

SIMULTANEOUS TRANSESTERIFICATION AND REACTIVE COUPLING FOR BIODIESEL AND POLYGLYCEROL PRODUCTION

Ibrahim Aris Mohammed^{1*}, Jonathan G.M. Lee¹, Adam P. Harvey¹

¹ School of Engineering, Newcastle University

ABSTRACT

Using conventional processes, biodiesel production is necessarily accompanied by the use of excess alcohol and production of a low value glycerol-rich co-product. There is currently a substantial worldwide surplus of this coproduct. While recovery of the alcohol is associated with high capital cost and energy requirement. This work tend to reduce the alcohol usage during biodiesel production and *in situ* convert the crude glycerol to an added valued product.

The biodiesel was produced batch-wise at 130 – 160 °C with sulfuric acid as the catalyst. The effects of reaction temperature, catalyst concentration and molar ratio of triglyceride to methanol were studied. Approximately 100% conversion of the triglyceride was achieved. The glycerol conversion increased with increasing temperature and decreasing molar ratio.

This represents proof-of-concept not only for reducing the excess methanol requirement, but also for combining production of fatty acid methyl esters with other added value products, whilst reducing glycerol production.

Keywords: reactive coupling, polyglycerols, transesterification, etherification, biodiesel.

NONMENCLATURE

Abbreviations

DG	Diglycerols
TG	Triglycerols
TTG	Tetraglycerols
FAME	Fatty acid methyl ester
PG	Polyglycerol

1. INTRODUCTION

Biodiesel production requires the use of excess alcohol to achieve sufficient conversion. Currently, distillation columns or flash evaporation are used for the methanol recovery step. However, the energy requirements and capital cost for these additional units increase the product cost.

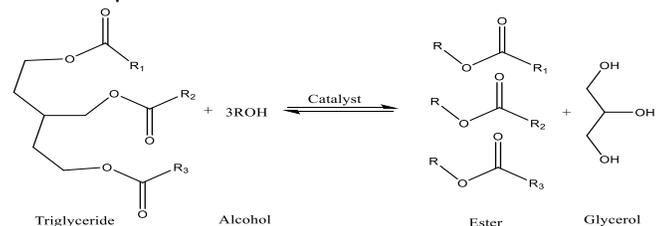


Fig 1 Transesterification reaction for biodiesel production

Also, the commercial production of biodiesel is on the increase which invariably increase the production of the crude glycerol as the major coproduct. The applications of pure glycerol in food, cosmetics and pharmaceutical industries among others also increases with the demands of the products. However, the glycerol formed during biodiesel production require various steps of purification before the coproduct will have an appreciable market value. The combined process of purifying the crude glycerol is costly and time consuming. Meanwhile the oversupply of the coproduct due to continuous increase in the biodiesel production will result in the disposal of the crude glycerol which has an effect to the environment [1-3].

Many reaction pathway is possibly to convert glycerol to other important added value or intermediate chemicals. This is possible due to the hydroxyl group (OH) attached to each of the carbon atom in the glycerol molecule [4].

Few of this pathway are shown in the Fig 2 below. Dehydration for the production of acrolein and acetol, fermentation can be apply for alcohol production, steam reforming in hydrogen production and etherification for polyglycerols production.

The aim of this research was to reduce the excess methanol used during biodiesel production. This can be achieved by converting the glycerol coproduct *in situ* into polyglycerol. By removing the glycerol, the equilibrium of

the transesterification reaction is pulled to the product side, reducing the methanol requirement.

The application of polyglycerols in food, pharmaceutical, biomedical, cosmetics and drug industries among others has make it significant in the science and engineering of polymers. It is produce by the condensation of two or more glycerol in presence of a selected catalyst to produce the oligomers of glycerol and water as a coproduct [5].

