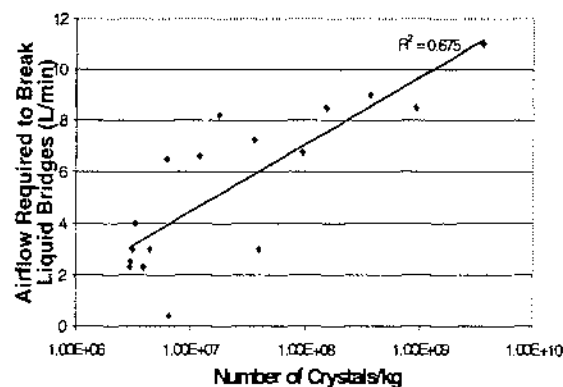


Figure 6.11 Correlation between number of crystals and blowtest result at a water activity of 0.59

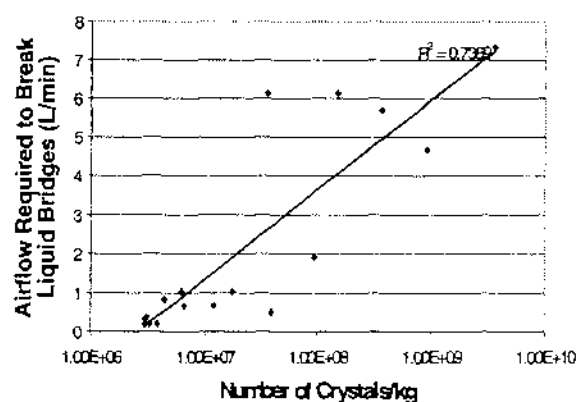


Figure 6.12 Correlation between number of crystals and blowtest result at a water activity of 0.65

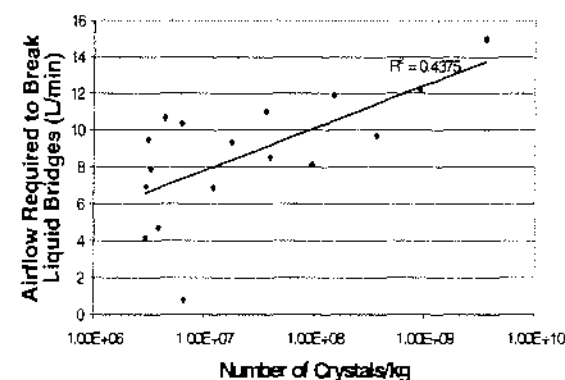


Figure 6.13 Correlation between number of crystals and blowtest result at a water activity of 0.69

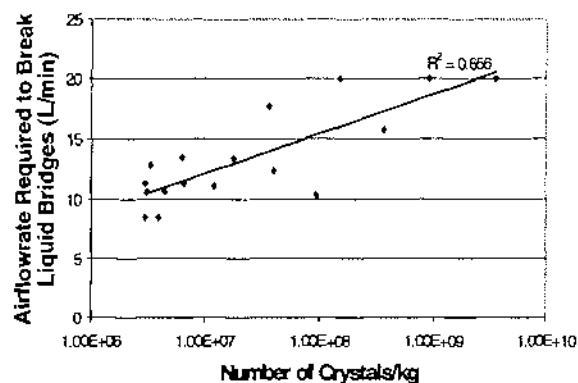


Figure 6.14 Correlation between number of crystals and blowtest result at a water activity of 0.75

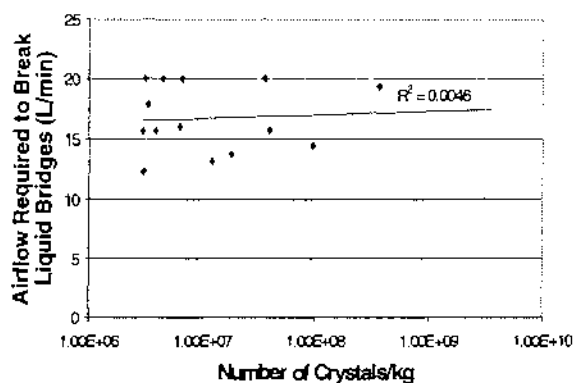


Figure 6.15 Correlation between number of crystals and blowtest result at a water activity of 0.81

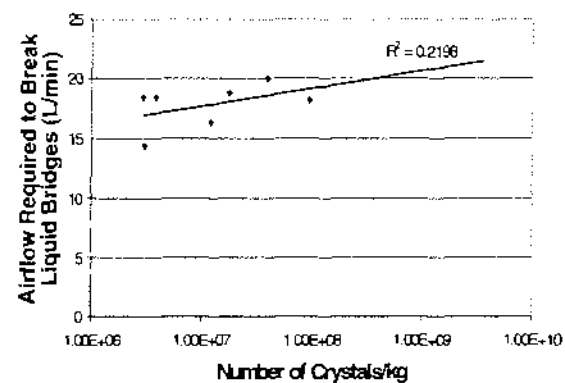


Figure 6.16 Correlation between number of crystals and blowtest result at a water activity of 0.87

6.4 Conclusions and Recommendations

It was found that the percentage of fine crystals, less than 150 μm , in standard 1A sugar was 0.1%, which is below the level required for caking to occur. The minimum amount of sugar required for caking is between 1% and 10%. In comparison nearly 10% of the caster sugar sample was found to be of this size.

There was no significant damage to sugar crystals as they were conveyed by a chain redler, however screw conveying does cause some damage to the crystals. This was found for both standard 1A sugar, and caster sugar. In addition, it was found that running conveying systems with less sugar in them made no difference to the amount of damage. This applies to both redlers and screw conveyors.

As this went to print the current caster screw conveyor post-grading (AC18) was being replaced with a redler conveyor. It is recommended that sampling is repeated once this new equipment is commissioned, and the results compared to those obtained from the current screw conveyor. This will allow the amount of damage to be accurately quantified because there will be no differences in either size of the sugar crystals, or the length of the conveyors being compared.

A correlation was found between the number of particles and the blowtest results for water activities in the 0.59 - 0.75 ranges. It is recommended more research be conducted to model the number of contact points per unit area in different mixtures. This will mean the level of caking that is likely to occur when sugar is stored at a given relative humidity will be known.

The amount of fines in the samples of both standard sugar and caster sugar are too low to affect caking. Also, there are not enough additional fines generated in the conveyors to change this conclusion.

In the next chapter any effects of damage, other than those related to particle size, will be explored.

Chapter 7

- Effect of Particle Damage -

7.1 Introduction

As crystals are broken, either by fraction or abrasion, not only does their size change, but also their shape. When this happens the previously smooth crystal surface becomes rough and uneven. It is possible this increase in roughness may cause the crystal surface to dissolve more readily than it would have otherwise, which in turn increases moisture absorption and caking. It is also possible that an amorphous layer could form on the outside of the crystals (Roth, 1976). This will also cause more moisture to be absorbed by the crystal, and has been shown to cause the onset of caking to occur earlier (Bressan & Mathlouthi, 1994).

It has been demonstrated in the previous section that damage to the crystals was occurring as crystals were conveyed using screw conveyors. The purpose of this chapter is to determine if this damage had more of an effect on caking than the actual size of the crystals.

7.2 Experimental

In order to determine the affect of damage, isotherms were created and caking tests carried out. To compose a series of isotherms the saturated salt method was used, as outlined in Chapter 3, and the amorphous content of these samples was found using the TAM at Fonterra, Kapuni, using the method given in Chapter 4. To measure the caking strength the blowtest and friability tests were carried out as outlined in Chapter 5.

Crystal samples from three places between the driers and graders were studied. These samples were taken from the bottom of the second drier, over the electromagnet and from the bottom of the silo. These sample points are shown on the plant diagram in Appendix A3, page A-8. The first sample point, the bottom of the driers, is the first place that a dry sample can be taken. The electromagnet is half way between the drier and the silo, so is also a good sample point. The sample from the bottom of the silo was taken from the clamgates, and is the last place representative samples can easily be taken before the sugar is graded into different products. Between each sample point the crystals are conveyed using several screws, redlers and elevators.

The particle size distributions of the three different process samples were measured by sieving, with particular care being taken to measure all particles below 200 μm . To increase the accuracy of this method with regard to the fine particles, a 4 d.p. Mettler Toledo AB104 (Switzerland) balance was utilized in conjunction with the following sieves:

- 45 μm , 75 μm , 150 μm , 315 μm , 500 μm , 600 μm , 850 μm

Three samples were taken from each sample point at different times and of different batches, since it would have been impossible to get a sample from the same batch from each of the drier, electromagnet and clamgates. These samples were then averaged and that particle size distribution used in further experiments.

Two sets of samples were then prepared. The first set was made up from samples recombined as follows. First, the sample taken from the electromagnet was separated into size fractions by sieving, using the above sieve series. This was then recombined in such a way that its new particle size mirrored that of the samples taken from the drier. In the same way the silo sample was recombined so that it had the same particle size distribution as the electromagnet sample.

This method of recombining samples means that the only difference between the original electromagnet sample and the new drier sample which has been recombined, is that the crystals in the original electromagnet sample have been through several conveyors and therefore, some damage to the crystals may have occurred. This means

any differences seen in the isotherms or caking tests between these samples will be due purely to crystal damage.

In the second set of samples all the fine crystals below 300 μm were removed and replaced with similar sized crystals obtained by milling. Crystals are milled by crushing and as a consequence crystal damage occurs, therefore the samples containing milled sugar will contain more damaged crystals than the samples without. The high temperatures generated by milling can also cause an amorphous layer to form on the crystal surface (Roth, 1976). To overcome this problem the milled sugar was recrystallised by leaving for a week over a saturated solution of potassium chloride. This gives a relative humidity of 87%, which will quickly recrystallise any amorphous sucrose that might be present, without liquefying the crystals.

7.3 Results and Discussion

7.3.1 Isotherms

The isotherms for both sample sets are very similar, as shown in Figures 7.1 and 7.2. They become exponential, at a water activity between 0.7 and 0.8. This is comparable to the GAB isotherm for literature, calculated in Chapter 2. Neither set shows any effect of having damaged crystals present.

The increase in moisture content shown by the electromagnet sample at a water activity of 0.44, is probably due to the salt solution not being saturated.

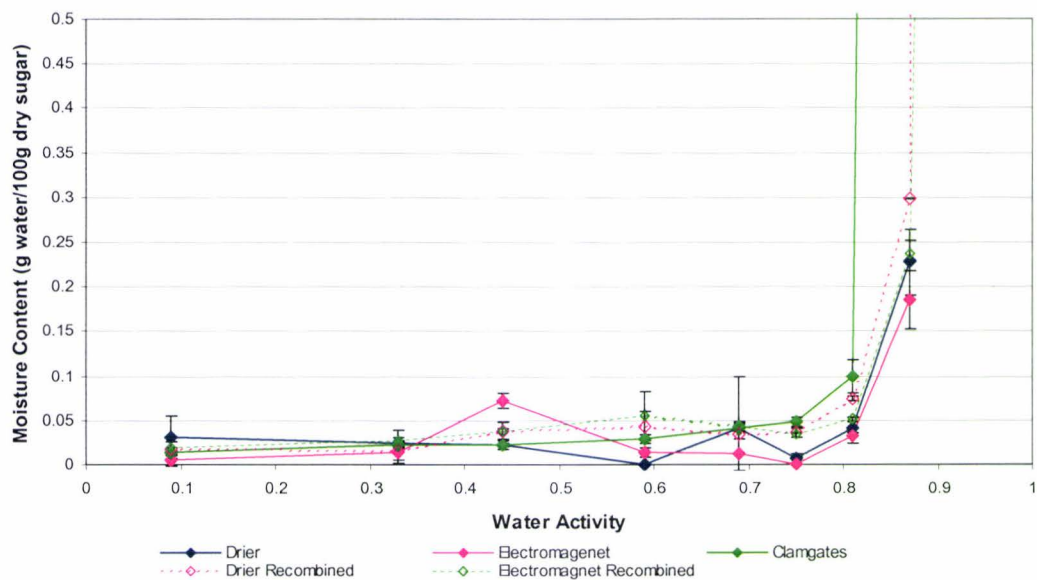


Figure 7.1 Working sorption isotherm for process samples and recombined process samples

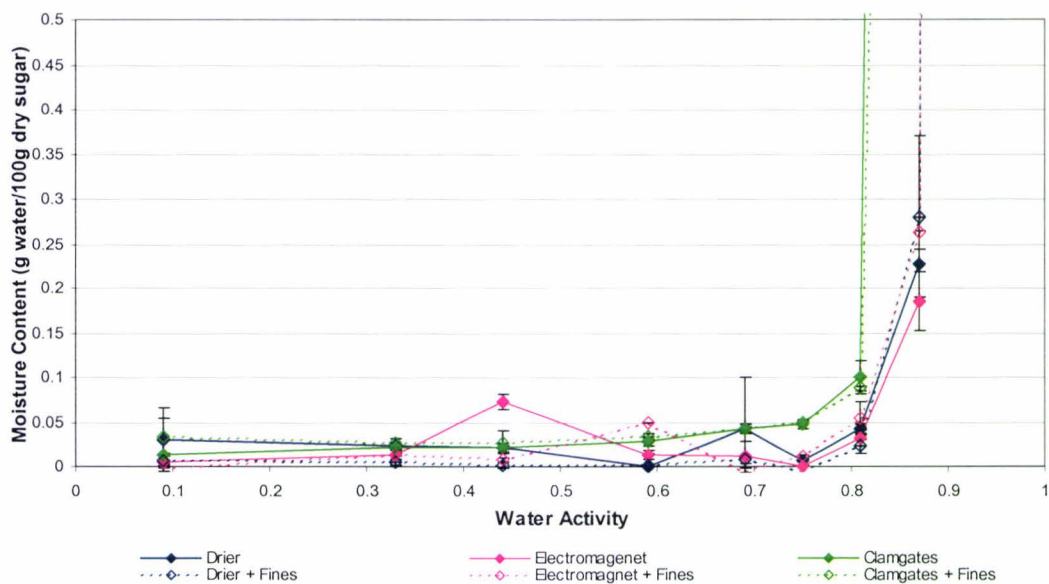


Figure 7.2 Working sorption isotherm for process samples and process samples with milled sugar added in place of fines

7.3.2 Friability

The results for the friability were also graphed. These are given in Appendix. Once again there was no difference between data sets.

7.3.3 Blowtester

The blowtest results were plotted against the water activity in Figures 7.3 and 7.4.

Figure 7.3 indicates a very small increase in the air flowrate required to dislodge surface particles at water activities greater than 0.59 for the recombined samples. If crystal damage was having an effect, the onset of caking, as shown by the increase in flowrate, for these recombined samples would be less than the sample they were recombined to mimic. This is because the samples that were used to create the recombined sample had been through less conveyers and subsequently any fine crystals present are likely to be from the crystallisation process and thus would not be damaged. Therefore, the differences in results that can be seen are likely to be caused by experimental errors, probably due to localised caking, rather than an actual effect of damage.

This conclusion is confirmed by the blowtester result shown in Figure 7.4. This graph shows no difference in caking between the original samples, and those containing milled sugar.

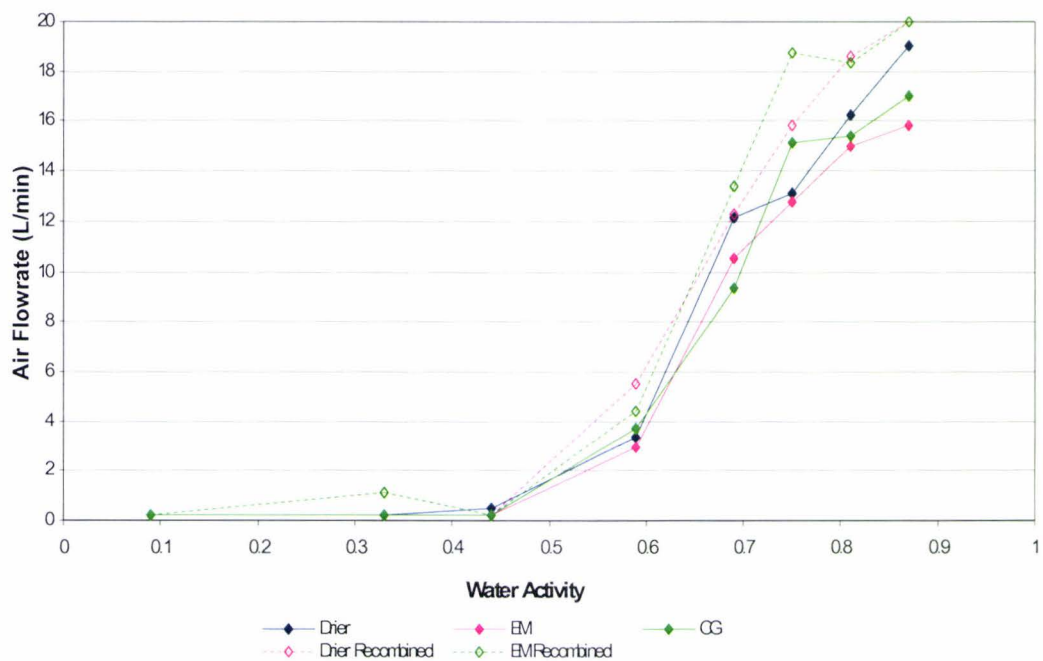


Figure 7.3 Liquid bridging strength for process samples and recombined process samples

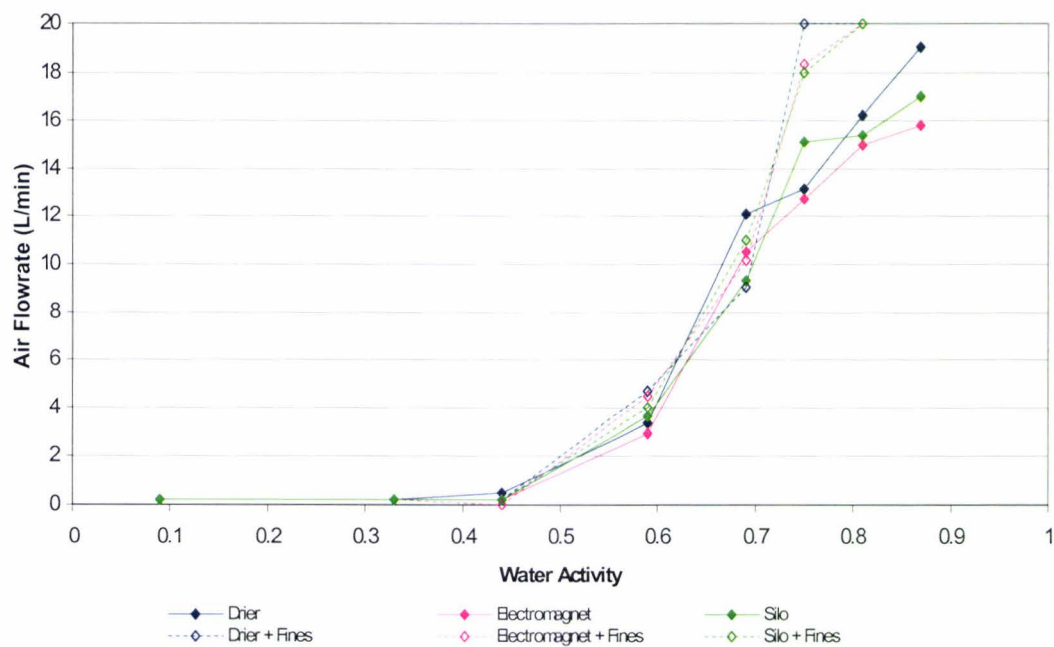


Figure 7.4 Liquid bridging strength for process samples and process samples with milled sugar added in place of fines

7.3.4 Kelvin Radius

The critical Kelvin radius was calculated for the process samples and damaged crystal using the method outlined in section 5.3.3. The results of this analysis are given below in Table 7.1.

Samples		Kelvin Radius (μm)	Water Activity
Process Samples	Drier	4.9	0.44
	Electromagnet	4.7	0.43
	Silo	6.3	0.53
	AC17	4.6	0.41
	Packing	7.7	0.59
Recombined	Drier	3.7	0.34
	Electromagnet	6.0	0.51
Added Fines	Drier	7.2	0.57
	Electromagnet	7.2	0.57
	Silo	6.6	0.54

Table 7.1 Critical Kelvin radiuses and water activities for different samples

It can be seen the critical Kelvin radius lies between 4.5 and 7.5 for most of the samples. This compares to a Kelvin radius of 7.5 for standard 600 – 850 μm sugar. If there were any differences in the critical Kelvin radiuses, it would be expected that the radius would decrease for the recombined samples and samples with added fines. One reason for the difference seen between the standard sample and the first three process samples is the process samples have not been graded, therefore, there is a large particle size variation. This means there is likely to be more smaller particles and more contact points, which has been shown in Section 5.3.3 to decrease the critical Kelvin radius. However, if the particle size distribution was significant it would be expected that the Kelvin radius for both AC17 and the packing sample would be much closer to the standard 600 – 850 μm sugar, since these are both standard 1A sugar, so contain a much narrower particle size distribution. Also, the

samples with added fines, which have the same particle size distributions as the first three process samples, had critical Kelvin radiuses of approximately the same as the standard sugar. Therefore, the variations are probably due to localised caking in the blowtest samples, giving an inaccurate blowtest value.

From these results it can be concluded the Kelvin radius does not show that caking occurs at a lower water activity where crystals have been damaged.

7.4 Conclusion and Recommendations

It was found, using the isotherm and caking tests, that the level of caking in sucrose was not greater for damaged crystals than for fine crystals. The Kelvin radius calculation also showed caking does not occur at a lower water activity for these samples. This means that the damage caused to small crystals during conveying is unlikely to be contributing to caking problems. It also indicates that damage does not result in a significant amount of amorphous sugar, as this would also have affected the isotherms and caking measurements. In addition, it is highly likely any amorphous sucrose that is formed will recrystallise almost instantaneously.

Chapter 8

- Conclusions and Recommendations -

Caking in sucrose is a problem in the sugar industry. This study found that the presence of fine crystals had some effect on caking, but this effect is minimal compared to the effect of differing relative humidities.

No differences due to size were detected in the sorption isotherms, and there was only a little difference shown in the friability tests. However, the blowtest was found to be a lot more sensitive to the differences found in the levels of caking between samples.

Even though fines are usually considered as any particle less than 300 μm in size, only the very fine particles, less than 150 μm were found to have any effect on caking, and only when they were present in large quantities. The smaller the particles, the smaller the amount needed for caking to occur. For example, the onset of caking occurs at a lower relative humidity for a sample containing 100% crystals 0-75 μm in size, than for a sample containing only 10% of this sized crystals, made up with 600-850 μm crystals, or a sample composed of 75-150 μm crystals. These differences in caking were insignificant for proportions of fine crystals below 1%, or samples where the fine crystals were larger than 150 μm .

Several different mechanisms could have caused the increased caking when smaller crystals are present. It is proposed that the mechanism by which caking is occurring is capillary condensation. This has an effect because in a sample containing fine crystals there are more contact points. Therefore, more capillary condensation occurs at a lower water activity, and thus caking also occurs at a lower water activity. This was shown in the earlier onset of caking in the blowtest, and also by the decrease in the size of the critical Kelvin radius, the size of the capillaries that a full of water when caking occurs. In addition, the number of contact points will be approximately

proportional to the number of crystals, and a correlation was found between this property and the blowtest result.

Other possible mechanisms were discounted because there was no amorphous sugar found in the samples, so this is not causing caking in this case. Also, there was not an increase in caking caused by crystal damage, over and above size effects. In addition, there was probably not an effect of small crystals dissolving earlier due to an increased surface area, because sugar is so soluble.

It was found the level of fines, in the 0-75 μm range, in standard 1A sugar at New Zealand Sugar was approximately 0.1%, which is below the level needed for caking to occur. This means that these fines should not contribute to caking problems when the sugar is transported.

This study also looked at where fine crystals were formed at New Zealand Sugar. Some small crystals originate from the crystallisation process, however these are separated from the standard 1A sugar during the grading process. It was also found that screw conveyors cause some crystal damage, whereas redler conveyors do not. At present both are used to convey sugar.

In summary, it was found that the level of fines should not be attributing to caking problems at New Zealand Sugar, but problems are more likely due to the differences in temperature and relative humidity that the bulk sugar is subjected to. These temperature differences create temperature gradients throughout the bulk product, causing changes to the equilibrium relative humidity, which results in moisture migration. In area of high relative humidity, liquid bridges form between the crystals. When these liquid bridges are subjected to lower relative humidities they dry out, leaving strong solid bridges.

8.1 Recommendations for Future Work

It is recommended that dynamic vapour sorption (DVS) be used to measure the isotherms again. This instrument is thought to be more sensitive than the saturated salt method used in this study, therefore would be able to show more accurately any differences that were present between samples.

It is recommended that the isotherm and caking experiments be repeated with crystals in a similar size range to the critical Kelvin radius, up to 10 μm . It is also recommended these experiments be repeated with samples containing between one and ten percent fine crystals to determine the critical level of fines needed for caking.

It is recommended that the effects of compaction and settling of crystals after they are packed be studied, because this would also increase the number of contact points and is therefore likely to affect caking. It is also recommended that the number of contact points be modelled so the expected caking strength of a sample can then be determined if it was subjected to any relative humidity.

