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# Advanced platform for shelf life extension in liquid foods

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#### Summary

The shelf life of lipid based foods is often determined by the development of rancid flavours attributed to lipid oxidation reactions. These reactions are highly complicated and readily change when the reaction system is altered. As a result, researchers have struggled to make significant advances in their understanding of the mechanisms and rates of lipid oxidation.

This thesis focuses on the generalised three step mechanism of lipid oxidation and develops understanding, through mathematical modelling exercises, about the factors that influence the rates of lipid oxidation. More specifically, this thesis focuses on bulk oils, bulk oils with added antioxidants, oil-in-water emulsions and the effects of oxygen supply and consumption rates in real food systems.

For this thesis, methods were developed to identify and validate findings that suggest that lipid hydroperoxides are the rate defining reactant in lipid oxidation reactions. These methods were then used to measure the solubility of oxygen in oil and to define the role oxygen plays in determining the rates of lipid oxidation in a range of systems.

The use of a newly developed batch oxidation apparatus led to the development and validation of models to predict the rates of oxygen consumption during oxidation. The model showed that the rates of oxygen consumption were half order with respect to the lipid hydroperoxide concentration. Through further validation experiments, it was shown that, during the initial stages of lipid oxidation before rancidity, each mole of lipid hydroperoxides formed required 5.04 moles of oxygen to be consumed when there was oxygen present.

The same model and methods were then used to predict the changes in rates of lipid oxidation triggered by changes in reaction temperature. From this work, it was found that the Arrhenius law was capable of predicting the rates of oxygen consumption.

The addition of butylated hydroxyanisole (BHA) to mixed fish oil samples brought with it a reduction in the rates of lipid oxidation, the magnitude of which was proportional to the concentration of BHA added. It was found that the inclusion of a modifier into the half order model was capable of predicting the rates of lipid oxidation when antioxidants were added. Methods to quantify the modifier were supplied for future use.

The dilution of bulk oils by the formation of oil-in-water emulsions was also studied. It was found that the rates of lipid oxidation were proportional to the concentration of

lipids in the emulsion. It was shown that the extent of oxidation during a batch oxidation was inversely proportional to the concentration of lipids in the emulsions as the aqueous phase acted as sump of oxygen for reaction in the oil droplets.

Through modelling and short validation exercises, it was shown that changes to the surface area to volume ratio of oil droplets in emulsions had no effect on the rates of oxygen supply/lipid oxidation and that any effects noted in literature are likely to be the result of other surface active compounds.

Finally, a modelling exercise showed that the rates of oxygen consumption via reaction were likely to be significantly faster than the rates of oxygen supply in unmixed systems in polymer packaging and, to some extent, open to the atmosphere. The diffusion of lipid hydroperoxides was shown to be important in bulk oils stored in polymer packaging as it allowed for a greater proportion of the oil to react with the oxygen transferred, thus reducing the potential for the oxygen supplied to take part in secondary and tertiary product formation. It was suggested that it is better, for a given quantity of oxygen supplied, for the entire oil product to react as it would result in fewer tertiary products being formed than if the oxygen were to be consumed at the surface of the oil only. Following this, it was suggested that an oil-in-water emulsion should be less stable than a bulk oil.

Short experimental work showed that storing bulk oils in the absence of oxygen brings with it a decrease in the rates of lipid oxidation caused by a decrease in the concentration of lipid hydroperoxides. This decrease, coupled with anecdotal evidence that products do become rancid over long periods of time, suggests that the radicals formed during lipid hydroperoxide breakdown can be used in two different sets of reactions. That is, the relative rates of reformation of lipid hydroperoxide via reaction with lipids and the formation of tertiary oxidation products will likely determine the rates of lipid hydroperoxide breakdown and rancidity in real food systems.

An indepth analysis of lipid hydroperoxide breakdown rates in the absence of oxygen as well as a set of validation experiments for the storage of bulk oils and oil-in-water emulsions in polymer films was suggested as being the final piece of information needed to complete a comprehensive model capable of quantitatively predicting the rates of lipid oxidation reactions and the shelf life of lipid oxidation prone foods.

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Figure XYZ: Ironically un-funny joke

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