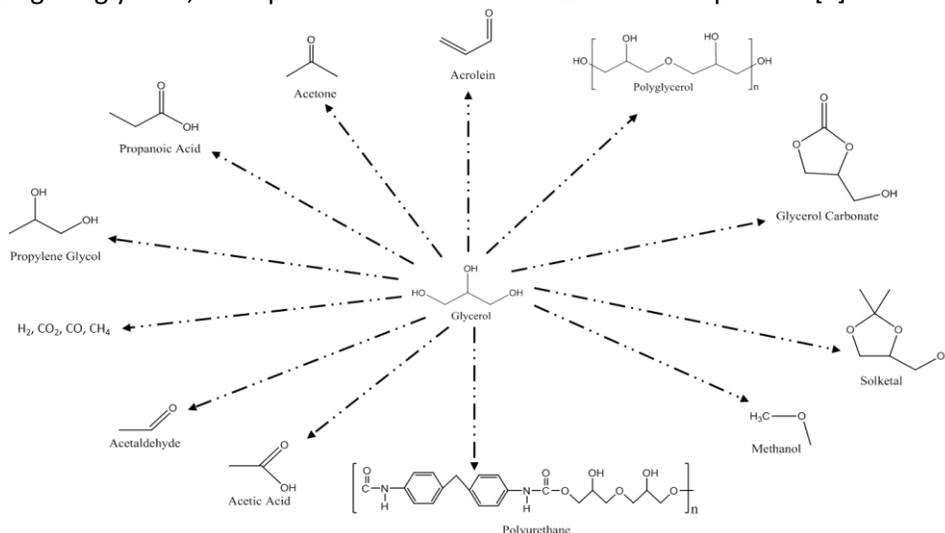


Fig 2 Different glycerol reaction pathways

2. MATERIALS AND METHOD

An anhydrous methanol with >99.5% purity, pyridine anhydrous (99.8%), N, O-Bis (trimethylsilyl) trifluoroacetamide > 98.5% with trimethylchlorosilane 1%, sulfuric acid (99.999%), methyl heptadecanoate (>99%) analytical standard all from Sigma-Aldrich. Propan-1-ol with 99.5% purity was obtained from Acros organics while diglycerol, polyglycerol – 3, and polyglycerol – 4 used as standard are from Inovyn.

The experiment begins by measuring an amount (100 ml) of triglyceride into the reaction vessel (A). It was then heated until the temperature reads 130 °C on the thermocouple. Methanol corresponding to the required mole ratio (4:1, 5:1, 6:1 and 8:1) and 1 % sulfuric acid as catalyst for the reaction were measured into the pressure vessel (B). Nitrogen gas was then allowed into the vessel (B) which flows the mixture of the methanol and catalyst into the main reactor (vessel A) at the required temperature. The reaction is conducted in nitrogen environment to minimize dehydration of the glycerol into acrolein and acetol. Liquid samples were collected at interval to determine the percentage FAME content. The gas was not collected during the reaction to avoid incomplete conversion of triglyceride to FAME. The gas samples were analysed with the GC at the end of the

reaction for its composition. The reaction was repeated with an increase temperature (140, 150 and 160 °C) and catalyst concentration (2, 3 and 5 %). The polyglycerol was analyzed with FTIR, HPLC and GC while the FAME was analyzed using GC.

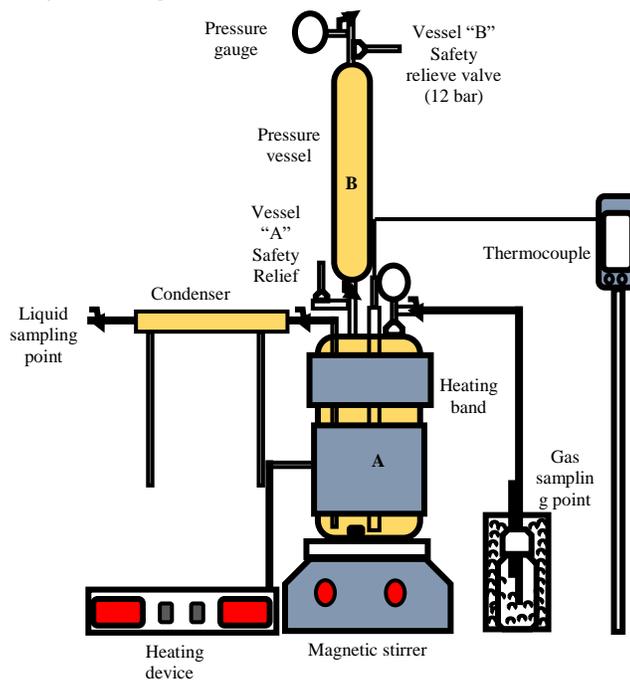


Fig 3 Reaction vessel equipped with thermocouple and pressuregauge.

