**Reactive coupling: A novel approach for glycerol free biodiesel production.**

Ibrahim A. Mohammed, Jonathan G.M. Lee, and Adam P. Harvey

*School of Engineering, Newcastle University*

*\*i.a.mohammed2@ncl.ac.uk*

**Highlights**

* Simultaneous production of biodiesel and polyglycerol.
* Reduction in the use of methanol during biodiesel production.
* Conversion of the excess methanol to added value product.

**1. Introduction**

Using conventional processes, biodiesel production is necessarily accompanied by the production of a low value glycerol-rich co-product. There is currently a substantial worldwide surplus of this coproduct, and it is of low value due to its low quality (due to the high level s of impurity present) and oversupply. The aim of this project was to develop a process to convert the glycerol produced into polyglycerol, a higher value product, in situ. In principle, this could improve the economics of biodiesel production. The improvement would not only be via the increased coproduct value, but also by reducing the methanol requirement of the process, which would reduce the load on the distillation column (used to recycle the methanol).

The “reactive coupling” proposed is given below:

**2. Methods**

The coproduct will undergo step-growth polycondensation in the same pot to produce polyglycerol and water. The reaction was performed in a pressurized vessel at 130 – 160 oC with sulfuric acid as the catalyst. The effect of reaction temperature, catalyst concentration and molar ratio of triglyceride to methanol was studied. Both FAME, polyglycerols and gas sample produced were analyzed using gas chromatography. Methyl heptadecanoate (C17) was used as internal standard for the FAME and N,O Bis(trimethylsilyl)trifluoroacetamide with trimethylchlorosilane (BSTFA) was used to silylate the polyglycerol sample before analysing with the GC.

**3. Results and discussion**

Conversion of the triglyceride of approximately 100% was achieved. The glycerol were majorly converted to diglycerols. The glycerol conversion increased with increasing temperature and with decreasing mole ratio. The diglycerols peaks are similar to previous reports (Barros *et al.* 2017, Guerrero-Urbaneja *et al.* 2014, Ayoub and Abdullah 2013) with the α,α diglycerols isomer more predominant than the α,β diglycerols and the β,β diglycerols. A high signal around 6 minutes was observed, which was presumed to be the cyclic diglycerols with two hydroxyl groups while the glycerol and diglycerols have three and four hydroxyl group attached to them respectively.

**Figure 1.** (a) Percentage FAME content after analysis with GC and (b) GC of the coupled glycerol during combined transesterification and reactive coupling showing the glycerol and isomers of diglycerols peaks.

The gas sample analysed were mostly methanol with few percentage of dimethyl ether (DME). This might be due to dehydration of the excess methanol in the reaction.

**4. Conclusions**

A proof-of-concept has been developed for this process to achieve high triglyceride conversion at low methanol-to-oil molar ratio and polyglycerols as the co-product of the reaction. The α,α diglycerols linear isomer was predominant among linear diglycerols which indicate the high selectivity of the homogeneous catalyst towards the etherification.

**References**

1. F.J.S Barros, R.Moreno-Tost, J.A. Cecilia, A.L. Ledesma-Munoz, L.C.C. de Oliveira, F.M.T. Luna, R.S. Vieira, Molecular Catalysis, 433 (2017) 282–290.
2. P. Guerrero-Urbaneja, C. Garcia-Sancho, R. Moreno-Tost, J. Merida-Robles, J. Santamaria-Gonzalez, A. Jimenez-Lopez, P. Maireles-Torres, Applied Catalysis A: General, 470 (2014) 199–207.
3. M. Ayoub, A.Z. Abdullah, Chemical Engineering Journal 225 (2013) 784–789.