References

- Abdullah, E. C., & Geldart, D. (1999). The use of bulk density measurements as flowability indicators. *Powder Technology*, 102(2), 151-165.
- Abou-Chakra, H., Tuzun, U., Bridle, I., Leaper, M., Bradley, M., & Reed, A. (2003). Assessing the potential of a fine powder to segregate using laser diffraction and sieve particle size measuring techniques. *Advanced Powder Technology*, 14(2), 167-176.
- Adamson, A. W. (1990). *Physical Properties of Surfaces*. New York, USA: John Wiley and Sons.
- Aguilera, J. M., del Valle, J. M., & Karel, M. (1995). Caking phenomena in amorphous food powders. *Trends in Food Science and Technology*, 6, 149 - 155.
- Allen, T. (1975). *Particle Size Measurement* (2 ed.). London: Chapman and Hall Ltd.
- Anonymous (year unknown). TAM. Thermal Activity Monitor for highly sensitive isothermal analyses. Brochure put out by Thermometric Company.
- Anonymous (2004). Chelsea Sugar - New Zealand website. Retrieved 23 September, 2004, from www.chelsea.co.nz
- Angberg, M. (1995). Lactose and thermal analysis with special emphasis on microcalorimetry. *Thermochimica acta*, 248, 161-176.
- Audu, T. O. K., Loncin, M., & Weisser, H. (1978). Sorption Isotherms of Sugars. *Lebensmittel-Wissenschaft & Technologie*, 11(1), 31-34.
- Bagster, D. F. (1970). Cause, prevention and measurement of the caking of refined sugar - a review (part 1). *International Sugar Journal*, 72(861), 263 - 267.
- Bakhit, R., & Schmidt, S. (1993). Sorption behavior of mechanically mixed and freeze-dried sucrose/casein mixtures. *Journal of Food Science*, 58(5), 1162-1165.
- Bell, L. N., & Labuza, T. P. (2000). *Moisture Sorption: Practical Aspects of Isotherm Measurement and Use* (2 ed.). St Paul, US: American Association of Cereal Chemists Inc.
- Bemrose, C. R., & Bridgwater, J. (1987). A review of attrition and attrition test methods. *Powder Technology*, 49(2), 97-126.
- Bergqvist, A., & Soderqvist, J. (1999). *Characterisation of Moisture Induced Crystallisation of Lactose by Isothermal Calorimetry*. Borlange, Germany?: Darna University.
- Bhandari, B. R., & Howes, T. (1999). Implication of glass transition for the drying and stability of dried foods. *Journal of Food Engineering*, 40(1-2), 71-79.
- Billings, S. W. (2002). *The Mathematical Modelling of Caking in Bulk Sucrose*. MEng thesis., Massey University, Palmerston North.
- Billings, S. W., Bronlund, J. E., & Paterson, A. H. J. (2005). Effects of capillary condensation on the caking of bulk sucrose. *In Press*.
- Bressan, C., & Mathlouthi, M. (1994). Thermodynamic activity of water and sucrose and the stability of crystalline sugar. *Zuckerindustrie*, 119(8), 652-658.
- Bronlund, J. (1997). *Modelling the Caking of Bulk Lactose*. PhD thesis. Palmerston North, New Zealand: Massey University.

- Bronlund, J., & Paterson, T. (2004). Moisture sorption isotherms for crystalline, amorphous and predominantly crystalline lactose powders. *International Dairy Journal*, 14, 247-254.
- Brooks, G. F. (2000). *The Sticking and Crystallisation of Amorphous Lactose*. MTech thesis. Palmerston North: Massey University.
- Bubnik, Z., Kadlek, P., Urban, D., & Bruhns, M. (1995). *Sugar Technologists Manual: Chemical and Physical Data for Sugar Manufacturers and Uses* (8th edition, formerly Zuckertechniker-Taschenbuch ed.). Berlin: Bartens.
- Buckton, G., & Beezer, A. E. (1991). The applications of microcalorimetry in the field of physical pharmacy. *International Journal of Pharmaceutics*, 72, 181-191.
- Buckton, G., & Darcy, P. (1995). The influence of additives on the recrystallisation of amorphous spray dried lactose. *International Journal of Pharmaceutics*, 121, 81-87.
- Chinachoti, P., & Steinberg, M. P. (1984). Interaction of sucrose with starch during dehydration as shown by water sorption. *Journal of Food Science*, 49, 1604-1608.
- Chinachoti, P., & Steinberg, M. P. (1986). Moisture hysteresis is due to amorphous sugar. *Journal of Food Science*, 51(2), 453-455.
- Chuy, L. E., & Labuza, T. P. (1994). Caking and stickiness of dairy-based food powders as related to glass-transition. *Journal of Food Science*, 59(1), 43-46.
- Doehlert, D. C., McMullen, S., Jannink, J., Panigrahi, S., Gu, H., & Riveland, N. R. (2004). Evaluation of oat kernel size uniformity. *Crop Science*, 44(4), 1178-1190.
- Eshel, G., Levy, G. J., Mingelgrin, U., & Singer, M. J. (2004). Critical evaluation of the use of laser diffraction for particle-size distribution analysis. *Soil Science Society of America Journal*, 68(3), 736-743.
- Feldman, R. F., & Sereda, P. J. (1965). Moisture content - its significance and interaction in a porous body. In P. N. Winn (Ed.), *Principles and Methods of Measuring Moisture in Liquids and Solids* (Vol. 4). New York: Reinhold Publishing Corporation.
- Foster, K. (2002). *The Prediction of Sticking in Dairy Powders*. PhD thesis. Palmerston North: Massey University.
- Foster, K., Bronlund, J., & Paterson, A. H. J. (2005). The contribution of milk fat towards the caking of dairy powders. *International Dairy Journal*, 15(1), 85-91.
- Franks, F. (1982). Water activity as a measure of biological viability and quality control. *Cereal Foods World*, 27(9), 403-407.
- Gan, M., Gopinathan, N., Jia, X., & Williams, R. A. (2004). Predicting packing characteristics of particles of arbitrary shapes. *Kona*, 22, 82-93.
- Gee, G. W., & Bauder, J. W. (1986). Particle-size analysis. In A. Klute (Ed.), *Methods of Soil Analysis. Part 1*. (2 ed.). Madison, USA: American Society of Agronomy.
- Ghadiri, M., & Zhang, Z. (2002). Impact attrition of particulate solids. Part 1: A theoretical model of chipping. *Chemical Engineering Science*, 57(17), 3659-3669.
- Greenspan, L. (1977). Humidity Fixed Points of Binary Saturated Aqueous Solutions. *Journal of Research of the National Bureau of Standards - A*, 81A(1), 89-96.

- Guinot, S., & Leveiller, F. (1999). The use of MTDSC to assess the amorphous phase content of a micronised drug substance. *International Journal of Pharmaceutics*, 192(1), 63-75.
- Hamano, M., & Sugimoto, H. (1978). Water sorption, reduction of caking and improvement of free flowingness of powdered soy and miso. *Journal of Food Processing and Preservation*, 2, 185-196.
- Iglesias, H. A., & Chirife, J. (1982). *Handbook of Food Isotherms: Water Sorption Parameters for Food and Food Components*. New York, United States: Academic Press.
- Iglesias, H. A., Chirife, J., & Boquet, R. (1980). Prediction of water sorption isotherms of food models from knowledge of components sorption behavior. *Journal of Food Science*, 45(3), 450-455.
- Iglesias, H. A., Chirife, J., & Lombardi, J. L. (1975). Comparison of water vapour sorption by sugar beet root components. *Journal of Food Technology*, 10, 385-391.
- Johanson, J. R., & Paul, B. O. (1996). Eliminating caking problems. *Chemical Processing*, 59(8), 71-75.
- Kalman, H. (1999). Attrition control by pneumatic conveying. *Powder Technology*, 104(3), 214-220.
- Kousaka, Y., & Okuyama, K. (1991). Particle Size. In K. Linoya, K. Gotoh & K. Higashitani (Eds.), *Powder Technology Handbook*. New York, USA: Marcel Dekker Inc.
- Laaksonen, T. J., Roos, Y. H., & Labuza, T. P. (2001). Comparison of the use of desiccators with or without vacuum for water sorption and glass transition studies. *International Journal of Food Properties*, 4(3), 545-563.
- Labuza, T. P., Nelson, K., & Coppersmith, C. (1992). *Glass transition temperatures of food systems*. Retrieved 27 April, 2004, from http://www.fsci.unm.edu/Ted_Labuza/PDF_files/Isotherm_Folder/Tg%20compilation.pdf
- Laitinen, N., Antikainen, O., & Yliruusi, J. (2002). Does a powder surface contain all necessary information for particle size distribution analysis? *European Journal of Pharmaceutical Sciences*, 17(4-5), 217-227.
- Leaper, M. C., Bradley, M. S. A., Cleaver, J. A. S., Bridle, I., Reed, A. R., Abou-Chakra, H., et al. (2002). Constructing an engineering model for moisture migration in bulk solids as a prelude to predicting moisture migration caking. *Advanced Powder Technology*, 13(4), 411-424.
- Linoya, K., Gotoh, K., & Higashitani, K. (1991). *Powder Technology Handbook*. New York, USA: Marcel Dekker Inc.
- Ludlow, D. K., & Aukland, N. R. (1990). Caking and flowability problems of sugar in a cold environment. *Powder Handling and Processing*, 2(1), 21 - 24.
- Mackin, L., Zanon, R., Park, J. M., Foster, K., Opalenik, H., & Demonte, M. (2002). Quantification of low levels (< 10%) of amorphous content in micronised active batches using dynamic vapour sorption and isothermal microcalorimetry. *International Journal of Pharmaceutics*, 231(2), 227-236.
- Makower, B., & Dye, W. B. (1956). Equilibrium moisture content and crystallisation of amorphous sucrose and glucose. *Agriculture and Food Chemistry*, 4(1), 72-77.
- Malvern Website. (2005). Retrieved 24 June, 2004, from www.malvern.com

- Mathlouthi, M. (1995). Amorphous sugar. In M. Mathlouthi & P. Reiser (Eds.), *Sucrose Properties and Applications* (pp. 126-152). London, Great Britain: Chapman and Hall.
- Mathlouthi, M., & Roge, B. (2001). Water content, water activity and water structure: three approaches to water/food interactions - application to the storage stability of crystalline sugar in silo. *Zuckerindustrie*, 126(11), 880-883.
- Mathlouthi, M., & Roge, B. (2003). Water vapour sorption isotherms and the caking of food powders. *Food Chemistry*, 82(1), 61-71.
- McLeod, J. (2002). *Lactose Smearing in Transport Lines*. MTech thesis. Massey University, Palmerston North.
- Merriam-Webster's Medical Desk Dictionary. (2002). Retrieved 1 November, 2004, from www.dictionary.com
- Mullin, J. W. (2001). *Crystallization* (4 ed.). Oxford, Great Britain: Butterworth-Heinemann.
- Neil, A. U., & Bridgwater, J. (1994). Attrition of particulate solids under shear. *Powder Technology*, 80(3), 207-219.
- Neil, A. U., & Bridgwater, J. (1999). Towards a parameter characterising attrition. *Powder Technology*, 106(1-2), 37-44.
- Nolan, G. T., & Kavanagh, P. E. (1995). Random packing of nonspherical particles. *Powder Technology*, 84, 199-205.
- Paterson, A. H. J., Bronlund, J., & Brooks, G. F. (2001). The blow test for measuring the stickiness of powders. *New Zealand Dairy Journal*.
- Pennington, N. L., & Baker, C. W. (1990). *Sugar, a Users Guide to Sucrose*. New York, U.S.A.: Van Nostrand Reinhold.
- Perry, R. H., & Green, D. W. (1997). *Perry's Chemical Engineers' Handbook* (7 ed.): McGraw-Hill Professional.
- Provent, B., Chulia, D., & Cary, J. (1993). Particle-size and the caking tendency of a powder. *European Journal of Pharmaceutics and Biopharmaceutics*, 39(5), 202-207.
- Rastikian, K., & Capart, R. (1998). Mathematical model of sugar dehydration during storage in a laboratory silo. *Journal of Food Engineering*, 35(4), 419-431.
- Rastikian, K., & Capart, R. (2000). Characterization of sugar caking during silo storage using penetrometric tests. *Zuckerindustrie*, 125(4), 240-243.
- Reiser, P., Birch, G. G., & Mathlouthi, M. (1995). Physical properties. In M. Mathlouthi & P. Reiser (Eds.), *Sucrose Properties and Applications* (pp. 186-221). London, Great Britain: Chapman and Hall.
- Rhodes, M. (1998). *Introduction to Particle Technology*. Chichester, England: John Wiley and Sons.
- Roge, B., & Mathlouthi, M. (2000). Caking of sucrose crystals: Effect of water content and crystal size. *Zuckerindustrie*, 125(5), 336-340.
- Roge, B., & Mathlouthi, M. (2003). Caking in white crystalline sugar. *International Sugar Journal*, 105(1251), 128-136.
- Rondeau, X., Affolter, C., Komunjer, L., Clausse, D., & Guigon, P. (2003). Experimental determination of capillary forces by crushing strength measurements. *Powder Technology*, 130, 124-131.
- Roos, Y. H., & Karel, M. (1990). Differential scanning calorimetry study of phase transitions affecting the quality of dehydrated materials. *Biotechnology Progress*, 6, 159-163.

- Roos, Y. H., & Karel, M. (1991a). Amorphous state and delayed ice formation in sucrose solutions. *International Journal of Food Science and Technology*, 26, 553-566.
- Roos, Y. H., & Karel, M. (1991b). Plasticizing effect of water on thermal behavior and crystallization of amorphous food models. *Journal of Food Science*, 56(1), 38-42.
- Roos, Y. H., & Karel, M. (1993). Effects of glass transitions on dynamic phenomena in sugar containing food systems. In J. M. V. Blanshard & P. J. Lilliford (Eds.), *Glass Transitions in Foods* (pp. 207-222). Nottingham: Nottingham University Press.
- Roth, T. (1976). *Amorphous Icing Sugar Produced During Crushing and Recrystallisation as the Cause of Agglomeration and Procedures for its Avoidance. PhD thesis. Translated from German by P.M.E. Merten.* University of Karlsruhe, Offenburg, Germany.
- Schwarz, P., Barr, J., Joyce, M., Power, J., & Horsley, R. (2002). Analysis of malt grist by manual sieve test. *Journal of the American Society of Brewing Chemists*, 60(1), 10-13.
- Sebhatu, T., Angberg, M., & Ahlneck, C. (1994). Assessment of the degree of disorder in crystalline solids by isothermal microcalorimetry. *International Journal of Pharmaceutics*, 104, 135-144.
- Seville, J. P. K., Tuzun, U., & R, C. (1997). *Processing Particulate Solids*. London: Blackie Academic and Professional.
- Sprague, M. A., & Blumenthal, W. R. (1997, May 4, 1997). *Characterization of the friction properties of ceramic powders*. Paper presented at the American Ceramic Society Meeting, Cincinnati, Ohio.
- Suzuki, M., & Oshima, T. (1983). Estimation of the co-ordination number in a multi-component mixture of spheres. *Powder Technology*, 35, 159-166.
- Terrill, S. (2003). *Chapter 13: Entropy and Free Energy and the Human Engine*, 2005, from www.norton.com/chemistry/concepts/chapter13/ch13_1.htm
- Troller, J. (1983). Methods to measure water activity. *Journal of Food Protection*, 46(2), 129-134.
- Troller, J., & Christian, J. H. B. (1978). *Water Activity and Food*. New York: Academic Press.
- Tselishchev, Y. G., & Val'tsifer, V. A. (2003). Influence of the type of contact between particles joined by a liquid bridge on the capillary cohesive forces. *Colloid Journal*, 65(3), 385-389.
- Vaccari, G., & Mantovani, G. (1995). Sucrose crystallisation. In M. Mathlouthi & P. Reiser (Eds.), *Sucrose Properties and Applications* (pp. 33-72). London, Great Britain: Chapman and Hall.
- Zou, R. P., & Yu, A. B. (1996). Evaluation of the packing characteristics of mono-sized non-spherical particles. *Powder Technology*, 88, 71-79.

Appendix 1

- Nomenclature -

a,b,c	GAB isotherm coefficients	
a_w	Water activity	
C	Constant (BET equation)	
C_1	Constant (GAB equation)	
C_p	Heat capacity	kJ/kgK
D	Average diameter	m
d	Diameter	m
K	Absolute temperature	K
k	Constant	
m	Mass of sample	kg
m	Moisture	g water/100g dry material
$M_{\text{crystalline}}$	Crystalline component of sample	g
m_o	Monolayer moisture content	g water/100g dry material
M_{total}	Total mass of water lost when sample is dried	g
n	Number of particles	
P_v	Wapour pressure of system	Pa
P_w	Wapour pressure of pure water	Pa
q	Heat energy	J
R	Gas constant	J/molK
RH	Relative humidity	%
r_k	Kelvin radius	m
S	Solubility	g sucrose/100g water
t	Temperature	°C
T_c	Collapse temperature	°C
T_g	Glass transitional temperature	°C
T_s	Sticky point temperature	°C
V_o	Liquid molar volume	m ³ /mol
$X_{\text{amorphous}}$	Mass fraction amorphous	
ΔT	Change in temperature	K or °C
θ	Wetting angle	radians
σ	Surface tension	N/m

Appendix 2

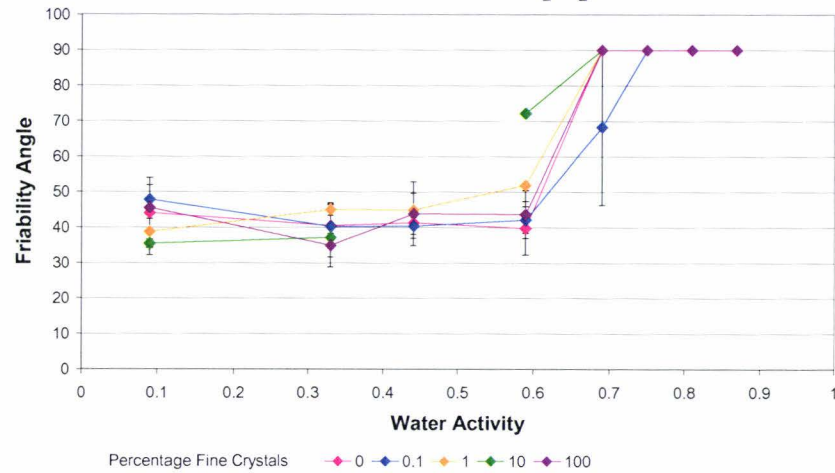


Figure A1 Angle required to break liquid bridges in samples containing different proportions of 150-212 μm crystals, mixed with 600-850 μm crystals

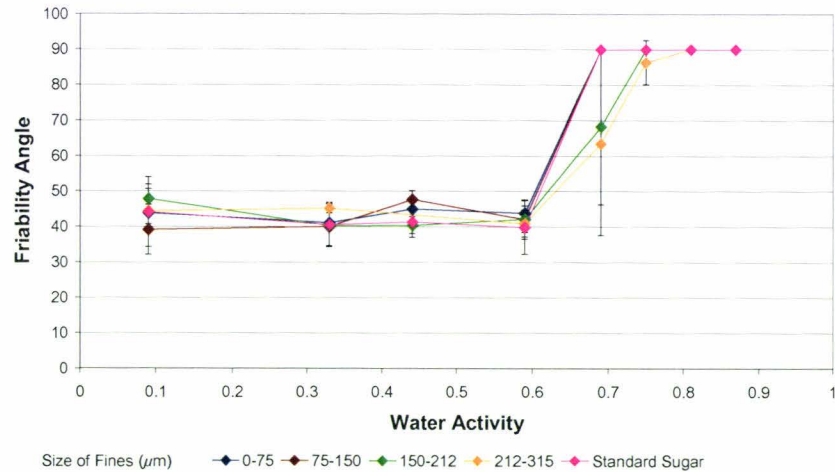


Figure A3 Angle required to break liquid bridges in samples containing 0.1% fine crystals, mixed with 600-850 μm crystals

- Caking Figures -

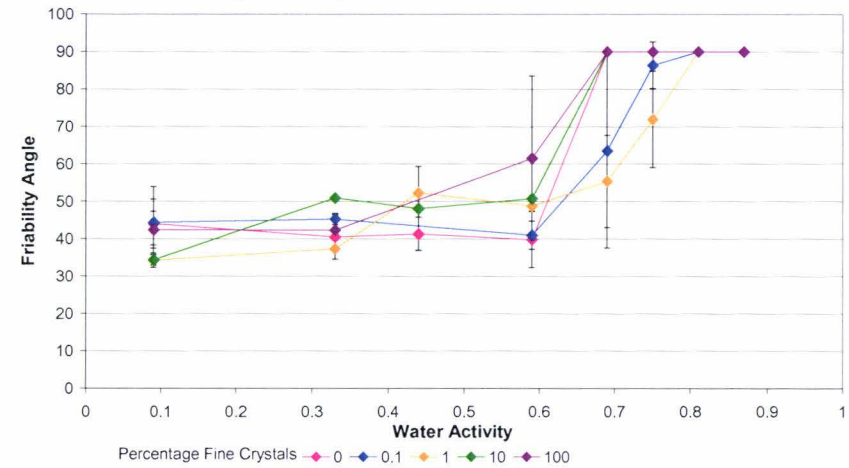


Figure A2 Angle required to break liquid bridges in samples containing different proportions of 212-315 μm crystals, mixed with 600-850 μm crystals

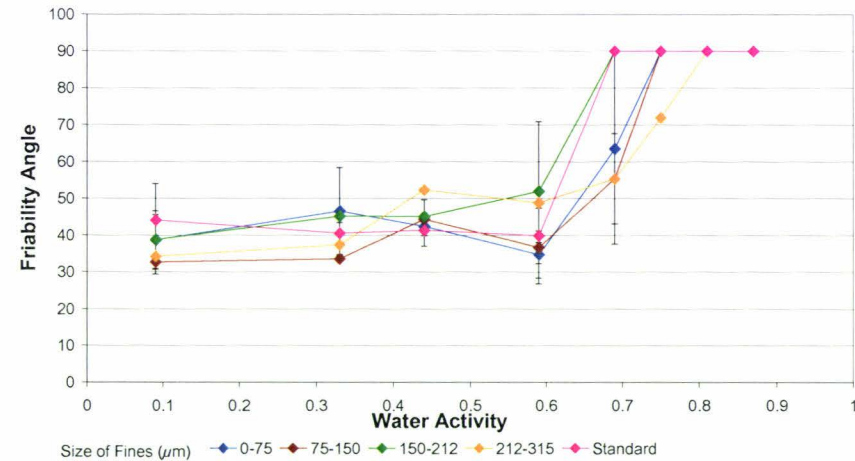


Figure A4 Angle required to break liquid bridges in samples containing 1% fine crystals, mixed with 600-850 μm crystals

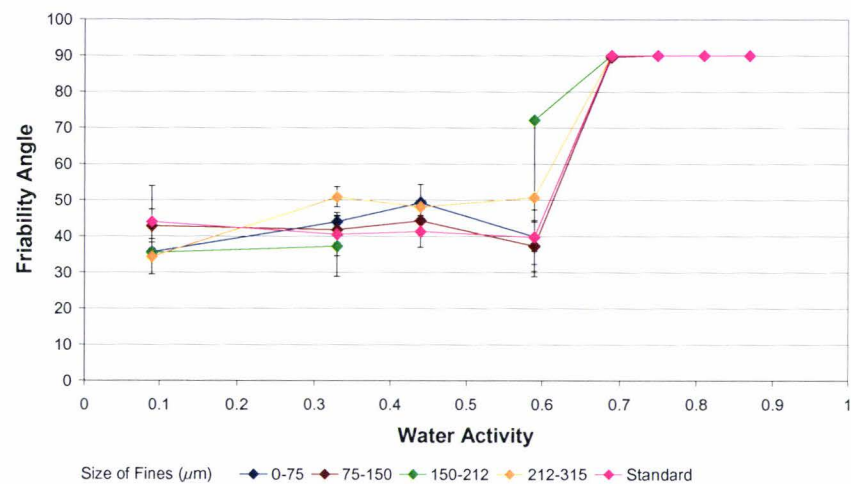


Figure A5 Angle required to break liquid bridges in samples containing 10% fine crystals, mixed with 600-850 μm crystals

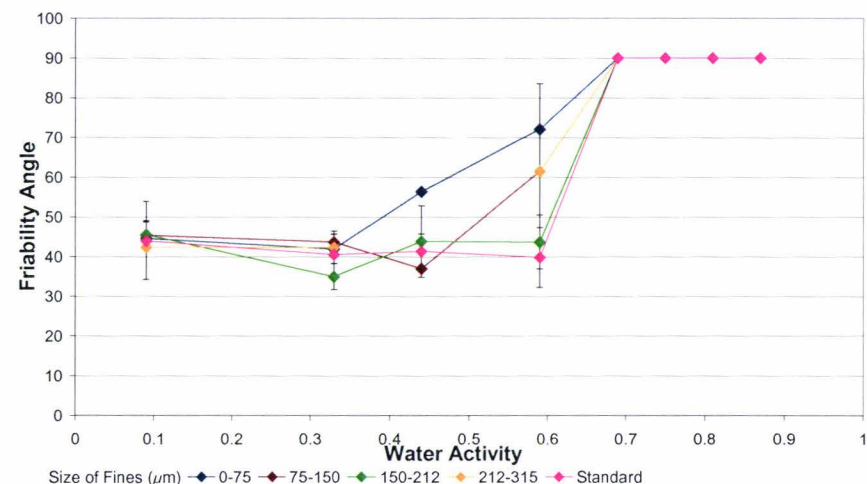


Figure A6 Angle required to break liquid bridges in samples containing 100% fine crystals

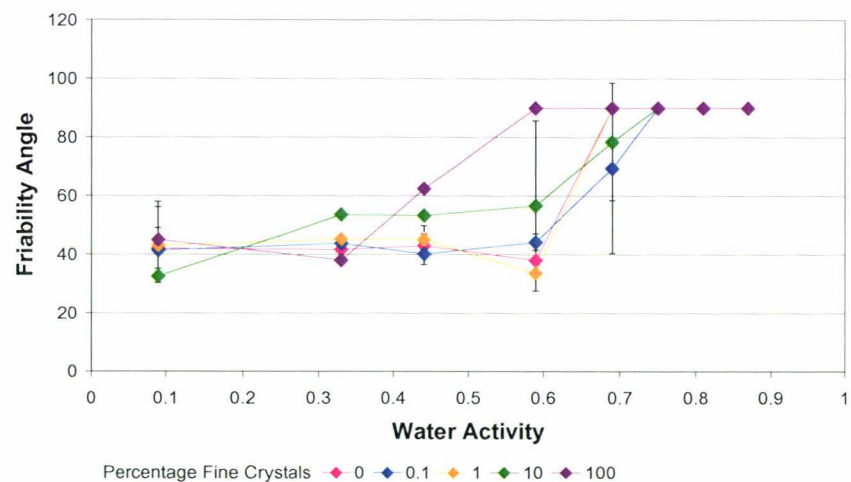


Figure A7 Angle required to break solid bridges in samples containing different proportions of 0-75 μm crystals, mixed with 600-850 μm crystals