3. RESULTS AND DISCUSSION

3.1 Polyglycerol

The FTIR spectra for the standard samples shows a decrease in the hydroxyl group (O – H bond) of the glycerol near $3000 - 3400 \text{ cm}^{-1}$ as shown in Fig 4. This implies the higher the degree of polyglycerol formed during etherification the more water will be formed and the less the hydroxyl group in the system. This can be buttress with the report of Ardila-Suárez, Rojas-Avellaneda and Ramirez-Caballero [6] that the hydroxyl number of the feed glycerol is higher than that of the polymerised sample.

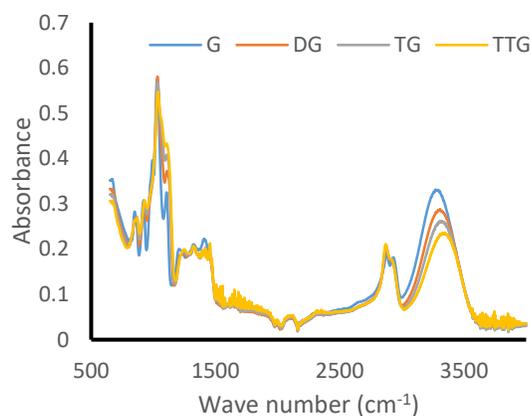


Fig 4 FTIR Spectra of the glycerol oligomers.

The decrease in the hydroxyl group was observed to with increase in reaction time, catalyst concentration and reaction temperature. The spectra's correspond to the work of Ardila-Suárez, Rojas-Avellaneda and Ramirez-Caballero [6] and Salehpour and Dubé [7]. The ether group with C – O – C stretch around wave number 1100 cm^{-1} was observed to increase from the glycerol to polyglycerol. It is pertinent to note that the appearance of the ether group (C – O – C) can only be noticed with the disappearance of the hydroxyl group (O – H) and the C – O stretch. The result from this work follows this sequence. The ether group peak was observed to increase with an increase in catalyst concentration, reaction temperature and reaction time. The result from the FTIR was able to show the increase in the total polyglycerol production, but not able to identify the different oligomers.

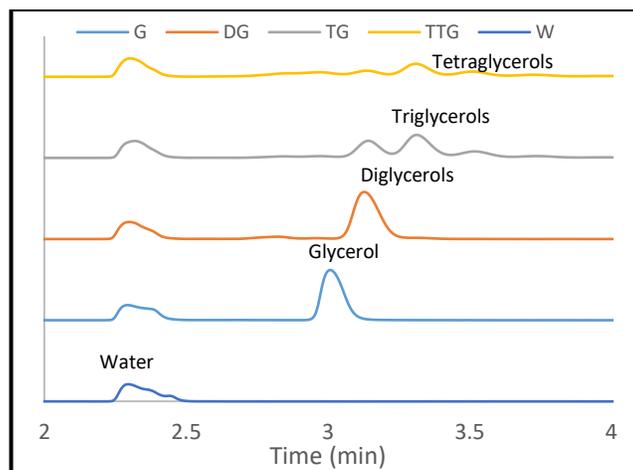


Fig 5 HPLC chromatogram of glycerol oligomers.

The chromatogram from the HPLC was able to give the different oligomers present in every sample. The yield and selectivity of each of the polymer can be determine from the chromatogram. Though this analytical method could not show the different isomers present in each oligomer.

