Kinetics of the pre-treatment of used cooking oil using Novozyme 435 for biodiesel production

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Biodiesel can be produced commercially by transesterification of vegetable oil to fatty acid methyl esters (FAME) using a homogenous catalyst such as sodium hydroxide and methanol. In order to reduce the cost and environmental impact of producing biodiesel, the use of heterogeneous catalysts and used cooking oil (UCO) is currently being investigated. UCO is a cheap raw material; however, due to the degradation of triglycerides during cooking it also contains free fatty acids (FFAs), mono and diglycerides. FFAs need to be removed from the UCO because it can cause saponification during the transesterification process and most biodiesel specifications impose an upper limit on the FFAs concentration. An esterification pre-treatment process can be used to convert the FFAs to biodiesel.

Novozyme 435, *Candida antarctica* Lipase B immobilized on acrylic resin, has been investigated as the catalyst for this reaction. It was found that at higher temperatures, 50-60 °C, the FFAs concentration initially decreased and then started to increase. A comparison of the FFAs and FAME concentration at 30 °C and 60 °C is shown in Figure 1. The esterification reaction schematic is shown in Figure 2 and from this it can be seen that 1 mol of FFAs should form 1 mol of biodiesel. However, the data in Figure 1 shows that the amount of biodiesel formed is significantly greater than expected from the esterification reaction.

Figure 1: Comparison of the FFAs and FAME concentrations for reactions carried out at 30 °C and 60 °C
This data indicates simultaneous esterification and transesterification of the mono-, di- and triglycerides. As a result, an experimental plan has been developed to monitor the FFAs mono-, di and triglycerides using UPLC-Ms, the FAME and glycerol concentrations using GC-MS and the water concentration using a Karl Fischer titration method. A detailed mechanism and associated kinetic model has been postulated and the experimental data will be used to test and possibly amend the model. This model can then be used to determine the optimum operating conditions for the pre-treatment process. Increasing the amount of biodiesel produced while minimising the FFA concentration should reduce the overall cost of the process.