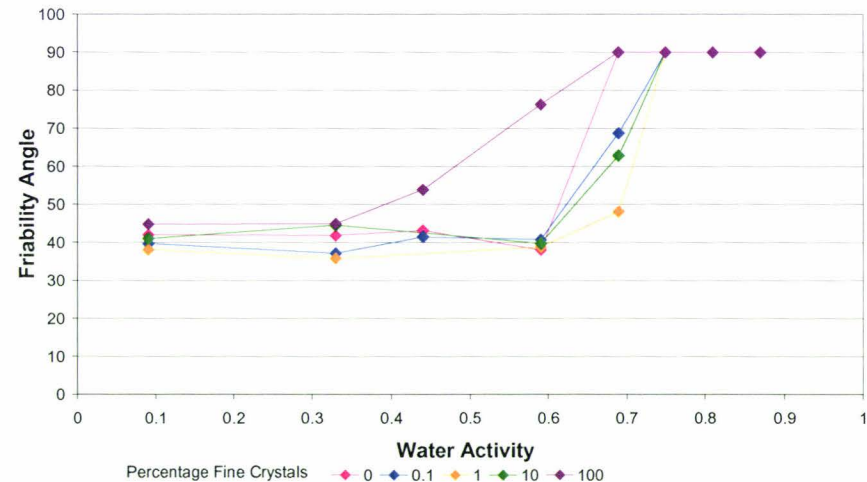


Figure A8 Angle required to break solid bridges in samples containing different proportions of 75-150 μm crystals, mixed with 600-850 μm crystals

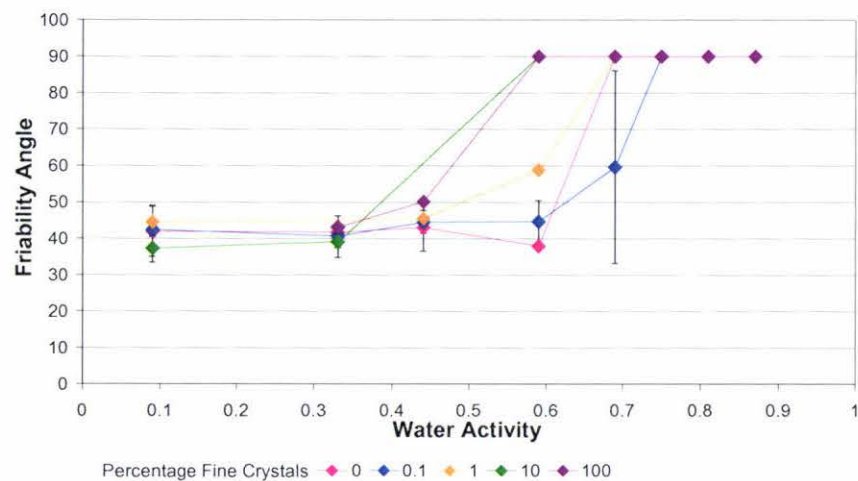


Figure A9 Angle required to break solid bridges in samples containing different proportions of 150-212 μm crystals, mixed with 600-850 μm crystals

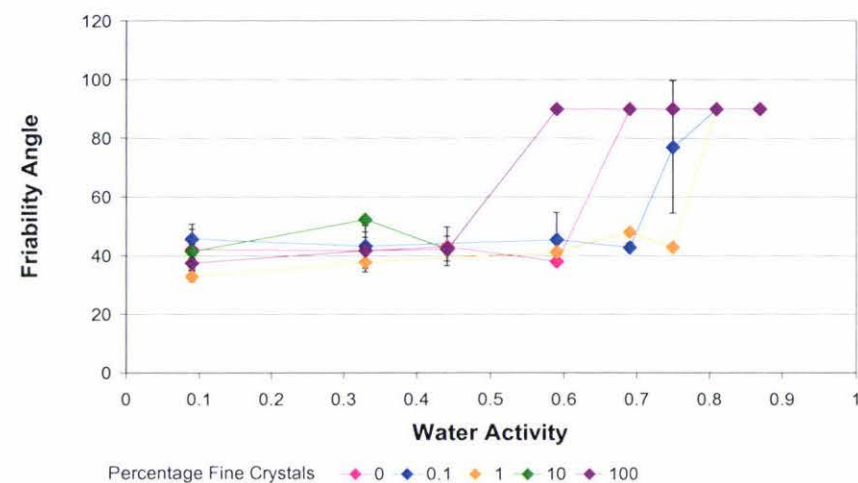


Figure A10 Angle required to break solid bridges in samples containing different proportions of 212-315 μm crystals, mixed with 600-850 μm crystals

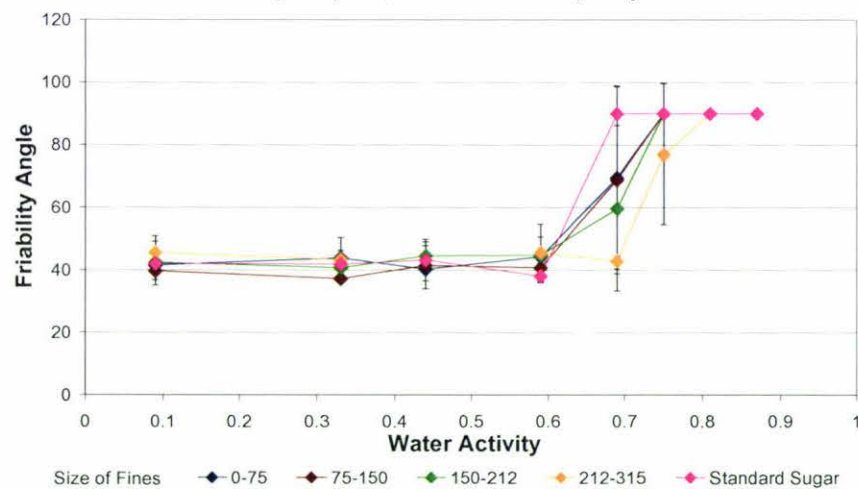


Figure A11 Angle required to break solid bridges in samples containing 0.1% fine crystals, mixed with 600-850 μm crystals

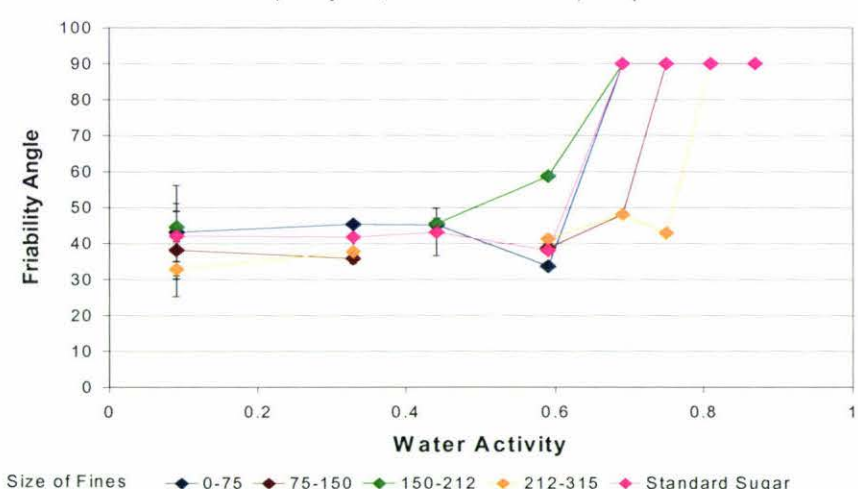


Figure A12 Angle required to break solid bridges in samples containing 1% fine crystals, mixed with 600-850 μm crystals

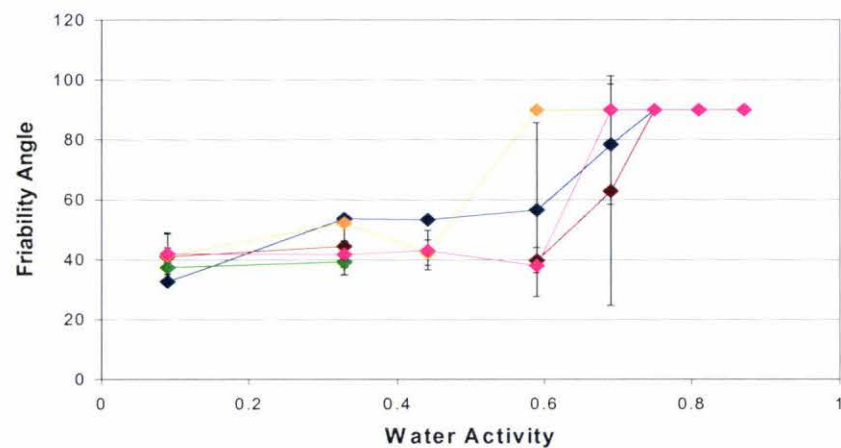


Figure A13 Angle required to break solid bridges in samples containing 10% fine crystals, mixed with 600-850 μm crystals

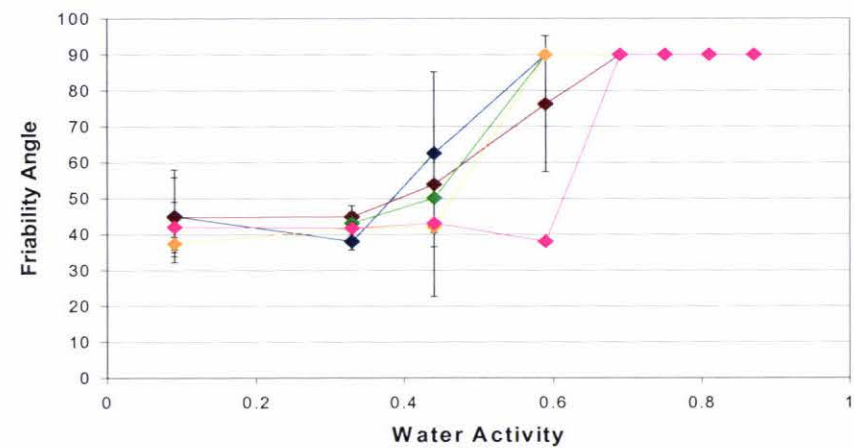


Figure A14 Angle required to break solid bridges in samples containing 100% fine crystals, mixed with 600-850 μm crystals

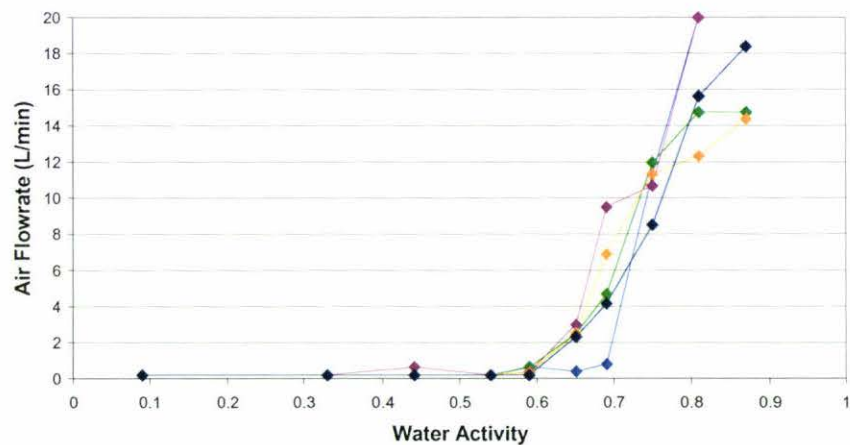


Figure A15 Airflow required to break liquid bridges in samples containing 0.1% fine crystals, mixed with 600-850 μm crystals

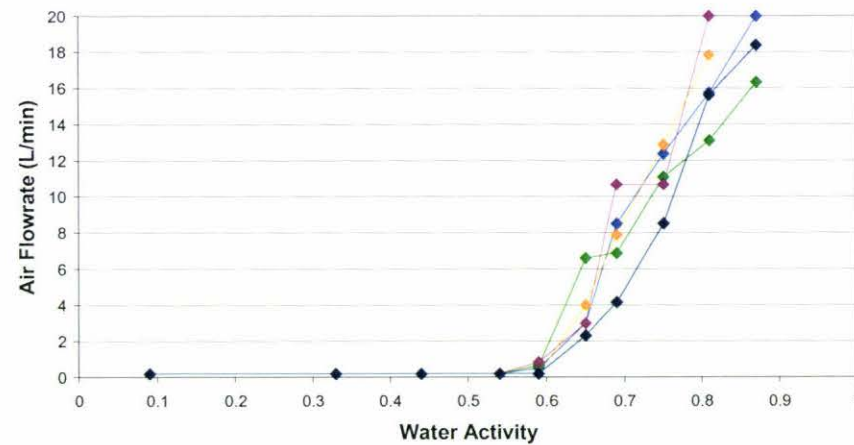


Figure A16 Airflow required to break liquid bridges in samples containing 1% fine crystals, mixed with 600-850 μm crystals

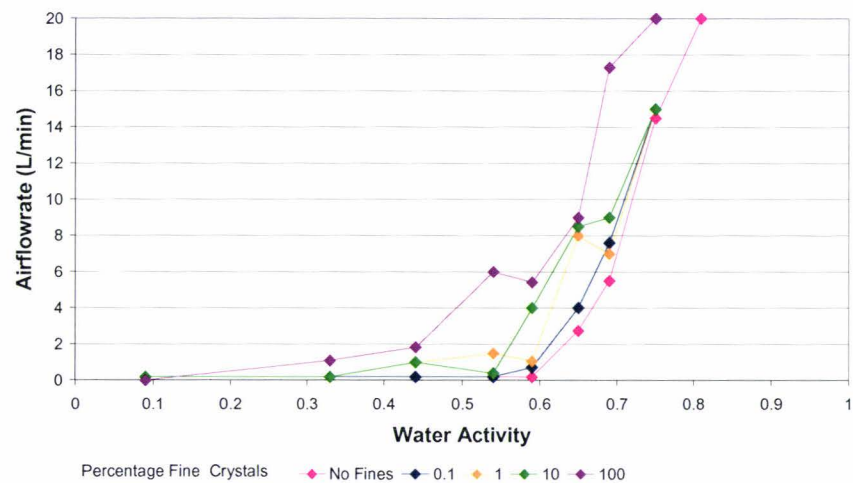


Figure A17 Airflow required to break solid bridges in samples containing different proportions of 75-150 μm crystals, mixed with 600-850 μm crystals

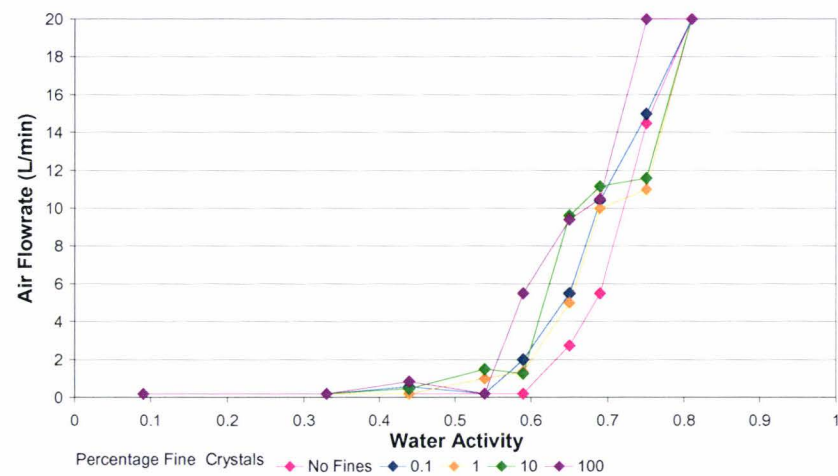


Figure A18 Airflow required to break solid bridges in samples containing different proportions of 150-212 μm crystals, mixed with 600-850 μm crystals

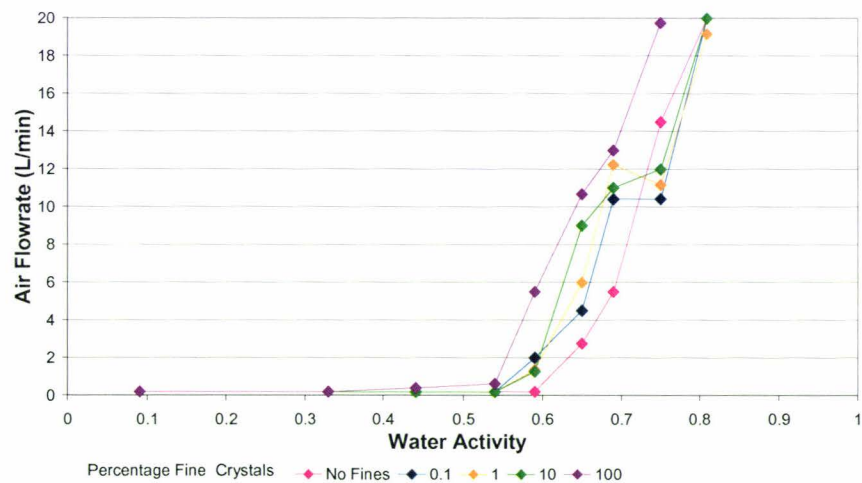


Figure A19 Airflow required to break solid bridges in samples containing different proportions of 212-315 μm crystals, mixed with 600-850 μm crystals

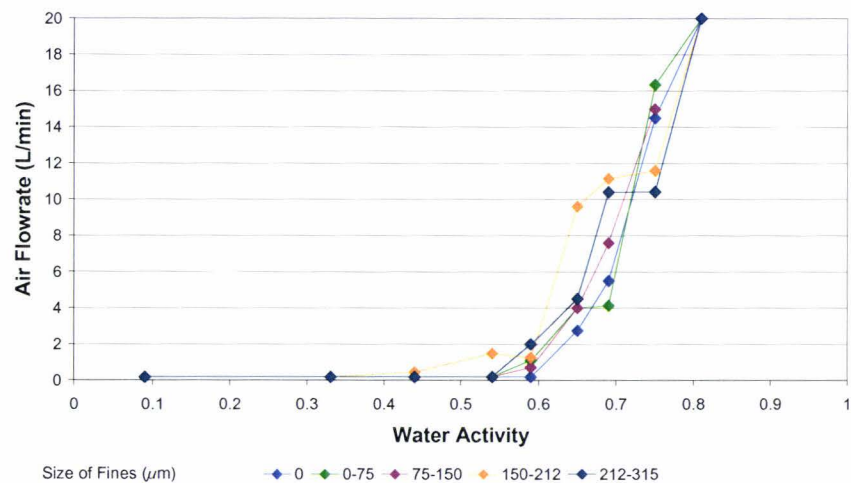


Figure A20 Airflow required to break solid bridges in samples containing 0.1% fine crystals, mixed with 600-850 μm crystals

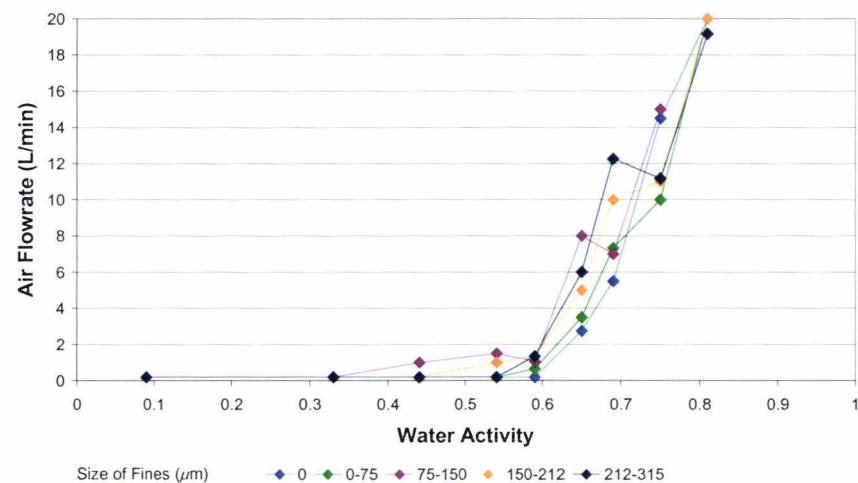


Figure A21 Airflow required to break solid bridges in samples containing 1% fine crystals, mixed with 600-850 μm crystals

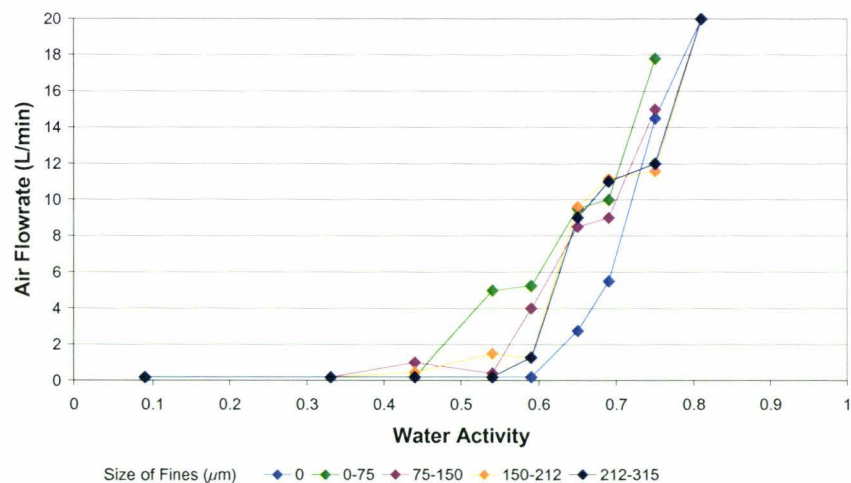


Figure A22 Airflow required to break solid bridges in samples containing 10% fine crystals, mixed with 600-850 μm crystals

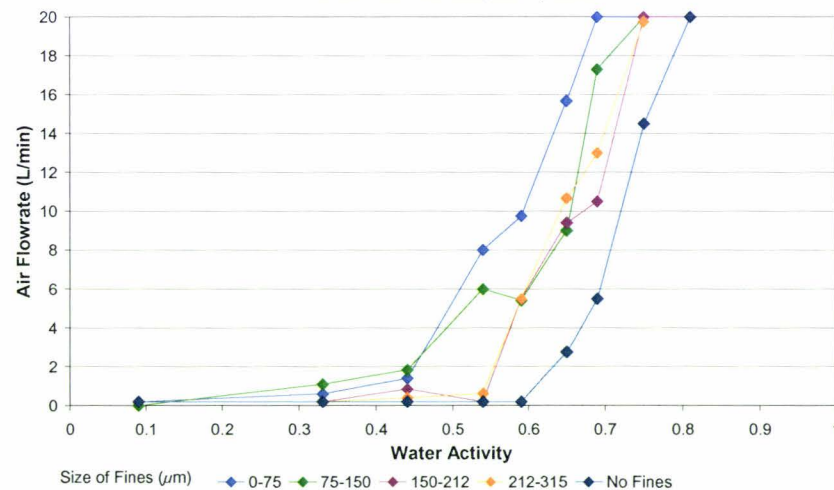


Figure A23 Airflow required to break solid bridges in samples containing 100% fine crystals

Appendix 3 - Sample Points -

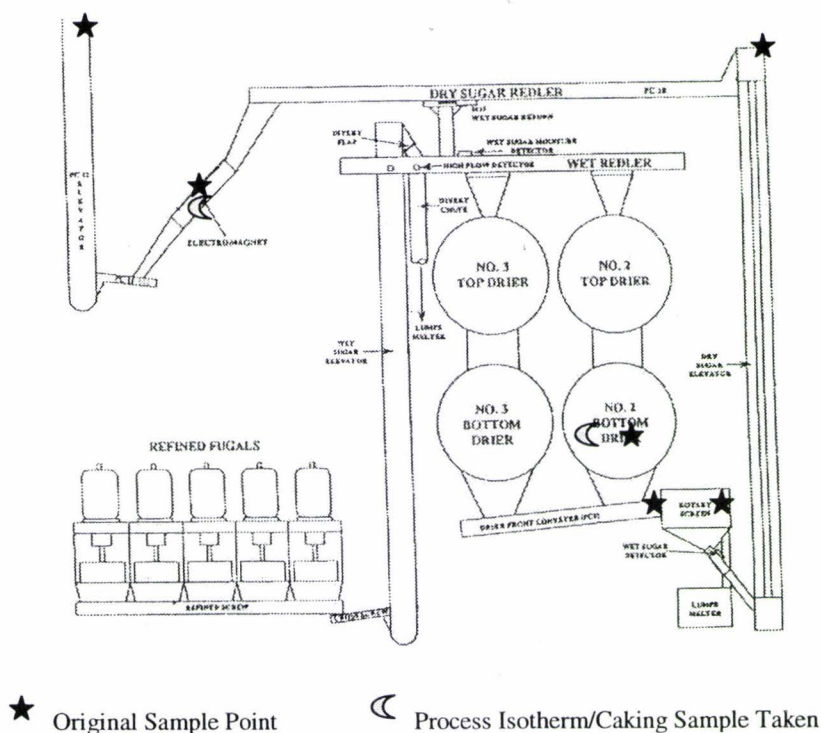


Figure A24 Sample points - drying

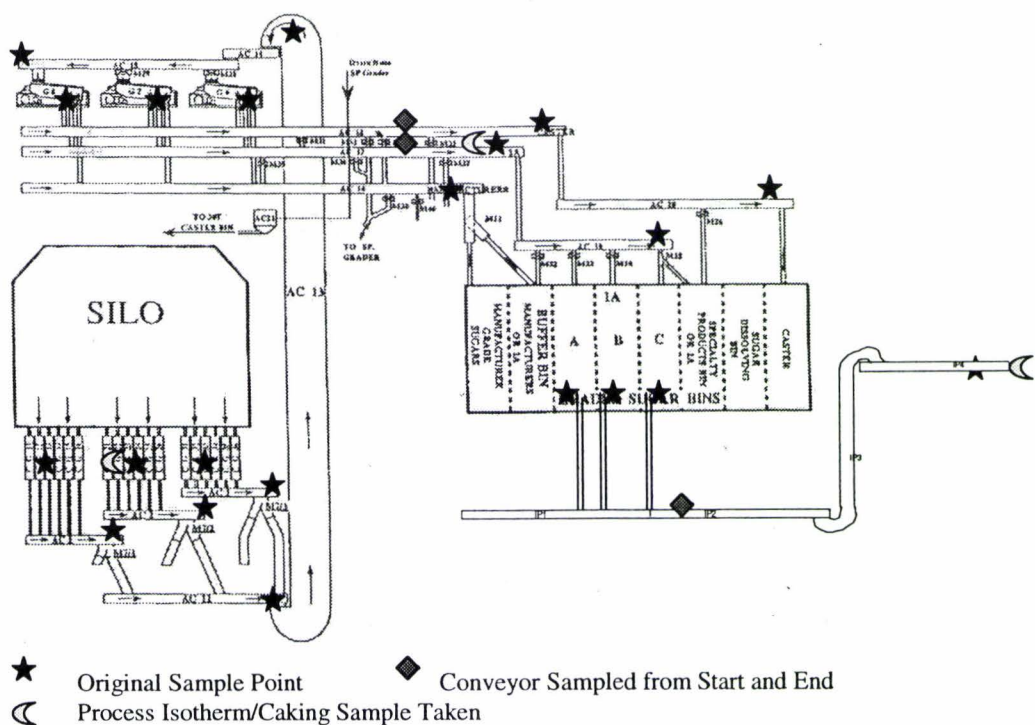


Figure A25 Sample points - conditioning

Appendix 4

- Calculations -

A4.1 Residence Time in Conveyors

Courtesy of Anthony Turnbull, New Zealand Sugar

Chain conveyors convey the sugar 'enmasse' at approximately the speed of the conveying chain, however there is some slippage. For this reason it is assumed that the conveyor is has an efficiency of 85%. Likewise, in screw conveyors there is some slippage of sugar, so an efficiency of 85% has been assumed.