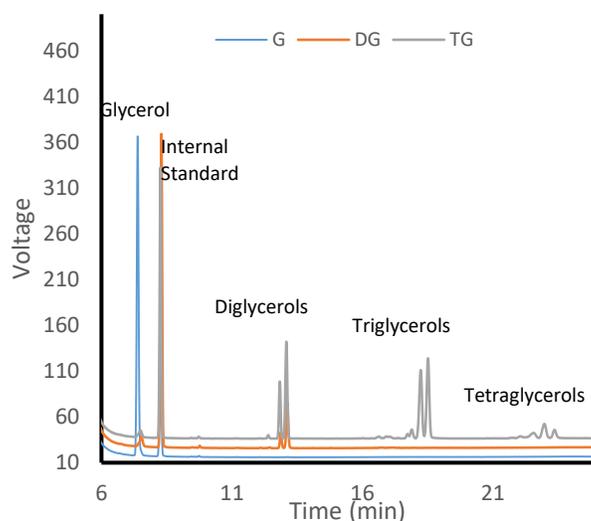


Fig 6 GC chromatogram of glycerol oligomers.

Different isomers (both linear and cyclic) is visible using the GC. The mechanism for this reaction indicates the production of α,α -diglycerols more often than α,β and β,β -diglycerols. This is because the energy required for the α,α -diglycerols is less. The cyclic compound is produce by dehydration of the different oligomers.

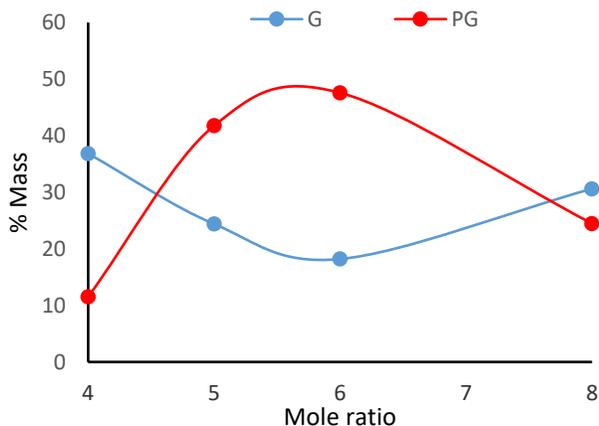


Fig 7 Polyglycerol production at 160°C and 6:1 mole ratio

As the reaction time increases, the production of the polyglycerol was observed to increase. The result is the same when catalyst concentration and temperature were varied. The total polyglycerol (PG) produced was observed to increase with increase in the mole ratio from 4:1 to 6:1. A decrease in the polyglycerol was observed when the mole ratio was increase above 6:1. This might be due to competitive reaction to produce other product (such as 1,3-methyl-propanediol) than polyglycerol.

3.2 Biodiesel

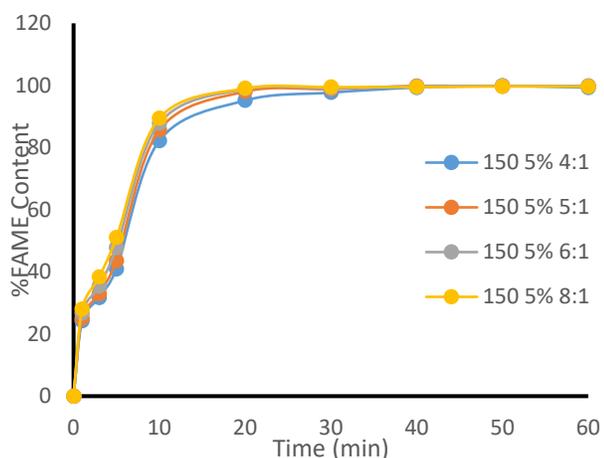


Fig 8 Percentage FAME at 150°C, 5% catalyst concentration and different mole ratio.

High conversion have been reported by several authors to occur close to the boiling point of the short chain alcohol. In the conventional method of biodiesel production, the loss of the alcohol through evaporation and low conversion to biodiesel is avoided by keeping the temperature of the reaction below the boiling point of the alcohol [8]. For this work, the use of a pressure vessel was to enable the application of higher temperature

above the boiling point of the alcohol. The advantage of using high temperature includes short reaction time and good miscibility of the reactant.

Conclusions

The proof-of-concept for the combine biodiesel and polyglycerol is possible, thereby converting the crude glycerol to an added value product. The conversion of the triglyceride to biodiesel was affected positively as the reaction is almost complete after 20 minutes with an acid catalyst.

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