AC17 Standard 1A Redler 'Enmasse' Chain Conveyor

Post-graders

Maximum throughput	30 t/hr
Maximum length	20 m
Chain velocity	315 mm/sec
Velocity of sugar mass	315 mm/sec
Residence time	63 secs
<i>Residence time (85% efficient)</i>	<i>74 secs</i>

AC18 Caster Screw Conveyor

Post-graders

Rotational speed	70 rpm
Length	20 m
Pitch of screw	275 mm
Conveying speed	0.32 m/sec
Residence time	62 sec
<i>Residence time (85% efficient)</i>	<i>70-75 sec</i>

IP1 – IP4 Standard 1A Screws Conveyors

Convey sugar from bulk bins to be packed

<i>IP1</i> Length	15 m
Pitch	0.475 m
Rotational speed	85 rpm
Conveying speed	0.67 m/sec
Residence time	22 sec
<i>Residence time (85% efficient)</i>	<i>26 sec</i>

<i>IP2</i> Length	15 m
Pitch	0.475
Rotational speed	85 rpm
Conveying speed	0.67 m/sec
Residence time	22 sec
<i>Residence time (85% efficient)</i>	<i>26 sec</i>

<i>IP4</i> Length	8 m
Pitch	0.475
Rotational speed	85 rpm
Conveying speed	0.67 m/sec
Residence time	12 sec
<i>Residence time (85% efficient)</i>	<i>14 sec</i>

<i>Total residence time</i>	<i>66 sec</i>
-----------------------------	---------------

A4.2 Packing If Small Crystals Fit Between Larger Crystals

In 1m³ of particles

$$\begin{aligned} \rho_b &= 831 \text{ kg/m}^3 \\ &= 831 \text{ kg} \end{aligned}$$

$$\varepsilon = 1 - \frac{\rho_{particle}}{\rho_b}$$

$$= 0.478$$

$$1 - 0.478 = 0.522 \text{ m}^3$$

For a sample 10% fines by mass

$$= 83.1 \text{ kg}$$

$$\rho_b = 756 \text{ kg/m}^3$$

$$\varepsilon = 0.525$$

$$\frac{83.1 \text{ kg}}{756 \text{ kg/m}^3} = 0.110 \text{ m}^3$$

Therefore, space remaining

$$= 1 - (0.522 + 0.110)$$

$$\varepsilon = 0.368$$

$$\rho_b = (1 - \varepsilon_{particle})$$

$$= (1 - \text{space remaining}) * \rho_{particle}$$

$$= (1 - 0.368) * 1590$$

$$= 1.005 \text{ kg/m}^3$$

Basis 1 m³

Sample	Mass Large	Mass Fines	Space Large	Space Fines	Space Remaining	Bulk Density
	kg	kg	m ³	m ³	m ³	kg/m ³
Std 1	830.6716					
0.10-75	830.6716	0.830672	0.522435	0.001001	0.476564	832.2626
0.175-150	830.6716	0.830672	0.522435	0.000997	0.476568	832.2573
0.1150-212	830.6716	0.830672	0.522435	0.000994	0.476571	832.2515
0.1212-315	830.6716	0.830672	0.522435	0.000998	0.476567	832.2579
10-75	830.6716	8.306716	0.522435	0.009914	0.467651	846.4352
175-150	830.6716	8.306716	0.522435	0.009936	0.46763	846.469
1150-212	830.6716	8.306716	0.522435	0.009851	0.467714	846.3344
1212-315	830.6716	8.306716	0.522435	0.009752	0.467813	846.1774
100-75	830.6716	83.06716	0.522435	0.099409	0.378156	988.7313
1075-150	830.6716	83.06716	0.522435	0.096002	0.381563	983.3149
10150-212	830.6716	83.06716	0.522435	0.096102	0.381463	983.4735
10212-315	830.6716	83.06716	0.522435	0.097009	0.380556	984.9166

A4.3 Packing If Small Crystals Form a Layer Around Large

The D [4,3] (average diameter of sphere with same volume) was calculated from the Malven Mastersizer 2000 data.

For the large particle

$$\text{Area} = \frac{4}{3} * \pi * r^3$$

$$\text{Mass} = \text{Area} * \rho_b$$

For particles surrounding large particle

$$\text{Mass 10\% fines} = 10\% \text{ of mass of large particle}$$

$$\text{Area occupied by fines} = \frac{\text{mass fines}}{\rho_b \text{ fines}}$$

$$\text{New 'particle' area} = \text{area fines} + \text{area large crystal}$$

$$\text{New 'particle' density} = \frac{\text{mass large crystals} + \text{mass fines}}{\text{Total 'particle' area}}$$

$$\rho_b = (1 - \epsilon_{\text{large crystals}}) * \rho_{\text{particle}}$$

Sample	D[4,3] m	Area um ³	Area m	Mass kg	Area fines m ³	Total Area m ³	Particle density kg/m ²	Bulk density kg/m ³
Std 1	738.645	2.11E+08	2.11E-10	3.36E-07				
0.10-75	69.275	174071.7	1.74E-13	3.36E-10	4.61E-13	2.11E-10	1590.448	830.9056
0.175-150	109.715	691507.1	6.92E-13	3.36E-10	4.45E-13	2.11E-10	1590.572	830.9702
0.1150-212	201.367	4275270	4.28E-12	3.36E-10	4.22E-13	2.11E-10	1590.742	831.059
0.1212-315	331.84	19133077	1.91E-11	3.36E-10	4.07E-13	2.11E-10	1590.851	831.1164
10-75	69.275	174071.7	1.74E-13	3.36E-09	4.61E-12	2.16E-10	1573.862	822.2407
175-150	109.715	691507.1	6.92E-13	3.36E-09	4.45E-12	2.15E-10	1575.064	822.8685
1150-212	201.367	4275270	4.28E-12	3.36E-09	4.22E-12	2.15E-10	1576.717	823.7319
1212-315	331.84	19133077	1.91E-11	3.36E-09	4.07E-12	2.15E-10	1577.787	824.2911
100-75	69.275	174071.7	1.74E-13	3.36E-08	4.61E-11	2.57E-10	1437.453	750.9756
1075-150	109.715	691507.1	6.92E-13	3.36E-08	4.45E-11	2.55E-10	1446.707	755.8106
10150-212	201.367	4275270	4.28E-12	3.36E-08	4.22E-11	2.53E-10	1459.61	762.5515
10212-315	331.84	19133077	1.91E-11	3.36E-08	4.07E-11	2.52E-10	1468.076	766.9742

A4.4 Estimation of Number of Crystals

From Malvern results know average (volume) crystal size

$$\text{Area} = \frac{4}{3} * \pi * r^3$$

$$\text{Mass} = \rho_{\text{particle}} * \text{volume}$$

Using 1kg basis can work out the mass of fine crystals

Therefore can work out mass of fine crystals

$$\text{Number of fine crystals} = \frac{\text{mass fines}}{\text{Mass 1 crystal}}$$

Likewise can calculate the number of larger crystals

Sample	# Fines
	2980554
0.10% 0-75	6593609
75-150	3890061
150-212	3127664
212-315	3013425
1% 0-75	39111110
75-150	12075628
150-212	4451651
212-315	3309268
10% 0-75	3.64E+08
75-150	93931293
150-212	17691531
212-315	6267693
100% 0-75	3.62E+09
75-150	9.12E+08
150-212	1.5E+08
212-315	35851942

- Appendix 5 - Laser Diffraction Analysis Reports



Result: Analysis Report

Sample Details Sample ID: 1A Sample File: REBECCA Sample Path: A: Sample Name: Run 1			
Run Number: 4	Record Number: 14	Measured: Sun 30 Mar 2003 3:03p.m.	Analysed: Sun 30 Mar 2003 3:03p.m.
Result Source: Analysed			
System Details Range Lens: 1000 mm Presentation: 3RHA Analysis Model: Compressed Range Modifications: None			
Beam Length: 10.00 mm [Particle R.I. = (1.4500, 0.1000), Dispersant R.I. = 1.0000] Sampler: MS64 Obscuration: 10.0 % Residual: 4.384 %			
Result Statistics Distribution Type: Volume Mean Diameter: D [4, 3] = 1002.05 um			
Concentration = 0.1558 %Vol D (v, 0.1) = 363.96 um D (v, 2) = 444.75 um			
Density = 1.567 g / cm ³ D (v, 0.5) = 625.18 um Span = 6.80E+01			
Specific S.A. = 0.0085 sq m / g D (v, 0.9) = 797.44 um Uniformity = 2.97E+01			
Size Low (um)	In %	Size High (um)	Under%
4.15	0.00	4.88	0.00
4.88	0.00	5.69	0.00
5.69	0.00	6.52	0.00
6.52	0.00	7.32	0.00
7.32	0.00	8.15	0.00
8.15	0.00	9.00	0.00
9.00	0.00	10.48	0.00
10.48	0.00	12.21	0.00
12.21	0.00	14.22	0.00
14.22	0.00	16.57	0.00
16.57	0.00	19.31	0.00
19.31	0.00	22.49	0.00
22.49	0.00	26.20	0.00
26.20	0.10	30.53	0.13
30.53	0.16	35.56	0.20
35.56	0.21	41.43	0.21
41.43	0.28	48.27	0.29
48.27	0.38	56.23	0.41
56.23	0.43	65.23	0.43
65.23	0.47	75.23	0.47
75.23	0.49	86.23	0.49
86.23	0.50	98.23	0.50
98.23	0.50	100.00	0.50

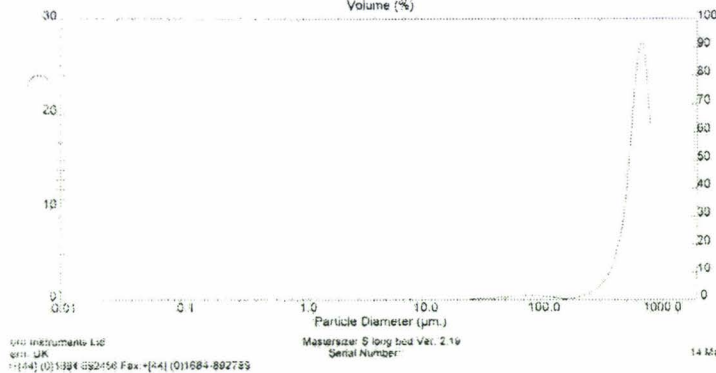


Figure A26 Malvern report for standard 1A sugar, sample 1



Result: Analysis Report

Sample Details Sample ID: AC 18 After Sample File: REBECCA Sample Path: A: Sample Name:			
Run Number: 8	Record Number: 4	Measured: Fri 5 Nov 2004 1:10p.m.	Analysed: Fri 5 Nov 2004 1:10p.m.
Result Source: Analysed			
System Details Range Lens: 1000 mm Presentation: 3RHA Analysis Model: Polydisperse Modifications: None			
Beam Length: 10.00 mm [Particle R.I. = (1.4500, 0.1000), Dispersant R.I. = 1.0000] Sampler: MS64 Obscuration: 5.9 % Residual: 5.21E %			
Result Statistics Distribution Type: Volume Mean Diameter: D [4, 3] = 1140.64 um			
Concentration = 0.0767 %Vol D (v, 0.1) = 232.14 um D (v, 2) = 384.55 um			
Density = 1.568 g / cm ³ D (v, 0.5) = 1161.85 um Span = 1.26E+01			
Specific S.A. = 0.0088 sq m / g D (v, 0.9) = 1823.84 um Uniformity = 3.68E+01			
Size Low (um)	In %	Size High (um)	Under%
4.15	0.00	4.88	0.00
4.88	0.00	5.69	0.00
5.69	0.00	6.52	0.00
6.52	0.00	7.32	0.00
7.32	0.00	8.15	0.00
8.15	0.00	9.00	0.00
9.00	0.00	10.48	0.00
10.48	0.00	12.21	0.00
12.21	0.00	14.22	0.00
14.22	0.00	16.57	0.00
16.57	0.00	19.31	0.00
19.31	0.00	22.49	0.00
22.49	0.00	26.20	0.00
26.20	0.00	30.53	0.00
30.53	0.00	35.56	0.00
35.56	0.00	41.43	0.00
41.43	0.00	48.27	0.00
48.27	0.00	56.23	0.00
56.23	0.00	65.23	0.00
65.23	0.00	75.23	0.00
75.23	0.00	86.23	0.00
86.23	0.00	98.23	0.00
98.23	0.00	100.00	0.00

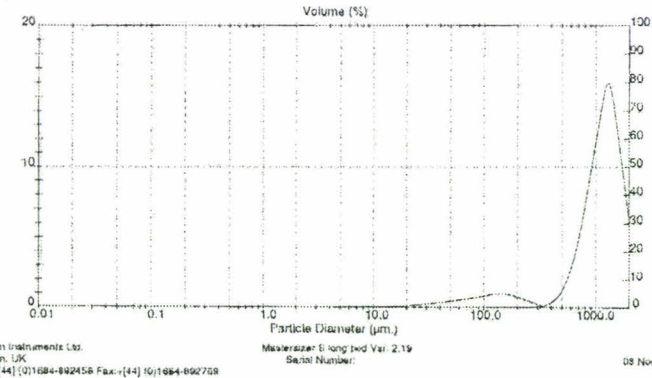


Figure A27 Malvern report for standard 1A sugar, sample 2

MASTERSIZER

Result: Analysis Report

Sample Details Sample ID: Manufacturers Sample File: REBECCA Sample Path: A Sample Notes: Run 1				System Details Range Lens: 1000 mm Beam Length: 10.00 mm Presentation: 2000 Analysis Mode: Compressed Range Modulations: None				Result Statistics Distribution Type: Volume Mean Diameter: D [4.2] = 597.28 µm Concentration = 0.1750 %Vol D (v, 0.1) = 386.35 µm D (v, 2) = 464.58 µm Density = 1.587 g/cub cm D (v, 0.5) = 528.32 µm Span = 7.26E-01 Specific S.A. = 0.0092 sq. m/g D (v, 0.9) = 811.78 µm Uniformity = 2.99E-01			
Sample Details Run Number: 3 Record Number: 13 Measured: Sun 30 Mar 2003 3:00p.m. Analysed: Sun 30 Mar 2003 3:00p.m. Result Source: Analysed				System Details Range Lens: 1000 mm Beam Length: 10.00 mm Presentation: 2000 Analysis Mode: Compressed Range Modulations: None				Result Statistics Distribution Type: Volume Mean Diameter: D [4.2] = 597.28 µm Concentration = 0.1750 %Vol D (v, 0.1) = 386.35 µm D (v, 2) = 464.58 µm Density = 1.587 g/cub cm D (v, 0.5) = 528.32 µm Span = 7.26E-01 Specific S.A. = 0.0092 sq. m/g D (v, 0.9) = 811.78 µm Uniformity = 2.99E-01			
Size Low (µm)	In %	Size High (µm)	Under%	Size Low (µm)	In %	Size High (µm)	Under%	Size Low (µm)	In %	Size High (µm)	Under%
4.19	0.00	4.88	0.00	65.51	0.38	76.22	1.69	75.32	0.92	88.91	3.29
4.68	0.00	5.68	0.00	76.32	0.35	88.91	2.04	88.91	1.39	103.58	4.88
5.68	0.00	6.63	0.00	88.91	0.34	103.58	2.39	103.58	2.06	120.67	6.74
6.63	0.00	7.72	0.00	103.58	0.27	120.67	2.69	120.67	2.97	140.26	9.71
7.72	0.00	9.00	0.00	120.67	0.19	140.26	2.94	140.26	4.11	163.77	13.83
9.00	0.00	10.45	0.00	140.26	0.19	163.77	3.04	163.77	5.42	190.60	19.29
10.45	0.00	12.21	0.00	163.77	0.35	190.60	3.29	190.60	6.79	222.28	26.94
12.21	0.00	14.22	0.00	190.60	0.66	222.28	4.08	222.28	8.09	258.55	34.14
14.22	0.00	16.57	0.00	222.28	1.13	258.55	5.21	258.55	9.24	301.68	43.36
16.57	0.00	19.31	0.00	258.55	1.75	301.68	6.96	301.68	10.25	351.46	53.93
19.31	0.00	22.49	0.00	301.68	2.73	351.46	9.69	351.46	11.13	409.45	64.77
22.49	0.00	26.20	0.00	351.46	4.46	409.45	14.14	409.45	10.59	477.01	75.39
26.20	0.08	30.63	0.06	409.45	7.65	477.01	21.75	477.01	9.27	555.71	84.52
30.63	0.12	35.95	0.20	477.01	13.34	555.71	35.13	555.71	7.43	647.41	92.05
35.95	0.17	41.45	0.37	555.71	19.74	647.41	54.87	647.41	5.19	754.23	97.25
41.45	0.24	48.27	0.61	647.41	24.85	754.23	79.77	754.23	2.75	876.67	100.00
48.27	0.31	56.23	0.92	754.23	20.23	876.67	100.00				
56.23	0.26	65.51	1.28								

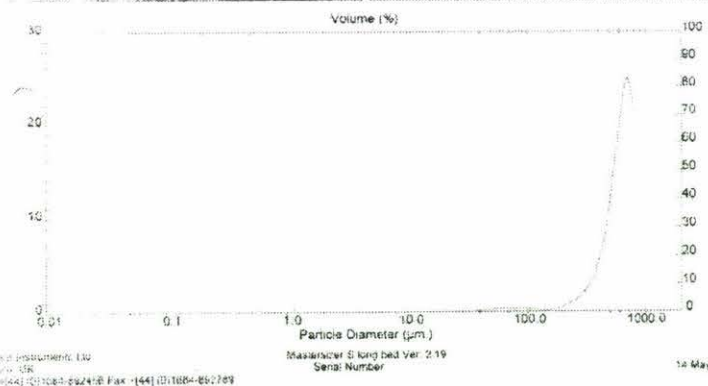


Figure A30 Malvern report for manufacturers sugar, sample 2

MASTERSIZER

Result: Analysis Report

Sample Details Sample ID: C3 Caster Sample File: REBECCA Sample Path: A Sample Notes: Run 2				System Details Range Lens: 1000 mm Beam Length: 10.00 mm Presentation: 2000 Analysis Mode: Compressed Range Modulations: None				Result Statistics Distribution Type: Volume Mean Diameter: D [4.2] = 587.51 µm Concentration = 0.1888 %Vol D (v, 0.1) = 342.26 µm D (v, 2) = 444.64 µm Density = 1.587 g/cub cm D (v, 0.5) = 533.57 µm Span = 1.420E+00 Specific S.A. = 0.0154 sq. m/g D (v, 0.9) = 817.97 µm Uniformity = 4.38E-01			
Sample Details Run Number: 6 Record Number: 19 Measured: Sun 30 Mar 2003 3:23p.m. Analysed: Sun 30 Mar 2003 3:23p.m. Result Source: Analysed				System Details Range Lens: 1000 mm Beam Length: 10.00 mm Presentation: 2000 Analysis Mode: Compressed Range Modulations: None				Result Statistics Distribution Type: Volume Mean Diameter: D [4.2] = 587.51 µm Concentration = 0.1888 %Vol D (v, 0.1) = 342.26 µm D (v, 2) = 444.64 µm Density = 1.587 g/cub cm D (v, 0.5) = 533.57 µm Span = 1.420E+00 Specific S.A. = 0.0154 sq. m/g D (v, 0.9) = 817.97 µm Uniformity = 4.38E-01			
Size Low (µm)	In %	Size High (µm)	Under%	Size Low (µm)	In %	Size High (µm)	Under%	Size Low (µm)	In %	Size High (µm)	Under%
4.19	0.00	4.68	0.00	75.32	0.92	88.91	3.29	75.32	0.92	88.91	3.29
4.68	0.00	5.68	0.00	88.91	1.39	103.58	4.88	88.91	1.39	103.58	4.88
5.68	0.00	6.63	0.00	103.58	2.06	120.67	6.74	103.58	2.06	120.67	6.74
6.63	0.00	7.72	0.00	120.67	2.97	140.26	9.71	120.67	2.97	140.26	9.71
7.72	0.00	9.00	0.00	140.26	4.11	163.77	13.83	140.26	4.11	163.77	13.83
9.00	0.00	10.45	0.00	163.77	5.42	190.60	19.29	163.77	5.42	190.60	19.29
10.45	0.00	12.21	0.00	190.60	6.79	222.28	26.94	190.60	6.79	222.28	26.94
12.21	0.00	14.22	0.00	222.28	8.09	258.55	34.14	222.28	8.09	258.55	34.14
14.22	0.04	16.57	0.08	258.55	9.24	301.68	43.36	258.55	9.24	301.68	43.36
16.57	0.06	19.31	0.13	301.68	10.25	351.46	53.93	301.68	10.25	351.46	53.93
19.31	0.08	22.49	0.21	351.46	11.13	409.45	64.77	351.46	11.13	409.45	64.77
22.49	0.10	26.20	0.31	409.45	10.59	477.01	75.39	409.45	10.59	477.01	75.39
26.20	0.12	30.63	0.44	477.01	9.27	555.71	84.52	477.01	9.27	555.71	84.52
30.63	0.16	35.95	0.61	555.71	7.43	647.41	92.05	555.71	7.43	647.41	92.05
35.95	0.20	41.45	0.80	647.41	5.19	754.23	97.25	647.41	5.19	754.23	97.25
41.45	0.24	48.27	1.04	754.23	2.75	876.67	100.00	754.23	2.75	876.67	100.00
48.27	0.31	56.23	1.35								
56.23	0.42	65.51	1.77								

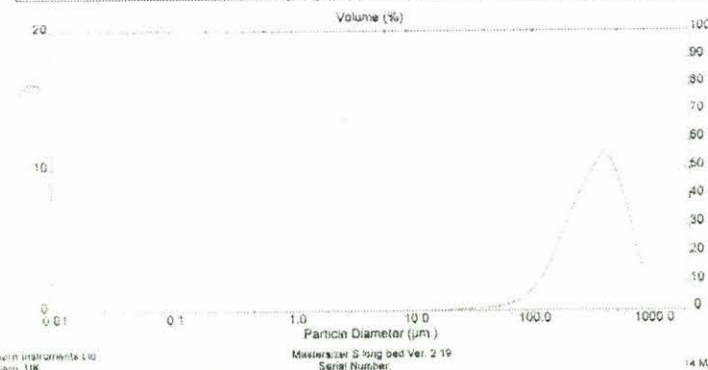


Figure A31 Malvern report for caster sugar, sample 1

MASTERSIZER

Result: Analysis Report

Sample Details		
Sample ID: 01-Caster	Run Number: 10	Measured: Sun 30 May 2023 12:32p
Sample File: RESECCA	Record Number: 10	Analysed: Sun 30 May 2023 2:32p
Sample Name: Run 1		Result Source: Analysed

System Details		
Sample Name: 01-Caster	Sample Weight: 10.00 g	Sample: M000
Sample File: RESECCA	Sample ID: 10	Sample: M000
Sample Name: Run 1		

Result Statistics		
Sample Name: 01-Caster	Sample Weight: 10.00 g	Sample: M000
Sample File: RESECCA	Sample ID: 10	Sample: M000
Sample Name: Run 1		

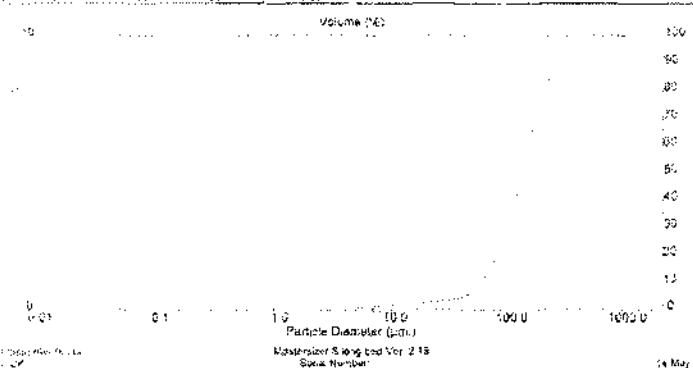


Figure A32 Malvern report for caster sugar, sample 2

MASTERSIZER

Result: Analysis Report

Sample Details		
Sample ID: 01-Caster	Run Number: 11	Measured: Sun 30 May 2023 12:32p
Sample File: RESECCA	Record Number: 11	Analysed: Sun 30 May 2023 2:32p
Sample Name: Run 2		Result Source: Analysed

System Details		
Sample Name: 01-Caster	Sample Weight: 10.00 g	Sample: M000
Sample File: RESECCA	Sample ID: 11	Sample: M000
Sample Name: Run 2		

Result Statistics		
Sample Name: 01-Caster	Sample Weight: 10.00 g	Sample: M000
Sample File: RESECCA	Sample ID: 11	Sample: M000
Sample Name: Run 2		

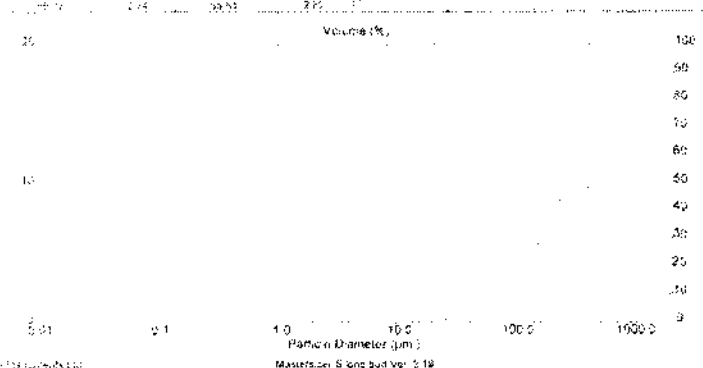
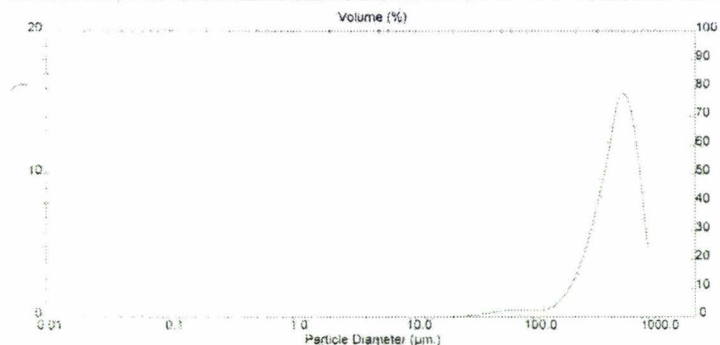


Figure A33 Malvern report for caster sugar, sample 3

MASTERSIZER

Result: Analysis Report

Sample Details			
Sample ID: FF Caster	Run Number: 1	Measured: Sun 30 Mar 2003 2:53p.m	
Sample File: REBECCA	Record Number: 11	Analysis: Sun 30 Mar 2003 2:53p.m	
Sample Path: A:\		Result Source: Analyzed	
Sample Notes: Run 1			
System Details			
Range Lens: 1000mm	Beam Length: 10.00 mm	Sampler: M300	Obscuration: 14.2 %
Presentation: 3RPA	[Particle R.I. = (1.4500, 0.1000);	Dispersant R.I. = 1.0000]	Residual: 2.270 %
Analysis Model: Compressed Range			
Modifications: None			
Result Statistics			
Distribution Type: Volume	Concentration = 0.1022 %Vol	Density = 1.557 g / cub cm	Specific S.A. = 0.0116 sq m / g
Mean Diameter:	D (v, 0.1) = 214.44 um	D (v, 0.5) = 441.43 um	D (v, 0.9) = 577.11 um
D (w, 0.1) = 442.61 um	D (w, 0.5) = 517.95 um	Span = 1.048E+00	Uniformity = 0.216E-01
Size Low (um)	In %	Size High (um)	Under%
4.18	0.00	4.88	0.00
4.95	0.00	5.59	0.00
5.99	0.00	6.63	0.00
6.63	0.00	7.72	0.00
7.72	0.00	9.00	0.00
9.00	0.00	10.46	0.00
10.46	0.00	12.21	0.00
12.21	0.00	14.22	0.00
14.22	0.00	16.57	0.00
16.57	0.00	19.31	0.00
19.31	0.06	22.49	0.06
22.49	0.08	26.20	0.14
26.20	0.13	30.52	0.27
30.52	0.19	35.58	0.49
35.58	0.27	41.43	0.72
41.43	0.35	48.27	1.08
48.27	0.43	56.23	1.51
56.23	0.48	65.51	1.99
65.51	0.49	76.32	2.47
76.32	0.46	88.91	2.93
88.91	0.44	103.58	3.37
103.58	0.53	120.67	3.87
120.67	0.73	140.58	4.81
140.58	1.21	163.77	5.92
163.77	1.97	190.00	7.76
190.00	3.20	222.26	10.83
222.26	4.54	258.95	15.37
258.95	6.59	301.68	21.96
301.68	9.10	351.46	31.06
351.46	11.85	409.45	42.92
409.45	14.92	477.01	57.84
477.01	16.48	550.71	73.31
550.71	13.40	647.41	89.51
647.41	9.33	754.23	99.54
754.23	4.10	878.07	100.00



m: Instruments Ltd
 m: UK
 t: (44) (0)1684-892456 Fax: (44) (0)1684-892789

Mastersizer S long bed Ver. 2.19
 Serial Number:

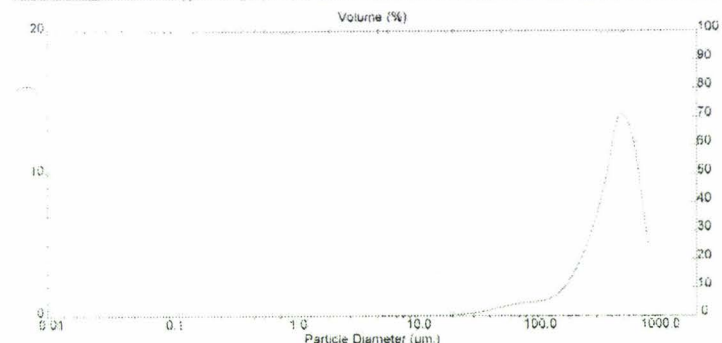
14 May 04 15:32

Figure A34 Malvern report for fines free caster sugar, sample 1

MASTERSIZER

Result: Analysis Report

Sample Details			
Sample ID: FF Caster	Run Number: 2	Measured: Sun 30 Mar 2003 2:57p.m	
Sample File: REBECCA	Record Number: 12	Analysis: Sun 30 Mar 2003 2:57p.m	
Sample Path: A:\		Result Source: Analyzed	
Sample Notes: Run 2			
System Details			
Range Lens: 1000mm	Beam Length: 10.00 mm	Sampler: M300	Obscuration: 13.9 %
Presentation: 3RPA	[Particle R.I. = (1.4500, 0.1000);	Dispersant R.I. = 1.0000]	Residual: 0.956 %
Analysis Model: Compressed Range			
Modifications: None			
Result Statistics			
Distribution Type: Volume	Concentration = 0.1140 %Vol	Density = 1.587 g / cub cm	Specific S.A. = 0.0162 sq m / g
Mean Diameter:	D (v, 0.1) = 103.33 um	D (v, 0.5) = 425.38 um	D (v, 0.9) = 676.93 um
D (w, 0.1) = 421.77 um	D (w, 0.5) = 232.84 um	Span = 1.238E+00	Uniformity = 3.732E-01
Size Low (um)	In %	Size High (um)	Under%
4.18	0.00	4.88	0.00
4.95	0.00	5.59	0.00
5.99	0.00	6.63	0.00
6.63	0.00	7.72	0.00
7.72	0.00	9.00	0.00
9.00	0.00	10.46	0.00
10.46	0.00	12.21	0.00
12.21	0.00	14.22	0.00
14.22	0.00	16.57	0.00
16.57	0.00	19.31	0.00
19.31	0.00	22.49	0.00
22.49	0.00	26.20	0.00
26.20	0.00	30.53	0.00
30.53	0.00	35.50	0.00
35.50	0.00	41.43	0.00
41.43	0.00	48.27	0.00
48.27	0.00	56.23	0.00
56.23	0.00	65.51	0.00
65.51	0.00	76.32	0.00
76.32	0.00	88.91	0.00
88.91	0.00	103.58	0.00
103.58	0.00	120.67	0.00
120.67	0.00	140.58	0.00
140.58	0.00	163.77	0.00
163.77	0.00	190.00	0.00
190.00	0.00	222.28	0.00
222.28	0.00	258.95	0.00
258.95	0.00	301.68	0.00
301.68	0.00	351.46	0.00
351.46	0.00	409.45	0.00
409.45	0.00	477.01	0.00
477.01	0.00	555.71	0.00
555.71	0.00	647.41	0.00
647.41	0.00	754.23	0.00
754.23	0.00	878.07	0.00



m: Instruments Ltd
 m: UK
 t: (44) (0)1684-892456 Fax: (44) (0)1684-892789

Mastersizer S long bed Ver. 2.19
 Serial Number:

14 May 04 15:32

Figure A35 Malvern report for fines free caster sugar, sample 2

MASTER SIZER

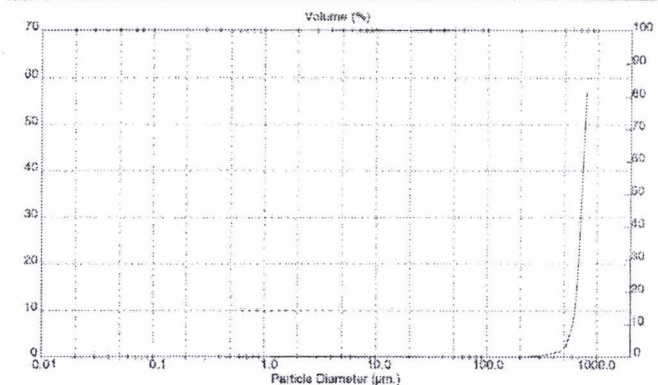
Result: Analysis Report

Sample Details		
Sample ID: standard 600-850	Run Number: 20	Measured: Tue 13 Jul 2004 11:54am
Sample File: REBECCA1	Record Number: 20	Analysed: Tue 13 Jul 2004 11:54am
Sample Path: C:\SIZER\DATA1		Result Source: Analysed
Sample Name:		

System Details			
Range Lens: 1000 mm	Beam Length: 10.00 mm	Dispersion: M365	Observation: 7.6 %
Presentation: 3R/1A	Particle F.I. = (1.4500, 0.1000)	Dispersion F.I. = 1.0000	Residual: 3.49 %
Analysis Mode: Compressed Range			
Modifications: None			

Result Statistics			
Distribution Type: Volume	Concentration = 0.1802 %Vol	Density = 1.588 g/cub cm	Specific S.A. = 0.0057 sq. m/g
Mean Diameter: D [v, 0.1] = 816.28 um	D [v, 0.5] = 790.53 um	D [v, 0.9] = 456.50 um	Uniformity = 3.85E-02
D [4, 3] = 744.99 um	D [2, 2] = 684.74 um	Span = 3.116E-01	

Size Low (um)	in %	Size High (um)	Under %	Size Low (um)	in %	Size High (um)	Under %
4.18	0.00	4.88	0.00	65.51	0.00	75.32	0.28
4.88	0.00	5.69	0.00	75.32	0.10	85.91	0.38
5.69	0.00	6.51	0.00	85.91	0.10	100.55	0.43
6.51	0.00	7.72	0.00	100.55	0.09	120.67	0.56
7.72	0.00	9.00	0.00	120.67	0.06	140.58	0.60
9.00	0.00	10.48	0.00	140.58	0.01	160.77	0.60
10.48	0.00	12.21	0.00	160.77	0.04	180.80	0.64
12.21	0.00	14.22	0.00	180.80	0.09	202.26	0.73
14.22	0.00	16.57	0.00	202.26	0.18	250.55	0.91
16.57	0.00	19.31	0.00	250.55	0.31	301.58	1.21
19.31	0.00	22.45	0.00	301.58	0.48	361.40	1.70
22.45	0.00	26.00	0.00	361.40	0.71	426.45	2.41
26.00	0.00	30.03	0.00	426.45	1.13	477.01	3.54
30.03	0.00	34.56	0.00	477.01	2.31	555.71	5.85
34.56	0.00	41.43	0.00	555.71	5.59	647.41	12.84
41.43	0.04	48.27	0.07	647.41	25.75	754.23	36.57
48.27	0.09	56.23	0.12	754.23	61.49	876.67	100.00
56.23	0.27	65.51	0.28				



Malvern Instruments Ltd
Malvern, UK
Tel: +44 (0)1684-892455 Fax: +44 (0)1684-892789

MasterSizer 5 Long Led Ver. 2.19
Serial Number

MASTER SIZER

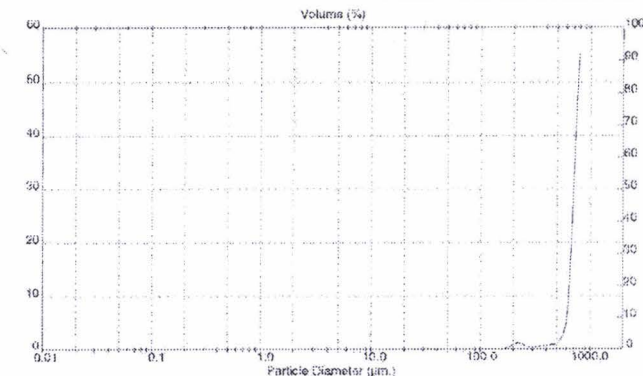
Result: Analysis Report

Sample Details		
Sample ID: Standard 1	Run Number: 1	Measured: Tue 13 Jul 2004 10:48am
Sample File: REBECCA1	Record Number: 2	Analysed: Tue 13 Jul 2004 10:48am
Sample Path: C:\SIZER\DATA1		Result Source: Analysed
Sample Name:		

System Details			
Range Lens: 1000 mm	Beam Length: 10.00 mm	Dispersion: M365	Observation: 0.7 %
Presentation: 3R/1A	Particle F.I. = (1.4500, 0.1000)	Dispersion F.I. = 1.0000	Residual: 3.41 %
Analysis Mode: Compressed Range			
Modifications: None			

Result Statistics			
Distribution Type: Volume	Concentration = 0.0434 %Vol	Density = 1.588 g/cub cm	Specific S.A. = 0.0077 sq. m/g
Mean Diameter: D [v, 0.1] = 623.40 um	D [v, 0.5] = 772.51 um	D [v, 0.9] = 357.50 um	Uniformity = 1.144E-01
D [4, 3] = 710.90 um	D [2, 2] = 489.48 um	Span = 3.000E-01	

Size Low (um)	in %	Size High (um)	Under %	Size Low (um)	in %	Size High (um)	Under %
4.18	0.01	4.88	0.01	65.51	0.00	75.32	0.98
4.88	0.02	5.69	0.03	75.32	0.00	85.91	0.99
5.69	0.03	6.51	0.06	85.91	0.00	100.55	0.99
6.51	0.03	7.72	0.15	100.55	0.00	120.67	0.99
7.72	0.04	9.00	0.13	120.67	0.01	140.58	0.99
9.00	0.04	10.48	0.17	140.58	0.00	160.77	1.00
10.48	0.06	12.21	0.22	160.77	0.33	180.80	1.36
12.21	0.06	14.22	0.28	180.80	0.38	202.26	2.41
14.22	0.07	16.57	0.30	202.26	1.09	250.55	3.40
16.57	0.09	19.31	0.44	250.55	0.38	301.58	0.90
19.31	0.00	22.45	0.54	301.58	0.00	361.40	4.08
22.45	0.00	26.00	0.80	361.40	0.80	426.45	5.04
26.00	0.08	30.03	0.71	426.45	0.83	477.01	5.87
30.03	0.30	34.56	0.79	477.01	1.29	555.71	7.14
34.56	0.39	41.43	0.38	555.71	4.45	647.41	11.01
41.43	0.07	48.27	0.25	647.41	30.46	754.23	42.07
48.27	0.03	56.23	0.36	754.23	27.59	876.67	100.00
56.23	0.01	65.51	0.58				



Malvern Instruments Ltd
Malvern, UK
Tel: +44 (0)1684-892455 Fax: +44 (0)1684-892789

MasterSizer 5 Long Led Ver. 2.19
Serial Number

13 Jul 04 10:48

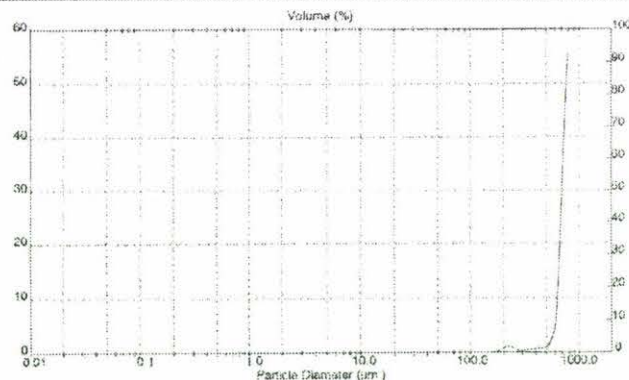
Figure A36 Malvern report for standard 600-850 µm sugar, sample 1

Figure A37 Malvern report for standard 600-850 µm sugar, sample 2

MASTERSIZER

Result: Analysis Report

Sample Details Sample ID: Standard 1 Sample File: REBECCO1 Sample Path: C:\SIZER\DATA\1 Sample Name:				System Details Range Lens: 1000 mm Presentation: 350A Analysis Model: Compressed Range Modulation: None																																																																																																																																																											
Sample Details Run Number: 2 Record Number: 3 Measured: Tue 10 Jul 2004 10:54 am Analyzed: Tue 10 Jul 2004 10:54 am Result Source: Analyst				System Details Range Lens: 1000 mm Presentation: 350A Analysis Model: Compressed Range Modulation: None																																																																																																																																																											
System Details Beam Length: 10.00 mm [Particle R.I. = 1.4500, D: 10000] Dispersion R.I. = 1.0000 Concentration: 2.7 % Backscat: 3.817 %				Result Statistics Distribution Type: Volume Mean Diameter: D [4.3] = 732.00 µm Concentration = 0.0434 % Vol D [v, 0.1] = 420.42 µm D [v, 2] = 489.40 µm Density = 1.588 g/ml µm D [v, 0.5] = 772.81 µm Span = 3.0068 Specific S.A. = 0.0077 sq. m/g D [v, 0.5] = 867.50 µm Uncertainty = 1.14E-01																																																																																																																																																											
<table border="1"> <thead> <tr> <th>Size (µm)</th> <th>D (%)</th> <th>Size (µm)</th> <th>D (%)</th> <th>Size (µm)</th> <th>D (%)</th> <th>Size (µm)</th> <th>D (%)</th> </tr> </thead> <tbody> <tr><td>4.19</td><td>0.01</td><td>4.68</td><td>0.01</td><td>15.51</td><td>0.00</td><td>76.32</td><td>0.08</td></tr> <tr><td>4.84</td><td>0.03</td><td>5.68</td><td>0.03</td><td>76.32</td><td>0.00</td><td>88.91</td><td>0.40</td></tr> <tr><td>5.80</td><td>0.10</td><td>6.62</td><td>0.06</td><td>98.91</td><td>0.00</td><td>103.18</td><td>0.96</td></tr> <tr><td>6.68</td><td>0.33</td><td>7.77</td><td>0.09</td><td>103.18</td><td>0.00</td><td>140.59</td><td>0.96</td></tr> <tr><td>7.72</td><td>0.04</td><td>9.00</td><td>0.12</td><td>120.87</td><td>0.01</td><td>140.59</td><td>0.96</td></tr> <tr><td>9.01</td><td>0.34</td><td>10.48</td><td>0.17</td><td>140.59</td><td>0.00</td><td>182.77</td><td>1.05</td></tr> <tr><td>10.48</td><td>0.90</td><td>12.81</td><td>0.22</td><td>182.77</td><td>0.00</td><td>190.20</td><td>1.29</td></tr> <tr><td>12.81</td><td>0.06</td><td>14.22</td><td>0.28</td><td>190.20</td><td>0.03</td><td>220.29</td><td>0.41</td></tr> <tr><td>14.22</td><td>0.07</td><td>16.57</td><td>0.30</td><td>220.29</td><td>0.00</td><td>289.99</td><td>0.49</td></tr> <tr><td>16.57</td><td>0.06</td><td>19.21</td><td>0.44</td><td>289.99</td><td>0.00</td><td>301.68</td><td>1.08</td></tr> <tr><td>19.21</td><td>0.09</td><td>22.46</td><td>0.54</td><td>301.68</td><td>0.00</td><td>361.45</td><td>0.99</td></tr> <tr><td>22.46</td><td>0.09</td><td>26.20</td><td>0.60</td><td>361.45</td><td>0.00</td><td>409.45</td><td>0.04</td></tr> <tr><td>26.20</td><td>0.06</td><td>30.53</td><td>0.71</td><td>409.45</td><td>0.00</td><td>477.03</td><td>0.87</td></tr> <tr><td>30.53</td><td>0.08</td><td>35.56</td><td>0.76</td><td>477.03</td><td>0.00</td><td>555.71</td><td>0.78</td></tr> <tr><td>35.56</td><td>0.09</td><td>41.42</td><td>0.88</td><td>555.71</td><td>0.00</td><td>647.41</td><td>1.60</td></tr> <tr><td>41.42</td><td>0.07</td><td>48.27</td><td>0.95</td><td>647.41</td><td>0.00</td><td>754.23</td><td>42.07</td></tr> <tr><td>48.27</td><td>0.03</td><td>56.23</td><td>0.08</td><td>754.23</td><td>97.93</td><td>870.67</td><td>100.00</td></tr> <tr><td>56.23</td><td>0.01</td><td>65.51</td><td>0.08</td><td></td><td></td><td></td><td></td></tr> </tbody> </table>				Size (µm)	D (%)	Size (µm)	D (%)	Size (µm)	D (%)	Size (µm)	D (%)	4.19	0.01	4.68	0.01	15.51	0.00	76.32	0.08	4.84	0.03	5.68	0.03	76.32	0.00	88.91	0.40	5.80	0.10	6.62	0.06	98.91	0.00	103.18	0.96	6.68	0.33	7.77	0.09	103.18	0.00	140.59	0.96	7.72	0.04	9.00	0.12	120.87	0.01	140.59	0.96	9.01	0.34	10.48	0.17	140.59	0.00	182.77	1.05	10.48	0.90	12.81	0.22	182.77	0.00	190.20	1.29	12.81	0.06	14.22	0.28	190.20	0.03	220.29	0.41	14.22	0.07	16.57	0.30	220.29	0.00	289.99	0.49	16.57	0.06	19.21	0.44	289.99	0.00	301.68	1.08	19.21	0.09	22.46	0.54	301.68	0.00	361.45	0.99	22.46	0.09	26.20	0.60	361.45	0.00	409.45	0.04	26.20	0.06	30.53	0.71	409.45	0.00	477.03	0.87	30.53	0.08	35.56	0.76	477.03	0.00	555.71	0.78	35.56	0.09	41.42	0.88	555.71	0.00	647.41	1.60	41.42	0.07	48.27	0.95	647.41	0.00	754.23	42.07	48.27	0.03	56.23	0.08	754.23	97.93	870.67	100.00	56.23	0.01	65.51	0.08								
Size (µm)	D (%)	Size (µm)	D (%)	Size (µm)	D (%)	Size (µm)	D (%)																																																																																																																																																								
4.19	0.01	4.68	0.01	15.51	0.00	76.32	0.08																																																																																																																																																								
4.84	0.03	5.68	0.03	76.32	0.00	88.91	0.40																																																																																																																																																								
5.80	0.10	6.62	0.06	98.91	0.00	103.18	0.96																																																																																																																																																								
6.68	0.33	7.77	0.09	103.18	0.00	140.59	0.96																																																																																																																																																								
7.72	0.04	9.00	0.12	120.87	0.01	140.59	0.96																																																																																																																																																								
9.01	0.34	10.48	0.17	140.59	0.00	182.77	1.05																																																																																																																																																								
10.48	0.90	12.81	0.22	182.77	0.00	190.20	1.29																																																																																																																																																								
12.81	0.06	14.22	0.28	190.20	0.03	220.29	0.41																																																																																																																																																								
14.22	0.07	16.57	0.30	220.29	0.00	289.99	0.49																																																																																																																																																								
16.57	0.06	19.21	0.44	289.99	0.00	301.68	1.08																																																																																																																																																								
19.21	0.09	22.46	0.54	301.68	0.00	361.45	0.99																																																																																																																																																								
22.46	0.09	26.20	0.60	361.45	0.00	409.45	0.04																																																																																																																																																								
26.20	0.06	30.53	0.71	409.45	0.00	477.03	0.87																																																																																																																																																								
30.53	0.08	35.56	0.76	477.03	0.00	555.71	0.78																																																																																																																																																								
35.56	0.09	41.42	0.88	555.71	0.00	647.41	1.60																																																																																																																																																								
41.42	0.07	48.27	0.95	647.41	0.00	754.23	42.07																																																																																																																																																								
48.27	0.03	56.23	0.08	754.23	97.93	870.67	100.00																																																																																																																																																								
56.23	0.01	65.51	0.08																																																																																																																																																												



Malvern Instruments Ltd.
 Malvern, UK
 Tel: +44 (0)1690-826456 Fax: +44 (0)1690-892089

Mastersizer 50 long bed Ver. 0.19
 Serial Number:

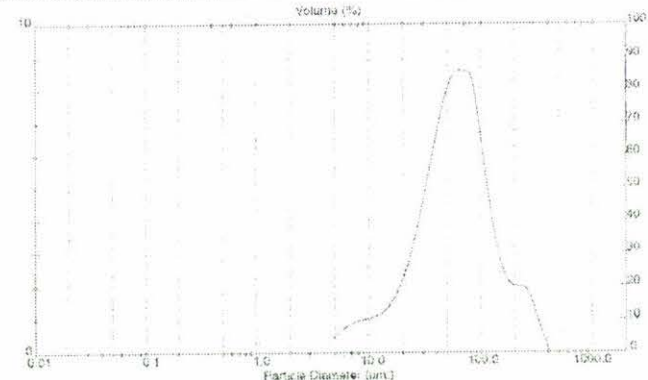
13 Jul 04 13:46

Figure A38 Malvern report for standard 600-850 µm sugar, sample 3

MASTERSIZER

Result: Analysis Report

Sample Details Sample ID: Focus Sample File: REBECCO1 Sample Path: C:\SIZER\DATA\1 Sample Name:				System Details Range Lens: 1000 mm Presentation: 350A Analysis Model: Compressed Range Modulation: None																																																																																																																																																											
Sample Details Run Number: 3 Record Number: 12 Measured: Tue 10 Jul 2004 11:02 am Analyzed: Tue 10 Jul 2004 11:02 am Result Source: Analyst				System Details Range Lens: 1000 mm Presentation: 350A Analysis Model: Compressed Range Modulation: None																																																																																																																																																											
System Details Beam Length: 10.00 mm [Particle R.I. = 1.4500, D: 10000] Dispersion R.I. = 1.0000 Concentration: 7.9 % Backscat: 1.759 %				Result Statistics Distribution Type: Volume Mean Diameter: D [4.3] = 76.78 µm Concentration = 0.0096 % Vol D [v, 0.1] = 19.24 µm D [v, 2] = 97.29 µm Density = 1.588 g/ml µm D [v, 0.5] = 19.47 µm Span = 2.286459																																																																																																																																																											
<table border="1"> <thead> <tr> <th>Size (µm)</th> <th>D (%)</th> <th>Size (µm)</th> <th>D (%)</th> <th>Size (µm)</th> <th>D (%)</th> <th>Size (µm)</th> <th>D (%)</th> </tr> </thead> <tbody> <tr><td>4.19</td><td>0.01</td><td>4.68</td><td>0.01</td><td>65.51</td><td>0.00</td><td>71.52</td><td>0.04</td></tr> <tr><td>4.84</td><td>0.17</td><td>5.68</td><td>0.01</td><td>71.52</td><td>0.00</td><td>88.91</td><td>0.40</td></tr> <tr><td>5.80</td><td>0.10</td><td>6.62</td><td>0.06</td><td>88.91</td><td>0.00</td><td>103.18</td><td>0.96</td></tr> <tr><td>6.68</td><td>0.34</td><td>7.77</td><td>0.09</td><td>103.18</td><td>0.00</td><td>140.59</td><td>0.96</td></tr> <tr><td>7.72</td><td>0.04</td><td>9.00</td><td>0.12</td><td>120.87</td><td>0.01</td><td>140.59</td><td>0.96</td></tr> <tr><td>9.01</td><td>0.34</td><td>10.48</td><td>0.17</td><td>140.59</td><td>0.00</td><td>182.77</td><td>1.05</td></tr> <tr><td>10.48</td><td>0.90</td><td>12.81</td><td>0.22</td><td>182.77</td><td>0.00</td><td>190.20</td><td>1.29</td></tr> <tr><td>12.81</td><td>0.06</td><td>14.22</td><td>0.28</td><td>190.20</td><td>0.03</td><td>220.29</td><td>0.41</td></tr> <tr><td>14.22</td><td>0.07</td><td>16.57</td><td>0.30</td><td>220.29</td><td>0.00</td><td>289.99</td><td>0.49</td></tr> <tr><td>16.57</td><td>0.06</td><td>19.21</td><td>0.44</td><td>289.99</td><td>0.00</td><td>301.68</td><td>1.08</td></tr> <tr><td>19.21</td><td>0.09</td><td>22.46</td><td>0.54</td><td>301.68</td><td>0.00</td><td>361.45</td><td>0.99</td></tr> <tr><td>22.46</td><td>0.09</td><td>26.20</td><td>0.60</td><td>361.45</td><td>0.00</td><td>409.45</td><td>0.04</td></tr> <tr><td>26.20</td><td>0.06</td><td>30.53</td><td>0.71</td><td>409.45</td><td>0.00</td><td>477.03</td><td>0.87</td></tr> <tr><td>30.53</td><td>0.08</td><td>35.56</td><td>0.76</td><td>477.03</td><td>0.00</td><td>555.71</td><td>0.78</td></tr> <tr><td>35.56</td><td>0.09</td><td>41.42</td><td>0.88</td><td>555.71</td><td>0.00</td><td>647.41</td><td>1.60</td></tr> <tr><td>41.42</td><td>0.07</td><td>48.27</td><td>0.95</td><td>647.41</td><td>0.00</td><td>754.23</td><td>42.07</td></tr> <tr><td>48.27</td><td>0.03</td><td>56.23</td><td>0.08</td><td>754.23</td><td>97.93</td><td>870.67</td><td>100.00</td></tr> <tr><td>56.23</td><td>0.01</td><td>65.51</td><td>0.08</td><td></td><td></td><td></td><td></td></tr> </tbody> </table>				Size (µm)	D (%)	Size (µm)	D (%)	Size (µm)	D (%)	Size (µm)	D (%)	4.19	0.01	4.68	0.01	65.51	0.00	71.52	0.04	4.84	0.17	5.68	0.01	71.52	0.00	88.91	0.40	5.80	0.10	6.62	0.06	88.91	0.00	103.18	0.96	6.68	0.34	7.77	0.09	103.18	0.00	140.59	0.96	7.72	0.04	9.00	0.12	120.87	0.01	140.59	0.96	9.01	0.34	10.48	0.17	140.59	0.00	182.77	1.05	10.48	0.90	12.81	0.22	182.77	0.00	190.20	1.29	12.81	0.06	14.22	0.28	190.20	0.03	220.29	0.41	14.22	0.07	16.57	0.30	220.29	0.00	289.99	0.49	16.57	0.06	19.21	0.44	289.99	0.00	301.68	1.08	19.21	0.09	22.46	0.54	301.68	0.00	361.45	0.99	22.46	0.09	26.20	0.60	361.45	0.00	409.45	0.04	26.20	0.06	30.53	0.71	409.45	0.00	477.03	0.87	30.53	0.08	35.56	0.76	477.03	0.00	555.71	0.78	35.56	0.09	41.42	0.88	555.71	0.00	647.41	1.60	41.42	0.07	48.27	0.95	647.41	0.00	754.23	42.07	48.27	0.03	56.23	0.08	754.23	97.93	870.67	100.00	56.23	0.01	65.51	0.08								
Size (µm)	D (%)	Size (µm)	D (%)	Size (µm)	D (%)	Size (µm)	D (%)																																																																																																																																																								
4.19	0.01	4.68	0.01	65.51	0.00	71.52	0.04																																																																																																																																																								
4.84	0.17	5.68	0.01	71.52	0.00	88.91	0.40																																																																																																																																																								
5.80	0.10	6.62	0.06	88.91	0.00	103.18	0.96																																																																																																																																																								
6.68	0.34	7.77	0.09	103.18	0.00	140.59	0.96																																																																																																																																																								
7.72	0.04	9.00	0.12	120.87	0.01	140.59	0.96																																																																																																																																																								
9.01	0.34	10.48	0.17	140.59	0.00	182.77	1.05																																																																																																																																																								
10.48	0.90	12.81	0.22	182.77	0.00	190.20	1.29																																																																																																																																																								
12.81	0.06	14.22	0.28	190.20	0.03	220.29	0.41																																																																																																																																																								
14.22	0.07	16.57	0.30	220.29	0.00	289.99	0.49																																																																																																																																																								
16.57	0.06	19.21	0.44	289.99	0.00	301.68	1.08																																																																																																																																																								
19.21	0.09	22.46	0.54	301.68	0.00	361.45	0.99																																																																																																																																																								
22.46	0.09	26.20	0.60	361.45	0.00	409.45	0.04																																																																																																																																																								
26.20	0.06	30.53	0.71	409.45	0.00	477.03	0.87																																																																																																																																																								
30.53	0.08	35.56	0.76	477.03	0.00	555.71	0.78																																																																																																																																																								
35.56	0.09	41.42	0.88	555.71	0.00	647.41	1.60																																																																																																																																																								
41.42	0.07	48.27	0.95	647.41	0.00	754.23	42.07																																																																																																																																																								
48.27	0.03	56.23	0.08	754.23	97.93	870.67	100.00																																																																																																																																																								
56.23	0.01	65.51	0.08																																																																																																																																																												



Malvern Instruments Ltd.
 Malvern, UK
 Tel: +44 (0)1690-826456 Fax: +44 (0)1690-892089

Mastersizer 50 long bed Ver. 0.19
 Serial Number:

10 Jul 04 10:44

Figure A39 Malvern report for 0-75 µm sugar, sample 1

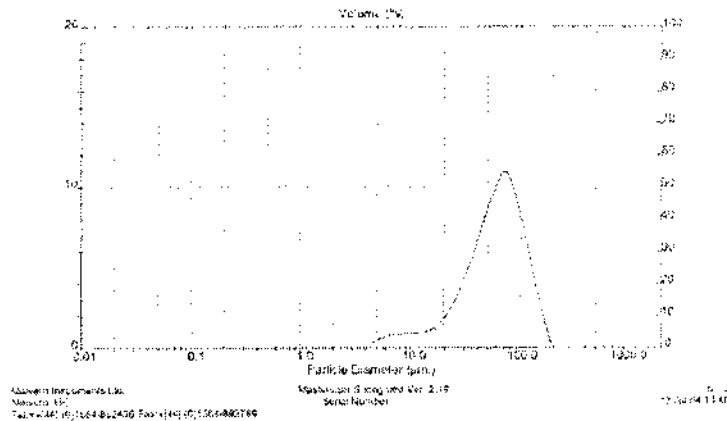
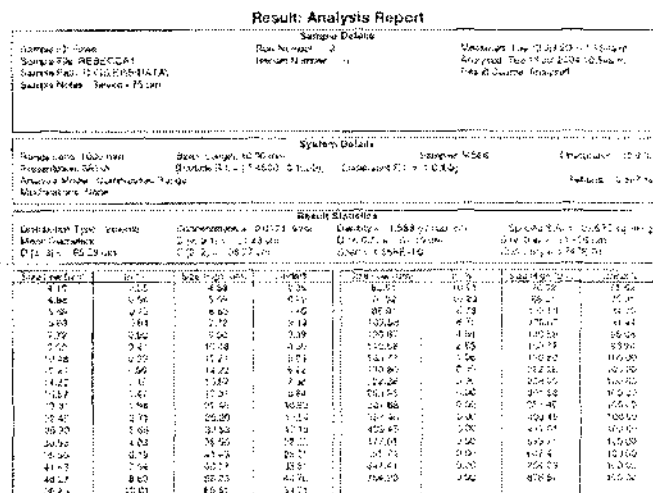


Figure A40 Malvern report for 0-75 μm sugar, sample 2

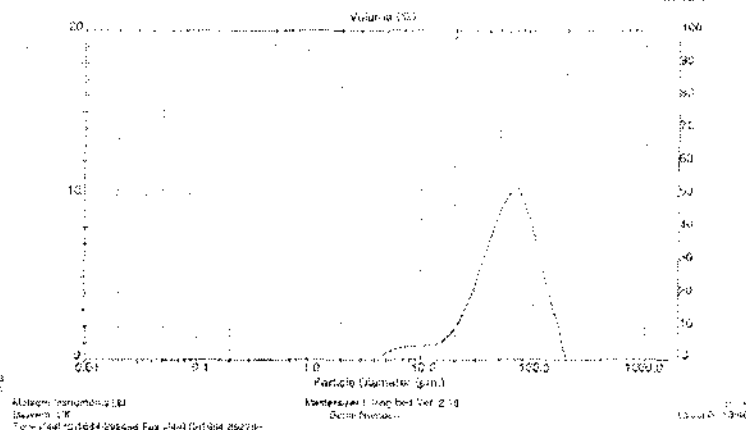
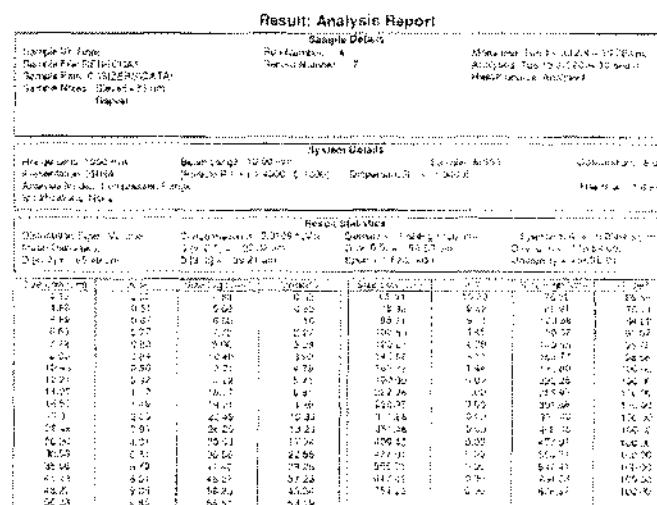
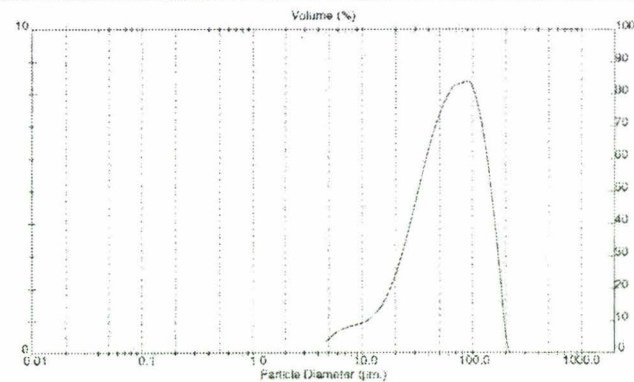


Figure A41 Malvern report for 0-75 μm sugar, sample 3

MALVERN MASTERSIZER

Result: Analysis Report

Sample Details			
Sample ID: Finex	Run Number: 8	Measured: Tue 15 Jul 2004 11:04am	
Sample File: HEREDCA1	Record Number: 9	Analyzed: Tue 15 Jul 2004 11:04am	
Sample Path: C:\SIZER\DATA1		Result Source: Analyzed	
Sample Notes: Sieved <75 um			
System Details			
Range Lens: 1000 mm	Beam Length: 10.00 mm	Sample: M360	Concentration: 6.7 %
Presentation: 3RHA	[Particle R.I.] = (1.4500, 0.1000)	Dispersion: R.I. = 1.0000	Refract: 2.902 %
Analysis Model: Compressed Range			
Modification: None			
Result Statistics			
Distribution Type: Volume	Concentration = 0.0006 % Vol	Density = 1.585 g/cc (m)	Specific S.A. = 0.0086 sq m/g
Mean Diameter:	D (v, 0.1) = 19.42 um	D (v, 0.5) = 61.28 um	D (v, 0.9) = 101.95 um
D (4, 0) = 84.26 um	D (3, 0) = 38.22 um	D (3, 0) = 1.8032 x 10 ⁻¹	Uncertainty = 5.8932 %
Size Low (um)	in %	Size High (um)	Under%
4.12	0.25	4.88	0.25
4.88	0.54	5.56	0.89
5.56	0.89	6.32	1.58
6.32	1.80	7.12	2.53
7.12	0.87	8.00	3.54
8.00	0.40	10.48	4.17
10.48	1.09	12.21	5.20
12.21	1.61	14.22	6.41
14.22	1.10	16.57	7.63
16.57	1.08	19.31	9.01
19.31	2.59	22.49	12.50
22.49	3.10	26.20	15.85
26.20	4.30	30.53	20.36
30.53	6.11	35.56	26.16
35.56	8.01	41.49	31.57
41.49	6.04	48.27	36.01
48.27	7.52	56.23	45.23
56.23	8.02	65.51	53.55
65.51	0.58	75.32	6.34
75.32	8.31	88.91	78.47
88.91	7.02	103.18	86.01
103.18	8.44	120.87	92.50
120.87	4.70	140.58	97.23
140.58	2.49	163.77	99.72
163.77	0.53	193.80	100.00
193.80	0.00	229.23	100.00
229.23	0.00	258.98	100.00
258.98	0.00	301.48	100.00
301.48	0.00	351.46	100.00
351.46	0.00	409.45	100.00
409.45	0.00	477.01	100.00
477.01	0.00	555.71	100.00
555.71	0.00	647.41	100.00
647.41	0.00	754.23	100.00
754.23	0.00	878.67	100.00



Malvern Instruments Ltd.
Malvern, UK
Tel: 01452 400214 Fax: 01452 400278

Mastersizer 9 long bed Ver. 2.13
Serial Number:

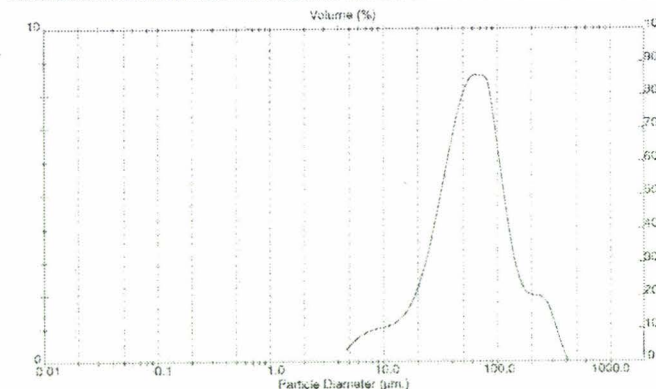
13 Jul 04 13:47

Figure A42 Malvern report for 0-75 µm sugar, sample 4

MALVERN MASTERSIZER

Result: Analysis Report

Sample Details			
Sample ID: Finex	Run Number: 8	Measured: Tue 13 Jul 2004 11:07am	
Sample File: HEREDCA1	Record Number: 11	Analyzed: Tue 13 Jul 2004 11:07am	
Sample Path: C:\SIZER\DATA1		Result Source: Analyzed	
Sample Notes: Sieved <75 um			
System Details			
Range Lens: 1000 mm	Beam Length: 10.01 mm	Sample: M360	Concentration: 7.0 %
Presentation: 3RHA	[Particle R.I.] = (1.4500, 0.1000)	Dispersion: R.I. = 1.0000	Refract: 1.716 %
Analysis Model: Compressed Range			
Modification: None			
Result Statistics			
Distribution Type: Volume	Concentration = 0.0006 % Vol	Density = 1.585 g/cc (m)	Effective S.A. = 0.0086 sq m/g
Mean Diameter:	D (v, 0.1) = 19.24 um	D (v, 0.5) = 58.47 um	D (v, 0.9) = 90.19 um
D (4, 0) = 78.78 um	D (3, 0) = 37.83 um	Spk = 2.2856 * 10 ⁻¹	Uncertainty = 7.1322 %
Size Low (um)	in %	Size High (um)	Under%
4.10	0.35	4.68	0.35
4.68	0.57	5.64	0.92
5.64	0.76	6.63	1.58
6.63	0.86	7.72	2.55
7.72	0.97	9.00	3.52
9.00	1.03	10.48	4.55
10.48	1.06	12.21	5.64
12.21	1.20	14.22	6.84
14.22	1.42	16.57	8.06
16.57	1.70	19.31	9.28
19.31	2.38	22.49	12.41
22.49	3.14	26.20	15.54
26.20	4.11	30.53	19.65
30.53	5.22	35.56	24.68
35.56	6.36	41.43	31.26
41.43	7.43	48.27	38.60
48.27	8.15	56.23	46.68
56.23	8.56	65.51	55.46
65.51	0.56	75.32	64.00
75.32	0.51	88.91	72.33
88.91	0.89	103.18	79.23
103.18	0.84	120.87	84.44
120.87	0.74	140.58	88.19
140.58	0.67	163.77	90.86
163.77	0.13	190.95	92.68
190.95	0.00	222.20	94.08
222.20	0.00	258.75	95.94
258.75	0.00	301.68	97.60
301.68	0.00	351.46	98.84
351.46	0.00	409.45	100.00
409.45	0.00	477.01	100.00
477.01	0.00	555.71	100.00
555.71	0.00	647.41	100.00
647.41	0.00	754.23	100.00
754.23	0.00	878.67	100.00



Malvern Instruments Ltd.
Malvern, UK
Tel: 01452 400214 Fax: 01452 400278

Mastersizer 9 long bed Ver. 2.19
Serial Number:

13 Jul 04 13:47

Figure A43 Malvern report for 0-75 µm sugar, sample 5

MASTERSIZER

Result: Analysis Report

Sample Details Sample ID: 75-150 µm Sample Name: 75-150 µm Sample Notes: 75-150 µm		Run Number: 11 Record Number: 14	Measured: Tue 10 Jul 2004 11:14:00 Analysed: Tue 10 Jul 2004 11:15:00 Result Owner: Analyst																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																												
System Details Range: 1000-10000 µm Beam Length: 1000 µm Dispersion: 1.0 Analysis Mode: Compressed Range Modifiers: None																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																															
Result Statistics Distribution Type: Volume Mean Diameter: 126.06 µm Span: 1.2606-1.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																															
<table border="1"> <thead> <tr> <th>Size (µm)</th><th>Vol %</th><th>Count</th><th>Area</th><th>Vol %</th><th>Count</th><th>Area</th><th>Vol %</th><th>Count</th></tr> </thead> <tbody> <tr><td>4.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>4.00</td><td>0.00</td><td>0.00</td><td>4.00</td><td>0.00</td></tr> <tr><td>4.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>4.50</td><td>0.00</td><td>0.00</td><td>4.50</td><td>0.00</td></tr> <tr><td>5.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>5.00</td><td>0.00</td><td>0.00</td><td>5.00</td><td>0.00</td></tr> <tr><td>5.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>5.50</td><td>0.00</td><td>0.00</td><td>5.50</td><td>0.00</td></tr> <tr><td>6.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>6.00</td><td>0.00</td><td>0.00</td><td>6.00</td><td>0.00</td></tr> <tr><td>6.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>6.50</td><td>0.00</td><td>0.00</td><td>6.50</td><td>0.00</td></tr> <tr><td>7.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>7.00</td><td>0.00</td><td>0.00</td><td>7.00</td><td>0.00</td></tr> <tr><td>7.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>7.50</td><td>0.00</td><td>0.00</td><td>7.50</td><td>0.00</td></tr> <tr><td>8.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>8.00</td><td>0.00</td><td>0.00</td><td>8.00</td><td>0.00</td></tr> <tr><td>8.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>8.50</td><td>0.00</td><td>0.00</td><td>8.50</td><td>0.00</td></tr> <tr><td>9.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>9.00</td><td>0.00</td><td>0.00</td><td>9.00</td><td>0.00</td></tr> <tr><td>9.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>9.50</td><td>0.00</td><td>0.00</td><td>9.50</td><td>0.00</td></tr> <tr><td>10.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>10.00</td><td>0.00</td><td>0.00</td><td>10.00</td><td>0.00</td></tr> <tr><td>10.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>10.50</td><td>0.00</td><td>0.00</td><td>10.50</td><td>0.00</td></tr> <tr><td>11.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>11.00</td><td>0.00</td><td>0.00</td><td>11.00</td><td>0.00</td></tr> <tr><td>11.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>11.50</td><td>0.00</td><td>0.00</td><td>11.50</td><td>0.00</td></tr> <tr><td>12.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>12.00</td><td>0.00</td><td>0.00</td><td>12.00</td><td>0.00</td></tr> <tr><td>12.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>12.50</td><td>0.00</td><td>0.00</td><td>12.50</td><td>0.00</td></tr> <tr><td>13.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>13.00</td><td>0.00</td><td>0.00</td><td>13.00</td><td>0.00</td></tr> <tr><td>13.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>13.50</td><td>0.00</td><td>0.00</td><td>13.50</td><td>0.00</td></tr> <tr><td>14.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>14.00</td><td>0.00</td><td>0.00</td><td>14.00</td><td>0.00</td></tr> <tr><td>14.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>14.50</td><td>0.00</td><td>0.00</td><td>14.50</td><td>0.00</td></tr> <tr><td>15.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>15.00</td><td>0.00</td><td>0.00</td><td>15.00</td><td>0.00</td></tr> <tr><td>15.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>15.50</td><td>0.00</td><td>0.00</td><td>15.50</td><td>0.00</td></tr> <tr><td>16.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>16.00</td><td>0.00</td><td>0.00</td><td>16.00</td><td>0.00</td></tr> <tr><td>16.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>16.50</td><td>0.00</td><td>0.00</td><td>16.50</td><td>0.00</td></tr> <tr><td>17.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>17.00</td><td>0.00</td><td>0.00</td><td>17.00</td><td>0.00</td></tr> <tr><td>17.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>17.50</td><td>0.00</td><td>0.00</td><td>17.50</td><td>0.00</td></tr> <tr><td>18.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>18.00</td><td>0.00</td><td>0.00</td><td>18.00</td><td>0.00</td></tr> <tr><td>18.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>18.50</td><td>0.00</td><td>0.00</td><td>18.50</td><td>0.00</td></tr> <tr><td>19.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>19.00</td><td>0.00</td><td>0.00</td><td>19.00</td><td>0.00</td></tr> <tr><td>19.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>19.50</td><td>0.00</td><td>0.00</td><td>19.50</td><td>0.00</td></tr> <tr><td>20.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>20.00</td><td>0.00</td><td>0.00</td><td>20.00</td><td>0.00</td></tr> <tr><td>20.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>20.50</td><td>0.00</td><td>0.00</td><td>20.50</td><td>0.00</td></tr> <tr><td>21.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>21.00</td><td>0.00</td><td>0.00</td><td>21.00</td><td>0.00</td></tr> <tr><td>21.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>21.50</td><td>0.00</td><td>0.00</td><td>21.50</td><td>0.00</td></tr> <tr><td>22.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>22.00</td><td>0.00</td><td>0.00</td><td>22.00</td><td>0.00</td></tr> <tr><td>22.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>22.50</td><td>0.00</td><td>0.00</td><td>22.50</td><td>0.00</td></tr> <tr><td>23.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>23.00</td><td>0.00</td><td>0.00</td><td>23.00</td><td>0.00</td></tr> <tr><td>23.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>23.50</td><td>0.00</td><td>0.00</td><td>23.50</td><td>0.00</td></tr> <tr><td>24.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>24.00</td><td>0.00</td><td>0.00</td><td>24.00</td><td>0.00</td></tr> <tr><td>24.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>24.50</td><td>0.00</td><td>0.00</td><td>24.50</td><td>0.00</td></tr> <tr><td>25.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>25.00</td><td>0.00</td><td>0.00</td><td>25.00</td><td>0.00</td></tr> <tr><td>25.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>25.50</td><td>0.00</td><td>0.00</td><td>25.50</td><td>0.00</td></tr> <tr><td>26.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>26.00</td><td>0.00</td><td>0.00</td><td>26.00</td><td>0.00</td></tr> <tr><td>26.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>26.50</td><td>0.00</td><td>0.00</td><td>26.50</td><td>0.00</td></tr> <tr><td>27.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>27.00</td><td>0.00</td><td>0.00</td><td>27.00</td><td>0.00</td></tr> <tr><td>27.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>27.50</td><td>0.00</td><td>0.00</td><td>27.50</td><td>0.00</td></tr> <tr><td>28.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>28.00</td><td>0.00</td><td>0.00</td><td>28.00</td><td>0.00</td></tr> <tr><td>28.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>28.50</td><td>0.00</td><td>0.00</td><td>28.50</td><td>0.00</td></tr> <tr><td>29.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>29.00</td><td>0.00</td><td>0.00</td><td>29.00</td><td>0.00</td></tr> <tr><td>29.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>29.50</td><td>0.00</td><td>0.00</td><td>29.50</td><td>0.00</td></tr> <tr><td>30.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>30.00</td><td>0.00</td><td>0.00</td><td>30.00</td><td>0.00</td></tr> <tr><td>30.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>30.50</td><td>0.00</td><td>0.00</td><td>30.50</td><td>0.00</td></tr> <tr><td>31.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>31.00</td><td>0.00</td><td>0.00</td><td>31.00</td><td>0.00</td></tr> <tr><td>31.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>31.50</td><td>0.00</td><td>0.00</td><td>31.50</td><td>0.00</td></tr> <tr><td>32.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>32.00</td><td>0.00</td><td>0.00</td><td>32.00</td><td>0.00</td></tr> <tr><td>32.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>32.50</td><td>0.00</td><td>0.00</td><td>32.50</td><td>0.00</td></tr> <tr><td>33.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>33.00</td><td>0.00</td><td>0.00</td><td>33.00</td><td>0.00</td></tr> <tr><td>33.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>33.50</td><td>0.00</td><td>0.00</td><td>33.50</td><td>0.00</td></tr> <tr><td>34.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>34.00</td><td>0.00</td><td>0.00</td><td>34.00</td><td>0.00</td></tr> <tr><td>34.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>34.50</td><td>0.00</td><td>0.00</td><td>34.50</td><td>0.00</td></tr> <tr><td>35.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>35.00</td><td>0.00</td><td>0.00</td><td>35.00</td><td>0.00</td></tr> <tr><td>35.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>35.50</td><td>0.00</td><td>0.00</td><td>35.50</td><td>0.00</td></tr> <tr><td>36.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>36.00</td><td>0.00</td><td>0.00</td><td>36.00</td><td>0.00</td></tr> <tr><td>36.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>36.50</td><td>0.00</td><td>0.00</td><td>36.50</td><td>0.00</td></tr> <tr><td>37.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>37.00</td><td>0.00</td><td>0.00</td><td>37.00</td><td>0.00</td></tr> <tr><td>37.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>37.50</td><td>0.00</td><td>0.00</td><td>37.50</td><td>0.00</td></tr> <tr><td>38.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>38.00</td><td>0.00</td><td>0.00</td><td>38.00</td><td>0.00</td></tr> <tr><td>38.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>38.50</td><td>0.00</td><td>0.00</td><td>38.50</td><td>0.00</td></tr> <tr><td>39.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>39.00</td><td>0.00</td><td>0.00</td><td>39.00</td><td>0.00</td></tr> <tr><td>39.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>39.50</td><td>0.00</td><td>0.00</td><td>39.50</td><td>0.00</td></tr> <tr><td>40.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>40.00</td><td>0.00</td><td>0.00</td><td>40.00</td><td>0.00</td></tr> <tr><td>40.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>40.50</td><td>0.00</td><td>0.00</td><td>40.50</td><td>0.00</td></tr> <tr><td>41.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>41.00</td><td>0.00</td><td>0.00</td><td>41.00</td><td>0.00</td></tr> <tr><td>41.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>41.50</td><td>0.00</td><td>0.00</td><td>41.50</td><td>0.00</td></tr> <tr><td>42.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>42.00</td><td>0.00</td><td>0.00</td><td>42.00</td><td>0.00</td></tr> <tr><td>42.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>42.50</td><td>0.00</td><td>0.00</td><td>42.50</td><td>0.00</td></tr> <tr><td>43.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>43.00</td><td>0.00</td><td>0.00</td><td>43.00</td><td>0.00</td></tr> <tr><td>43.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>43.50</td><td>0.00</td><td>0.00</td><td>43.50</td><td>0.00</td></tr> <tr><td>44.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>44.00</td><td>0.00</td><td>0.00</td><td>44.00</td><td>0.00</td></tr> <tr><td>44.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>44.50</td><td>0.00</td><td>0.00</td><td>44.50</td><td>0.00</td></tr> <tr><td>45.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>45.00</td><td>0.00</td><td>0.00</td><td>45.00</td><td>0.00</td></tr> <tr><td>45.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>45.50</td><td>0.00</td><td>0.00</td><td>45.50</td><td>0.00</td></tr> <tr><td>46.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>46.00</td><td>0.00</td><td>0.00</td><td>46.00</td><td>0.00</td></tr> <tr><td>46.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>46.50</td><td>0.00</td><td>0.00</td><td>46.50</td><td>0.00</td></tr> <tr><td>47.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>47.00</td><td>0.00</td><td>0.00</td><td>47.00</td><td>0.00</td></tr> <tr><td>47.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>47.50</td><td>0.00</td><td>0.00</td><td>47.50</td><td>0.00</td></tr> <tr><td>48.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>48.00</td><td>0.00</td><td>0.00</td><td>48.00</td><td>0.00</td></tr> <tr><td>48.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>48.50</td><td>0.00</td><td>0.00</td><td>48.50</td><td>0.00</td></tr> <tr><td>49.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>49.00</td><td>0.00</td><td>0.00</td><td>49.00</td><td>0.00</td></tr> <tr><td>49.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>49.50</td><td>0.00</td><td>0.00</td><td>49.50</td><td>0.00</td></tr> <tr><td>50.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>50.00</td><td>0.00</td><td>0.00</td><td>50.00</td><td>0.00</td></tr> <tr><td>50.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>50.50</td><td>0.00</td><td>0.00</td><td>50.50</td><td>0.00</td></tr> <tr><td>51.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>51.00</td><td>0.00</td><td>0.00</td><td>51.00</td><td>0.00</td></tr> <tr><td>51.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>51.50</td><td>0.00</td><td>0.00</td><td>51.50</td><td>0.00</td></tr> <tr><td>52.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>52.00</td><td>0.00</td><td>0.00</td><td>52.00</td><td>0.00</td></tr> <tr><td>52.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>52.50</td><td>0.00</td><td>0.00</td><td>52.50</td><td>0.00</td></tr> <tr><td>53.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>53.00</td><td>0.00</td><td>0.00</td><td>53.00</td><td>0.00</td></tr> <tr><td>53.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>53.50</td><td>0.00</td><td>0.00</td><td>53.50</td><td>0.00</td></tr> <tr><td>54.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>54.00</td><td>0.00</td><td>0.00</td><td>54.00</td><td>0.00</td></tr> <tr><td>54.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>54.50</td><td>0.00</td><td>0.00</td><td>54.50</td><td>0.00</td></tr> <tr><td>55.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>55.00</td><td>0.00</td><td>0.00</td><td>55.00</td><td>0.00</td></tr> <tr><td>55.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>55.50</td><td>0.00</td><td>0.00</td><td>55.50</td><td>0.00</td></tr> <tr><td>56.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>56.00</td><td>0.00</td><td>0.00</td><td>56.00</td><td>0.00</td></tr> <tr><td>56.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>56.50</td><td>0.00</td><td>0.00</td><td>56.50</td><td>0.00</td></tr> <tr><td>57.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>57.00</td><td>0.00</td><td>0.00</td><td>57.00</td><td>0.00</td></tr> <tr><td>57.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>57.50</td><td>0.00</td><td>0.00</td><td>57.50</td><td>0.00</td></tr> <tr><td>58.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>58.00</td><td>0.00</td><td>0.00</td><td>58.00</td><td>0.00</td></tr> <tr><td>58.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>58.50</td><td>0.00</td><td>0.00</td><td>58.50</td><td>0.00</td></tr> <tr><td>59.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>59.00</td><td>0.00</td><td>0.00</td><td>59.00</td><td>0.00</td></tr> <tr><td>59.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>59.50</td><td>0.00</td><td>0.00</td><td>59.50</td><td>0.00</td></tr> <tr><td>60.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>60.00</td><td>0.00</td><td>0.00</td><td>60.00</td><td>0.00</td></tr> <tr><td>60.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>60.50</td><td>0.00</td><td>0.00</td><td>60.50</td><td>0.00</td></tr> <tr><td>61.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>61.00</td><td>0.00</td><td>0.00</td><td>61.00</td><td>0.00</td></tr> <tr><td>61.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>61.50</td><td>0.00</td><td>0.00</td><td>61.50</td><td>0.00</td></tr> <tr><td>62.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>62.00</td><td>0.00</td><td>0.00</td><td>62.00</td><td>0.00</td></tr> <tr><td>62.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>62.50</td><td>0.00</td><td>0.00</td><td>62.50</td><td>0.00</td></tr> <tr><td>63.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>63.00</td><td>0.00</td><td>0.00</td><td>63.00</td><td>0.00</td></tr> <tr><td>63.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>63.50</td><td>0.00</td><td>0.00</td><td>63.50</td><td>0.00</td></tr> <tr><td>64.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>64.00</td><td>0.00</td><td>0.00</td><td>64.00</td><td>0.00</td></tr> <tr><td>64.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>64.50</td><td>0.00</td><td>0.00</td><td>64.50</td><td>0.00</td></tr> <tr><td>65.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>65.00</td><td>0.00</td><td>0.00</td><td>65.00</td><td>0.00</td></tr> <tr><td>65.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>65.50</td><td>0.00</td><td>0.00</td><td>65.50</td><td>0.00</td></tr> <tr><td>66.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>66.00</td><td>0.00</td><td>0.00</td><td>66.00</td><td>0.00</td></tr> <tr><td>66.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>66.50</td><td>0.00</td><td>0.00</td><td>66.50</td><td>0.00</td></tr> <tr><td>67.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>67.00</td><td>0.00</td><td>0.00</td><td>67.00</td><td>0.00</td></tr> <tr><td>67.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>67.50</td><td>0.00</td><td>0.00</td><td>67.50</td><td>0.00</td></tr> <tr><td>68.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>68.00</td><td>0.00</td><td>0.00</td><td>68.00</td><td>0.00</td></tr> <tr><td>68.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>68.50</td><td>0.00</td><td>0.00</td><td>68.50</td><td>0.00</td></tr> <tr><td>69.00</td><td>0.00</td><td>0.00</td><td>0.00</td><td>69.00</td><td>0.00</td><td>0.00</td><td>69.00</td><td>0.00</td></tr> <tr><td>69.50</td><td>0.00</td><td>0.00</td><td>0.00</td><td>69.50</td><td>0.00</td><td>0.00</td><td>69.50</td><td>0.00</td></tr> <tr><td>70.00</td><td>0.00</td></tr></tbody></table>	Size (µm)	Vol %	Count	Area	Vol %	Count	Area	Vol %	Count	4.00	0.00	0.00	0.00	4.00	0.00	0.00	4.00	0.00	4.50	0.00	0.00	0.00	4.50	0.00	0.00	4.50	0.00	5.00	0.00	0.00	0.00	5.00	0.00	0.00	5.00	0.00	5.50	0.00	0.00	0.00	5.50	0.00	0.00	5.50	0.00	6.00	0.00	0.00	0.00	6.00	0.00	0.00	6.00	0.00	6.50	0.00	0.00	0.00	6.50	0.00	0.00	6.50	0.00	7.00	0.00	0.00	0.00	7.00	0.00	0.00	7.00	0.00	7.50	0.00	0.00	0.00	7.50	0.00	0.00	7.50	0.00	8.00	0.00	0.00	0.00	8.00	0.00	0.00	8.00	0.00	8.50	0.00	0.00	0.00	8.50	0.00	0.00	8.50	0.00	9.00	0.00	0.00	0.00	9.00	0.00	0.00	9.00	0.00	9.50	0.00	0.00	0.00	9.50	0.00	0.00	9.50	0.00	10.00	0.00	0.00	0.00	10.00	0.00	0.00	10.00	0.00	10.50	0.00	0.00	0.00	10.50	0.00	0.00	10.50	0.00	11.00	0.00	0.00	0.00	11.00	0.00	0.00	11.00	0.00	11.50	0.00	0.00	0.00	11.50	0.00	0.00	11.50	0.00	12.00	0.00	0.00	0.00	12.00	0.00	0.00	12.00	0.00	12.50	0.00	0.00	0.00	12.50	0.00	0.00	12.50	0.00	13.00	0.00	0.00	0.00	13.00	0.00	0.00	13.00	0.00	13.50	0.00	0.00	0.00	13.50	0.00	0.00	13.50	0.00	14.00	0.00	0.00	0.00	14.00	0.00	0.00	14.00	0.00	14.50	0.00	0.00	0.00	14.50	0.00	0.00	14.50	0.00	15.00	0.00	0.00	0.00	15.00	0.00	0.00	15.00	0.00	15.50	0.00	0.00	0.00	15.50	0.00	0.00	15.50	0.00	16.00	0.00	0.00	0.00	16.00	0.00	0.00	16.00	0.00	16.50	0.00	0.00	0.00	16.50	0.00	0.00	16.50	0.00	17.00	0.00	0.00	0.00	17.00	0.00	0.00	17.00	0.00	17.50	0.00	0.00	0.00	17.50	0.00	0.00	17.50	0.00	18.00	0.00	0.00	0.00	18.00	0.00	0.00	18.00	0.00	18.50	0.00	0.00	0.00	18.50	0.00	0.00	18.50	0.00	19.00	0.00	0.00	0.00	19.00	0.00	0.00	19.00	0.00	19.50	0.00	0.00	0.00	19.50	0.00	0.00	19.50	0.00	20.00	0.00	0.00	0.00	20.00	0.00	0.00	20.00	0.00	20.50	0.00	0.00	0.00	20.50	0.00	0.00	20.50	0.00	21.00	0.00	0.00	0.00	21.00	0.00	0.00	21.00	0.00	21.50	0.00	0.00	0.00	21.50	0.00	0.00	21.50	0.00	22.00	0.00	0.00	0.00	22.00	0.00	0.00	22.00	0.00	22.50	0.00	0.00	0.00	22.50	0.00	0.00	22.50	0.00	23.00	0.00	0.00	0.00	23.00	0.00	0.00	23.00	0.00	23.50	0.00	0.00	0.00	23.50	0.00	0.00	23.50	0.00	24.00	0.00	0.00	0.00	24.00	0.00	0.00	24.00	0.00	24.50	0.00	0.00	0.00	24.50	0.00	0.00	24.50	0.00	25.00	0.00	0.00	0.00	25.00	0.00	0.00	25.00	0.00	25.50	0.00	0.00	0.00	25.50	0.00	0.00	25.50	0.00	26.00	0.00	0.00	0.00	26.00	0.00	0.00	26.00	0.00	26.50	0.00	0.00	0.00	26.50	0.00	0.00	26.50	0.00	27.00	0.00	0.00	0.00	27.00	0.00	0.00	27.00	0.00	27.50	0.00	0.00	0.00	27.50	0.00	0.00	27.50	0.00	28.00	0.00	0.00	0.00	28.00	0.00	0.00	28.00	0.00	28.50	0.00	0.00	0.00	28.50	0.00	0.00	28.50	0.00	29.00	0.00	0.00	0.00	29.00	0.00	0.00	29.00	0.00	29.50	0.00	0.00	0.00	29.50	0.00	0.00	29.50	0.00	30.00	0.00	0.00	0.00	30.00	0.00	0.00	30.00	0.00	30.50	0.00	0.00	0.00	30.50	0.00	0.00	30.50	0.00	31.00	0.00	0.00	0.00	31.00	0.00	0.00	31.00	0.00	31.50	0.00	0.00	0.00	31.50	0.00	0.00	31.50	0.00	32.00	0.00	0.00	0.00	32.00	0.00	0.00	32.00	0.00	32.50	0.00	0.00	0.00	32.50	0.00	0.00	32.50	0.00	33.00	0.00	0.00	0.00	33.00	0.00	0.00	33.00	0.00	33.50	0.00	0.00	0.00	33.50	0.00	0.00	33.50	0.00	34.00	0.00	0.00	0.00	34.00	0.00	0.00	34.00	0.00	34.50	0.00	0.00	0.00	34.50	0.00	0.00	34.50	0.00	35.00	0.00	0.00	0.00	35.00	0.00	0.00	35.00	0.00	35.50	0.00	0.00	0.00	35.50	0.00	0.00	35.50	0.00	36.00	0.00	0.00	0.00	36.00	0.00	0.00	36.00	0.00	36.50	0.00	0.00	0.00	36.50	0.00	0.00	36.50	0.00	37.00	0.00	0.00	0.00	37.00	0.00	0.00	37.00	0.00	37.50	0.00	0.00	0.00	37.50	0.00	0.00	37.50	0.00	38.00	0.00	0.00	0.00	38.00	0.00	0.00	38.00	0.00	38.50	0.00	0.00	0.00	38.50	0.00	0.00	38.50	0.00	39.00	0.00	0.00	0.00	39.00	0.00	0.00	39.00	0.00	39.50	0.00	0.00	0.00	39.50	0.00	0.00	39.50	0.00	40.00	0.00	0.00	0.00	40.00	0.00	0.00	40.00	0.00	40.50	0.00	0.00	0.00	40.50	0.00	0.00	40.50	0.00	41.00	0.00	0.00	0.00	41.00	0.00	0.00	41.00	0.00	41.50	0.00	0.00	0.00	41.50	0.00	0.00	41.50	0.00	42.00	0.00	0.00	0.00	42.00	0.00	0.00	42.00	0.00	42.50	0.00	0.00	0.00	42.50	0.00	0.00	42.50	0.00	43.00	0.00	0.00	0.00	43.00	0.00	0.00	43.00	0.00	43.50	0.00	0.00	0.00	43.50	0.00	0.00	43.50	0.00	44.00	0.00	0.00	0.00	44.00	0.00	0.00	44.00	0.00	44.50	0.00	0.00	0.00	44.50	0.00	0.00	44.50	0.00	45.00	0.00	0.00	0.00	45.00	0.00	0.00	45.00	0.00	45.50	0.00	0.00	0.00	45.50	0.00	0.00	45.50	0.00	46.00	0.00	0.00	0.00	46.00	0.00	0.00	46.00	0.00	46.50	0.00	0.00	0.00	46.50	0.00	0.00	46.50	0.00	47.00	0.00	0.00	0.00	47.00	0.00	0.00	47.00	0.00	47.50	0.00	0.00	0.00	47.50	0.00	0.00	47.50	0.00	48.00	0.00	0.00	0.00	48.00	0.00	0.00	48.00	0.00	48.50	0.00	0.00	0.00	48.50	0.00	0.00	48.50	0.00	49.00	0.00	0.00	0.00	49.00	0.00	0.00	49.00	0.00	49.50	0.00	0.00	0.00	49.50	0.00	0.00	49.50	0.00	50.00	0.00	0.00	0.00	50.00	0.00	0.00	50.00	0.00	50.50	0.00	0.00	0.00	50.50	0.00	0.00	50.50	0.00	51.00	0.00	0.00	0.00	51.00	0.00	0.00	51.00	0.00	51.50	0.00	0.00	0.00	51.50	0.00	0.00	51.50	0.00	52.00	0.00	0.00	0.00	52.00	0.00	0.00	52.00	0.00	52.50	0.00	0.00	0.00	52.50	0.00	0.00	52.50	0.00	53.00	0.00	0.00	0.00	53.00	0.00	0.00	53.00	0.00	53.50	0.00	0.00	0.00	53.50	0.00	0.00	53.50	0.00	54.00	0.00	0.00	0.00	54.00	0.00	0.00	54.00	0.00	54.50	0.00	0.00	0.00	54.50	0.00	0.00	54.50	0.00	55.00	0.00	0.00	0.00	55.00	0.00	0.00	55.00	0.00	55.50	0.00	0.00	0.00	55.50	0.00	0.00	55.50	0.00	56.00	0.00	0.00	0.00	56.00	0.00	0.00	56.00	0.00	56.50	0.00	0.00	0.00	56.50	0.00	0.00	56.50	0.00	57.00	0.00	0.00	0.00	57.00	0.00	0.00	57.00	0.00	57.50	0.00	0.00	0.00	57.50	0.00	0.00	57.50	0.00	58.00	0.00	0.00	0.00	58.00	0.00	0.00	58.00	0.00	58.50	0.00	0.00	0.00	58.50	0.00	0.00	58.50	0.00	59.00	0.00	0.00	0.00	59.00	0.00	0.00	59.00	0.00	59.50	0.00	0.00	0.00	59.50	0.00	0.00	59.50	0.00	60.00	0.00	0.00	0.00	60.00	0.00	0.00	60.00	0.00	60.50	0.00	0.00	0.00	60.50	0.00	0.00	60.50	0.00	61.00	0.00	0.00	0.00	61.00	0.00	0.00	61.00	0.00	61.50	0.00	0.00	0.00	61.50	0.00	0.00	61.50	0.00	62.00	0.00	0.00	0.00	62.00	0.00	0.00	62.00	0.00	62.50	0.00	0.00	0.00	62.50	0.00	0.00	62.50	0.00	63.00	0.00	0.00	0.00	63.00	0.00	0.00	63.00	0.00	63.50	0.00	0.00	0.00	63.50	0.00	0.00	63.50	0.00	64.00	0.00	0.00	0.00	64.00	0.00	0.00	64.00	0.00	64.50	0.00	0.00	0.00	64.50	0.00	0.00	64.50	0.00	65.00	0.00	0.00	0.00	65.00	0.00	0.00	65.00	0.00	65.50	0.00	0.00	0.00	65.50	0.00	0.00	65.50	0.00	66.00	0.00	0.00	0.00	66.00	0.00	0.00	66.00	0.00	66.50	0.00	0.00	0.00	66.50	0.00	0.00	66.50	0.00	67.00	0.00	0.00	0.00	67.00	0.00	0.00	67.00	0.00	67.50	0.00	0.00	0.00	67.50	0.00	0.00	67.50	0.00	68.00	0.00	0.00	0.00	68.00	0.00	0.00	68.00	0.00	68.50	0.00	0.00	0.00	68.50	0.00	0.00	68.50	0.00	69.00	0.00	0.00	0.00	69.00	0.00	0.00	69.00	0.00	69.50	0.00	0.00	0.00	69.50	0.00	0.00	69.50	0.00	70.00	0.00
Size (µm)	Vol %	Count	Area	Vol %	Count	Area	Vol %	Count																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
4.00	0.00	0.00	0.00	4.00	0.00	0.00	4.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
4.50	0.00	0.00	0.00	4.50	0.00	0.00	4.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
5.00	0.00	0.00	0.00	5.00	0.00	0.00	5.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
5.50	0.00	0.00	0.00	5.50	0.00	0.00	5.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
6.00	0.00	0.00	0.00	6.00	0.00	0.00	6.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
6.50	0.00	0.00	0.00	6.50	0.00	0.00	6.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
7.00	0.00	0.00	0.00	7.00	0.00	0.00	7.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
7.50	0.00	0.00	0.00	7.50	0.00	0.00	7.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
8.00	0.00	0.00	0.00	8.00	0.00	0.00	8.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
8.50	0.00	0.00	0.00	8.50	0.00	0.00	8.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
9.00	0.00	0.00	0.00	9.00	0.00	0.00	9.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
9.50	0.00	0.00	0.00	9.50	0.00	0.00	9.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
10.00	0.00	0.00	0.00	10.00	0.00	0.00	10.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
10.50	0.00	0.00	0.00	10.50	0.00	0.00	10.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
11.00	0.00	0.00	0.00	11.00	0.00	0.00	11.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
11.50	0.00	0.00	0.00	11.50	0.00	0.00	11.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
12.00	0.00	0.00	0.00	12.00	0.00	0.00	12.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
12.50	0.00	0.00	0.00	12.50	0.00	0.00	12.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
13.00	0.00	0.00	0.00	13.00	0.00	0.00	13.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
13.50	0.00	0.00	0.00	13.50	0.00	0.00	13.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
14.00	0.00	0.00	0.00	14.00	0.00	0.00	14.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
14.50	0.00	0.00	0.00	14.50	0.00	0.00	14.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
15.00	0.00	0.00	0.00	15.00	0.00	0.00	15.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
15.50	0.00	0.00	0.00	15.50	0.00	0.00	15.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
16.00	0.00	0.00	0.00	16.00	0.00	0.00	16.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
16.50	0.00	0.00	0.00	16.50	0.00	0.00	16.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
17.00	0.00	0.00	0.00	17.00	0.00	0.00	17.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
17.50	0.00	0.00	0.00	17.50	0.00	0.00	17.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
18.00	0.00	0.00	0.00	18.00	0.00	0.00	18.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
18.50	0.00	0.00	0.00	18.50	0.00	0.00	18.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
19.00	0.00	0.00	0.00	19.00	0.00	0.00	19.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
19.50	0.00	0.00	0.00	19.50	0.00	0.00	19.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
20.00	0.00	0.00	0.00	20.00	0.00	0.00	20.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
20.50	0.00	0.00	0.00	20.50	0.00	0.00	20.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
21.00	0.00	0.00	0.00	21.00	0.00	0.00	21.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
21.50	0.00	0.00	0.00	21.50	0.00	0.00	21.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
22.00	0.00	0.00	0.00	22.00	0.00	0.00	22.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
22.50	0.00	0.00	0.00	22.50	0.00	0.00	22.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
23.00	0.00	0.00	0.00	23.00	0.00	0.00	23.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
23.50	0.00	0.00	0.00	23.50	0.00	0.00	23.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
24.00	0.00	0.00	0.00	24.00	0.00	0.00	24.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
24.50	0.00	0.00	0.00	24.50	0.00	0.00	24.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
25.00	0.00	0.00	0.00	25.00	0.00	0.00	25.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
25.50	0.00	0.00	0.00	25.50	0.00	0.00	25.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
26.00	0.00	0.00	0.00	26.00	0.00	0.00	26.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
26.50	0.00	0.00	0.00	26.50	0.00	0.00	26.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
27.00	0.00	0.00	0.00	27.00	0.00	0.00	27.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
27.50	0.00	0.00	0.00	27.50	0.00	0.00	27.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
28.00	0.00	0.00	0.00	28.00	0.00	0.00	28.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
28.50	0.00	0.00	0.00	28.50	0.00	0.00	28.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
29.00	0.00	0.00	0.00	29.00	0.00	0.00	29.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
29.50	0.00	0.00	0.00	29.50	0.00	0.00	29.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
30.00	0.00	0.00	0.00	30.00	0.00	0.00	30.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
30.50	0.00	0.00	0.00	30.50	0.00	0.00	30.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
31.00	0.00	0.00	0.00	31.00	0.00	0.00	31.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
31.50	0.00	0.00	0.00	31.50	0.00	0.00	31.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
32.00	0.00	0.00	0.00	32.00	0.00	0.00	32.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
32.50	0.00	0.00	0.00	32.50	0.00	0.00	32.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
33.00	0.00	0.00	0.00	33.00	0.00	0.00	33.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
33.50	0.00	0.00	0.00	33.50	0.00	0.00	33.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
34.00	0.00	0.00	0.00	34.00	0.00	0.00	34.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
34.50	0.00	0.00	0.00	34.50	0.00	0.00	34.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
35.00	0.00	0.00	0.00	35.00	0.00	0.00	35.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
35.50	0.00	0.00	0.00	35.50	0.00	0.00	35.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
36.00	0.00	0.00	0.00	36.00	0.00	0.00	36.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
36.50	0.00	0.00	0.00	36.50	0.00	0.00	36.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
37.00	0.00	0.00	0.00	37.00	0.00	0.00	37.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
37.50	0.00	0.00	0.00	37.50	0.00	0.00	37.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
38.00	0.00	0.00	0.00	38.00	0.00	0.00	38.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
38.50	0.00	0.00	0.00	38.50	0.00	0.00	38.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
39.00	0.00	0.00	0.00	39.00	0.00	0.00	39.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
39.50	0.00	0.00	0.00	39.50	0.00	0.00	39.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
40.00	0.00	0.00	0.00	40.00	0.00	0.00	40.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
40.50	0.00	0.00	0.00	40.50	0.00	0.00	40.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
41.00	0.00	0.00	0.00	41.00	0.00	0.00	41.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
41.50	0.00	0.00	0.00	41.50	0.00	0.00	41.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
42.00	0.00	0.00	0.00	42.00	0.00	0.00	42.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
42.50	0.00	0.00	0.00	42.50	0.00	0.00	42.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
43.00	0.00	0.00	0.00	43.00	0.00	0.00	43.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
43.50	0.00	0.00	0.00	43.50	0.00	0.00	43.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
44.00	0.00	0.00	0.00	44.00	0.00	0.00	44.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
44.50	0.00	0.00	0.00	44.50	0.00	0.00	44.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
45.00	0.00	0.00	0.00	45.00	0.00	0.00	45.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
45.50	0.00	0.00	0.00	45.50	0.00	0.00	45.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
46.00	0.00	0.00	0.00	46.00	0.00	0.00	46.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
46.50	0.00	0.00	0.00	46.50	0.00	0.00	46.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
47.00	0.00	0.00	0.00	47.00	0.00	0.00	47.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
47.50	0.00	0.00	0.00	47.50	0.00	0.00	47.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
48.00	0.00	0.00	0.00	48.00	0.00	0.00	48.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
48.50	0.00	0.00	0.00	48.50	0.00	0.00	48.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
49.00	0.00	0.00	0.00	49.00	0.00	0.00	49.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
49.50	0.00	0.00	0.00	49.50	0.00	0.00	49.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
50.00	0.00	0.00	0.00	50.00	0.00	0.00	50.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
50.50	0.00	0.00	0.00	50.50	0.00	0.00	50.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
51.00	0.00	0.00	0.00	51.00	0.00	0.00	51.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
51.50	0.00	0.00	0.00	51.50	0.00	0.00	51.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
52.00	0.00	0.00	0.00	52.00	0.00	0.00	52.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
52.50	0.00	0.00	0.00	52.50	0.00	0.00	52.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
53.00	0.00	0.00	0.00	53.00	0.00	0.00	53.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
53.50	0.00	0.00	0.00	53.50	0.00	0.00	53.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
54.00	0.00	0.00	0.00	54.00	0.00	0.00	54.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
54.50	0.00	0.00	0.00	54.50	0.00	0.00	54.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
55.00	0.00	0.00	0.00	55.00	0.00	0.00	55.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
55.50	0.00	0.00	0.00	55.50	0.00	0.00	55.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
56.00	0.00	0.00	0.00	56.00	0.00	0.00	56.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
56.50	0.00	0.00	0.00	56.50	0.00	0.00	56.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
57.00	0.00	0.00	0.00	57.00	0.00	0.00	57.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
57.50	0.00	0.00	0.00	57.50	0.00	0.00	57.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
58.00	0.00	0.00	0.00	58.00	0.00	0.00	58.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
58.50	0.00	0.00	0.00	58.50	0.00	0.00	58.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
59.00	0.00	0.00	0.00	59.00	0.00	0.00	59.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
59.50	0.00	0.00	0.00	59.50	0.00	0.00	59.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
60.00	0.00	0.00	0.00	60.00	0.00	0.00	60.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
60.50	0.00	0.00	0.00	60.50	0.00	0.00	60.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
61.00	0.00	0.00	0.00	61.00	0.00	0.00	61.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
61.50	0.00	0.00	0.00	61.50	0.00	0.00	61.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
62.00	0.00	0.00	0.00	62.00	0.00	0.00	62.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
62.50	0.00	0.00	0.00	62.50	0.00	0.00	62.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
63.00	0.00	0.00	0.00	63.00	0.00	0.00	63.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
63.50	0.00	0.00	0.00	63.50	0.00	0.00	63.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
64.00	0.00	0.00	0.00	64.00	0.00	0.00	64.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
64.50	0.00	0.00	0.00	64.50	0.00	0.00	64.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
65.00	0.00	0.00	0.00	65.00	0.00	0.00	65.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
65.50	0.00	0.00	0.00	65.50	0.00	0.00	65.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
66.00	0.00	0.00	0.00	66.00	0.00	0.00	66.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
66.50	0.00	0.00	0.00	66.50	0.00	0.00	66.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
67.00	0.00	0.00	0.00	67.00	0.00	0.00	67.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
67.50	0.00	0.00	0.00	67.50	0.00	0.00	67.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
68.00	0.00	0.00	0.00	68.00	0.00	0.00	68.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
68.50	0.00	0.00	0.00	68.50	0.00	0.00	68.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
69.00	0.00	0.00	0.00	69.00	0.00	0.00	69.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
69.50	0.00	0.00	0.00	69.50	0.00	0.00	69.50	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
70.00	0.00																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																														

MALVERN MASTERSIZER

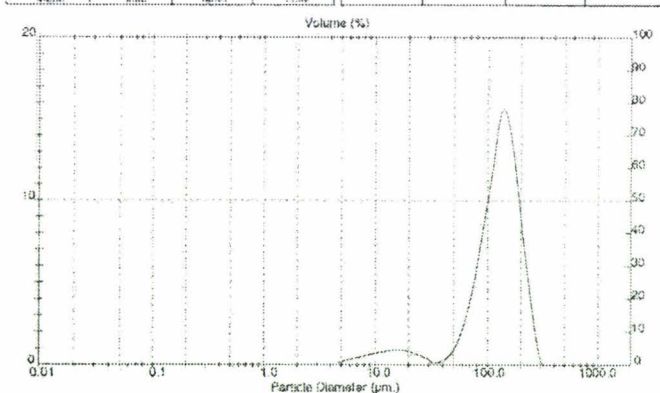
Result: Analysis Report

Sample Details		
Sample ID: Fines	Run Number: 12	Measured: Tue 13 Jul 2004 11:21am
Sample File: REBECCA1	Record Number: 15	Analyzed: Tue 13 Jul 2004 11:21am
Sample Path: C:\SIZERS\DATA\		Result Status: Analyzed
Sample Notes: Sieved 75 - 150 um		

System Details		
Range Lens: 1000 mm	Beam Length: 10.00 mm	Samples: MS66
Preselection: SRHA	(Particle R.I. = 1.4500, 0.1000)	Dispersion R.I. = 1.0000
Analysis Model: Compressed Range		Observation: 83.3%
Modifications: None		Refractive: 1.925%

Result Statistics		
Distribution Type: Volume	Concentration = 0.0145 %/d	Density = 1.898 g/cub.cm
Mean Diameter:	D (v, 0.1) = 57.44 um	D (v, 0.5) = 138.56 um
D (4, 5) = 128.93 um	D (v, 0.9) = 49.45 um	Span = 3.49E+00
		Specific S.A. = 0.0543 sq m/g
		Uniformity = 9.49E+01

Size Low (um)	in %	Size High (um)	in %	Size Low (um)	in %	Size High (um)	in %
4.76	0.14	4.76	0.14	55.51	3.87	75.92	15.95
4.80	0.05	5.08	0.37	61.82	0.97	88.91	22.90
5.69	0.37	6.62	0.72	86.41	0.24	131.58	01.90
6.60	0.08	7.72	1.26	100.58	12.27	120.97	43.83
7.72	0.68	9.00	1.83	120.87	15.93	140.56	55.20
9.00	0.09	10.48	3.52	140.58	14.50	162.77	74.64
10.48	0.79	12.21	3.31	162.77	12.00	180.80	08.17
12.21	0.88	14.22	4.17	180.80	8.11	202.28	94.26
14.22	0.93	16.57	5.07	202.28	4.45	258.88	88.73
16.57	0.88	19.31	5.55	258.88	1.27	301.68	100.00
19.31	0.79	22.49	6.24	301.68	0.03	351.46	100.00
22.49	0.62	26.20	7.36	351.46	0.00	409.45	100.00
26.20	0.44	30.55	7.75	409.45	0.00	477.91	100.00
30.55	0.17	35.56	7.96	477.91	0.00	555.71	100.00
35.56	0.22	41.43	8.18	555.71	0.03	647.41	100.00
41.43	0.49	48.27	8.67	647.41	0.00	754.23	100.00
48.27	1.10	56.25	9.77	754.23	0.00	873.07	100.00
56.25	2.22	66.51	11.86				



Malvern Instruments Ltd
Malvern, UK
Tel: +44 (0)1684-892456 Fax: +44 (0)1684-892789

MasterSizer 5 (any bed Ver. 2.19)
Serial Number:

Figure A46 Malvern report for 75-150 µm sugar, sample 3

MALVERN MASTERSIZER

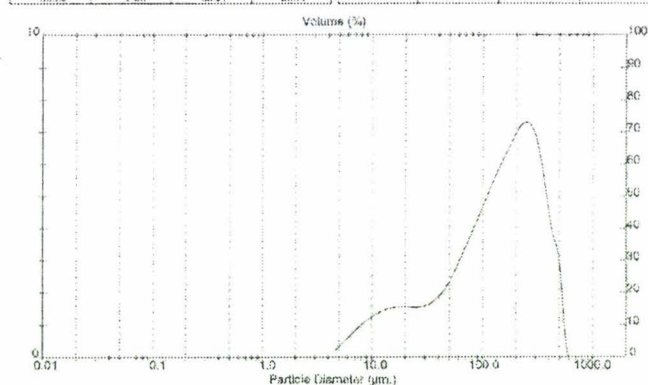
Result: Analysis Report

Sample Details		
Sample ID: Fines	Run Number: 14	Measured: Tue 13 Jul 2004 11:33am
Sample File: REBECCA1	Record Number: 17	Analyzed: Tue 13 Jul 2004 11:32am
Sample Path: C:\SIZERS\DATA\		Result Status: Analyzed
Sample Notes: Sieved 150-212 um		

System Details		
Range Lens: 1000 mm	Beam Length: 10.00 mm	Samples: MS66
Preselection: SRHA	(Particle R.I. = 1.4500, 0.1000)	Dispersion R.I. = 1.0000
Analysis Model: Compressed Range		Observation: 7.9%
Modifications: None		Refractive: 1.691%

Result Statistics		
Distribution Type: Volume	Concentration = 0.0138 %/d	Density = 1.598 g/cub.cm
Mean Diameter:	D (v, 0.1) = 18.72 um	D (v, 0.5) = 148.64 um
D (4, 5) = 171.51 um	D (v, 0.9) = 56.75 um	Span = 2.34E+00
		Specific S.A. = 0.0717 sq m/g
		Uniformity = 7.23E+01

Size Low (um)	in %	Size High (um)	in %	Size Low (um)	in %	Size High (um)	in %
3.19	0.21	3.19	0.21	63.51	3.40	75.92	29.14
4.68	0.43	5.00	0.64	75.92	2.96	88.91	59.17
5.69	0.84	6.62	1.29	88.91	4.53	100.58	97.70
6.60	0.05	7.72	0.14	100.58	5.07	120.97	42.77
7.72	1.05	9.00	3.16	120.97	5.56	140.56	48.38
9.00	1.00	10.48	4.40	140.56	6.08	162.77	94.63
10.48	1.30	12.21	5.77	162.77	6.54	180.80	50.98
12.21	1.47	14.22	7.23	180.80	7.54	202.28	88.03
14.22	1.53	16.57	8.78	202.28	7.70	258.88	75.32
16.57	1.55	19.31	10.31	258.88	7.13	301.68	82.45
19.31	1.56	22.49	11.06	301.68	6.40	351.46	88.80
22.49	1.54	26.20	13.40	351.46	5.06	409.45	58.91
26.20	1.55	30.55	14.85	409.45	3.72	477.91	97.47
30.55	1.53	35.56	16.58	477.91	2.38	555.71	100.00
35.56	1.39	41.43	18.97	555.71	0.90	647.41	100.00
41.43	2.06	48.27	20.43	647.41	0.00	754.23	100.00
48.27	2.44	56.25	22.87	754.23	0.00	873.07	100.00
56.25	2.81	66.51	25.77				



Malvern Instruments Ltd
Malvern, UK
Tel: +44 (0)1684-892456 Fax: +44 (0)1684-892789

MasterSizer 5 (any bed Ver. 2.19)
Serial Number:

Figure A47 Malvern report for 150-212 µm sugar, sample 1

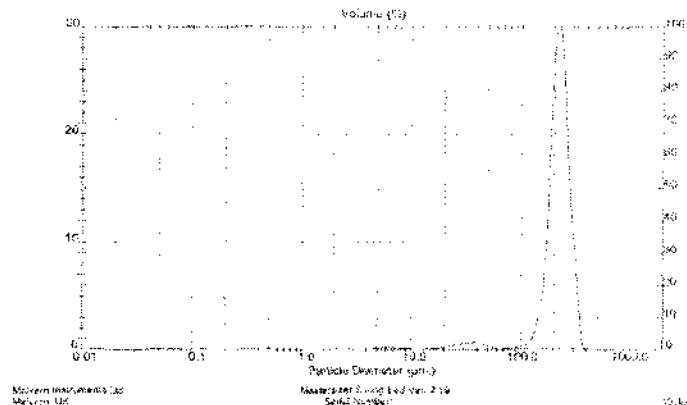
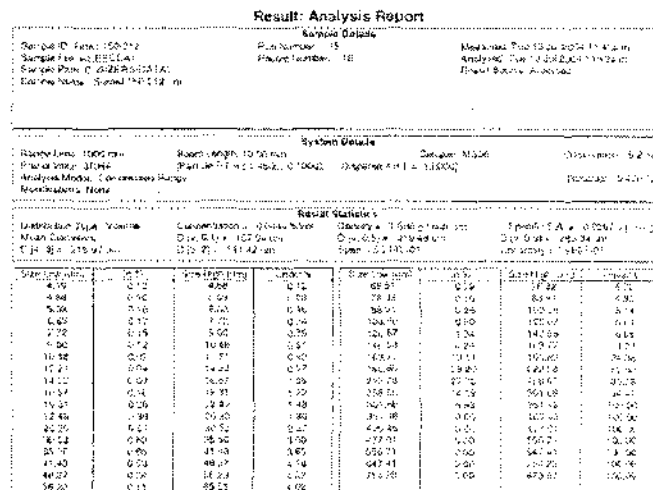


Figure A48 Malvern report for 150-212 μm sugar, sample 2

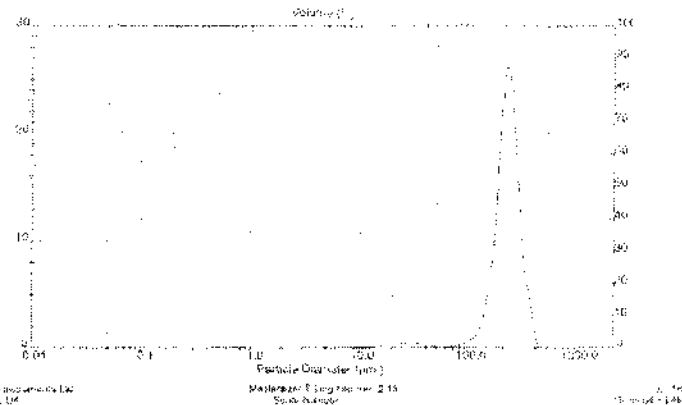
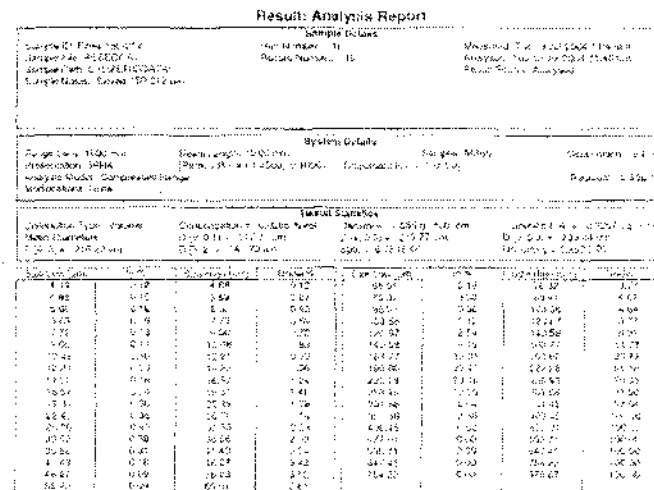


Figure A49 Malvern report for 150-212 μm sugar, sample 3

MALVERN MASTERSIZER

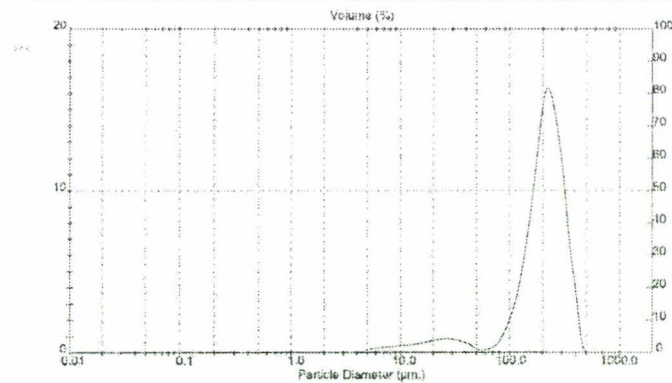
Result: Analysis Report

Sample Details		
Sample ID: Free	Run Number: 13	Measured: Tue 13 Jul 2004 11:29:41
Sample File: REBECCA1	Report Number: 1E	Analysed: Tue 13 Jul 2004 11:29:41
Sample Path: C:\SIZEHSD\DATA\		Result Source: Analyzed
Sample Name: Sugar 150-212 µm		

System Details		
Range Lens: 1000 mm	Beam Length: 10.00 mm	Sample: M560
Prism/Tube: 30/1A	Particle Size: 1-4500, 0-1000	Dispersion: R.I. = 1.0000
Analysis Mode: Compressed Range		Observation: 5.9 %
Modifications: None		Refractive: 1.490 %

Result Statistics		
Distribution Type: Volume	Concentration = 0.0167 %Vol	Density = 1.585 g/cm³
Mean Diameter: D [4,3] = 202.17 µm	D [v,0.1] = 20.64 µm	D [v,0.5] = 211.27 µm
	D [x,0] = 65.68 µm	Span = 1.138E+00

Size Low (µm)	in %	Size High (µm)	in %	Size Low (µm)	in %	Size High (µm)	in %
4.19	0.14	4.88	0.14	65.51	0.38	75.32	0.45
4.38	0.13	5.19	0.17	76.38	0.45	88.41	0.38
5.09	0.31	5.83	0.65	85.31	1.71	105.58	11.58
6.53	0.38	7.72	1.04	100.58	3.04	110.67	15.03
7.72	0.40	8.00	1.44	120.67	5.02	140.58	20.06
9.00	0.44	10.45	1.88	140.58	7.95	161.77	23.50
10.48	0.46	12.21	2.35	161.77	11.78	190.50	33.75
12.21	0.53	14.22	2.87	190.50	15.88	222.28	55.48
14.22	0.60	16.37	3.49	222.28	15.95	258.95	71.00
16.37	0.68	18.31	4.15	258.95	13.31	301.68	65.61
18.31	0.75	22.42	4.87	301.68	2.23	361.46	10.80
22.42	0.85	25.21	5.87	361.46	4.93	439.45	69.70
25.21	0.87	30.53	6.88	439.45	1.21	477.01	100.00
30.53	0.91	35.55	7.91	477.01	0.30	525.71	100.00
35.55	0.87	41.43	8.18	525.71	0.30	647.41	100.00
41.43	0.90	48.27	8.68	647.41	0.50	784.23	100.00
48.27	0.19	56.53	8.93	784.23	0.03	878.67	100.00
56.53	0.20	65.61	9.05				



Malvern Instruments Ltd.
Malvern, UK
Tel: +44 (0)1684 892456 Fax: +44 (0)1684 892789

MasterSizer 3 long bed Ver. 2.15
Serial Number:

p. 13
13 Jul 04 13:47

Figure A50 Malvern report for 150-212 µm sugar, sample 4

MALVERN MASTERSIZER

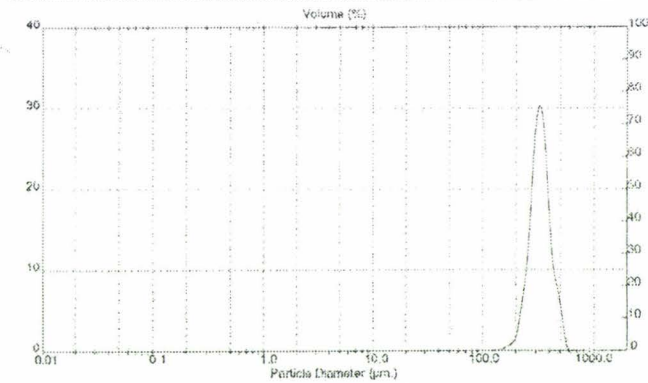
Result: Analysis Report

Sample Details		
Sample ID: Free 212-315	Run Number: 18	Measured: Tue 13 Jul 2004 11:45:41
Sample File: REBECCA1	Report Number: 22	Analysed: Tue 13 Jul 2004 11:45:41
Sample Path: C:\SIZEHSD\DATA\		Result Source: Analyzed
Sample Name:		

System Details		
Range Lens: 1000 mm	Beam Length: 10.00 mm	Sample: M560
Prism/Tube: 30/1A	Particle Size: 1-4500, 0-1000	Dispersion: R.I. = 1.0000
Analysis Mode: Compressed Range		Observation: 8.7 %
Modifications: None		Refractive: 0.502 %

Result Statistics		
Distribution Type: Volume	Concentration = 0.0766 %Vol	Density = 1.588 g/cm³
Mean Diameter: D [4,3] = 301.53 µm	D [v,0.1] = 247.40 µm	D [v,0.5] = 325.29 µm
	D [x,0] = 301.53 µm	Span = 5.681E-01

Size Low (µm)	in %	Size High (µm)	in %	Size Low (µm)	in %	Size High (µm)	in %
4.19	0.11	4.88	0.11	65.51	0.02	75.32	1.03
4.38	0.03	5.19	0.04	76.38	0.01	88.41	1.06
5.09	0.04	5.83	0.08	85.31	0.02	105.58	1.91
6.53	0.05	7.72	0.13	100.58	0.08	110.67	1.14
7.72	0.08	8.00	0.19	120.67	0.18	140.58	1.77
9.00	0.09	10.45	0.25	140.58	0.30	161.77	1.07
10.48	0.05	12.21	0.30	161.77	0.19	190.50	2.30
12.21	0.14	14.22	0.34	190.50	2.40	222.28	4.73
14.22	0.03	16.37	0.37	222.28	8.21	258.95	12.93
16.37	0.04	18.31	0.40	258.95	21.67	301.68	44.41
18.31	0.16	22.42	0.46	301.68	10.80	361.46	64.07
22.42	0.09	25.21	0.54	361.46	13.44	439.45	86.10
25.21	0.09	30.53	0.63	439.45	9.42	477.01	85.52
30.53	0.09	35.55	0.72	477.01	4.48	525.71	100.00
35.55	0.09	41.43	0.88	525.71	0.50	647.41	100.00
41.43	0.08	48.27	0.91	647.41	0.50	784.23	100.00
48.27	0.07	56.53	0.98	784.23	0.03	878.67	100.00
56.53	0.06	65.61	1.05				



Malvern Instruments Ltd.
Malvern, UK
Tel: +44 (0)1684 892456 Fax: +44 (0)1684 892789

MasterSizer 3 long bed Ver. 2.15
Serial Number:

p. 13
13 Jul 04 13:46

Figure A51 Malvern report for 212-315 µm sugar, sample 1

MALVERN MASTERSIZER

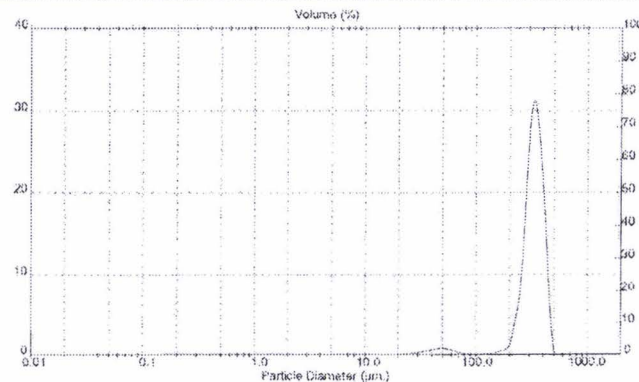
Result: Analysis Report

Sample Details		
Sample ID: Pops 212-315	Run Number: 17	Measured Time: 13 Jul 2004 11:47am
Sample File: REEBC001	Record Number: 21	Analysis: Tue 13 Jul 2004 11:47am
Sample Path: C:\SIZER\DATA\		Result Source: Analysis
Sample Notes:		

System Details			
Range Lens: 1000 mm	Beam Length: 10.00 mm	Sample: M366	Concentration: 7.9 %
Preventative: 3H-A	Particle R.I.: (1.4500, 0.1000)	Dispersant R.I.: 1.0000	Refractive: 0.680 %
Analysis Model: Compressed Range			
Modulation: None			

Result Statistics			
Distribution Type: Volume	Concentration = 0.0261 % Vol	Density = 1.588 g/cm ³	Specific S.A. = 0.0185 sq m/g
Mean (Sauter):	D (v, 0.1) = 238.23 µm	D (v, 0.5) = 329.21 µm	D (v, 0.9) = 412.65 µm
D [4, 3] = 310.20 µm	D [3, 2] = 200.74 µm	Span = 5.9061 (v)	Uniformity = 0.9145 (v)

Size Low (µm)	in %	Size High (µm)	Under %	Size Low (µm)	in %	Size High (µm)	Under %
4.19	0.04	4.88	0.04	65.51	0.05	76.32	4.87
4.88	0.07	5.69	0.10	76.32	0.18	88.91	5.05
5.69	0.09	6.51	0.20	88.91	0.07	100.58	5.12
6.51	0.12	7.72	0.31	100.58	0.07	110.67	5.19
7.72	0.13	8.90	0.44	110.67	0.16	140.58	5.55
8.90	0.15	10.48	0.57	140.58	0.50	163.77	5.95
10.48	0.18	12.21	0.69	163.77	0.63	190.80	6.28
12.21	0.01	14.22	0.70	190.80	1.75	225.23	6.03
14.22	0.02	16.57	0.73	225.23	5.10	259.95	14.22
16.57	0.05	19.31	0.77	259.95	18.45	301.88	32.71
19.31	0.09	22.49	0.83	301.88	30.85	351.46	83.56
22.49	0.16	26.20	1.03	351.46	25.52	409.43	89.06
26.20	0.26	30.53	1.29	409.43	16.92	477.31	130.00
30.53	0.41	35.58	1.70	477.31	0.00	555.31	100.00
35.58	0.60	41.33	2.31	555.71	0.00	647.41	100.00
41.33	0.78	48.27	3.08	647.41	0.00	754.23	100.00
48.27	0.91	56.23	3.89	754.23	0.00	879.07	100.00
56.23	0.63	65.51	4.52				



Malvern Instruments Ltd. Mastersizer Elong bed Ver. 2.10
 Malvern, UK Date Number:
 Tel: +44 (0)1684 892456 Fax: +44 (0)1684 892782 13 Jul 04 13:48

Figure A52 Malvern report for 212-315 µm sugar, sample 2