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Compounds and Molecular Transition during Biodiesel Glycerol Hydrothermal Liquefaction

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Abstract: Hydrothermal liquefaction of biomass with acids, bases, neutral, mixed oxides or ionic liquids catalysts into fuels (bio-char bio-oil and syngas) and renewable chemicals is economically valuable technology. However, issues including poor selectivity, reactor corrosion and high cost have not been properly addressed. Glycerol waste from biodiesel production was liquefied under different reaction conditions such as temperature (250°C-350°C), time (5-15 min) and biomass to solvent ratio (5-15). Varied concentration of Choline chlorides based ionic liquids substitutes (deep eutectic solvents) were prepared and used as catalysts and co-solvents in the liquefaction. The results revealed the FTIR analysis indicated the increasing aldehydes, acetals and phenols and decreasing hydrocarbons. Reaction temperature, biomass composition and catalysts selectivity were the most influencing factors determining molecular and compounds transition. Also, increasing of total acidity (7.62% to 5.73%), peroxide values (134.52 mg/KOH/g-88.52 mg/KOH/g) and decreasing TRS (0.826 % - 0.732 %). High temperature favors the production of low molecular weights compounds while catalysts greatly determine the conversion ratio. It was concluded that during hydrothermal liquefaction molecular degradation, polymerization, rearrangement, elimination and other reactions not determined were taking place sequentially.

Keywords: Liquefaction; glycerol; acid compounds; temperature

1. INTRODUCTION

There is unlikely available biomass to replace fossil fuel energy. A comprehensive study of the bottom-up biomass availability potentials from different countries suggested the increasing biofuels supply potentials, specifically in transportation fuel, which will be sourced from biomass, agricultural residue and energy crops [1]. Greater than 80% total cost of most biofuels is the cost of feedstocks cultivation, transportation, sorting and pretreatment [2]. As such, feedstock is an integral part of biofuels production and economics. Generation by generation, feedstocks from different biomass including cellulosic, algae, waste sludge,

wastewater and waste papers have demonstrated suitable biofuels potentials. However, until date, seed oils have been the major source of biodiesel.

Glycerol from biodiesel production constitutes more than ten percent of the total produce during transesterification of vegetable oils and a major by-product in biorefinery. However, limited market is available for the consumption of such crude glycerol. Glycerol can be converted into many useful products. According to Wang et al., [3] sorbitol is converted into mono-functionalized oxygenated intermediates in the first stage of the reaction and proceeds to form jet fuel via aromatization of the intermediates. Aromatic, alcohol and alkane fuels are blended with gasoline to form gasohols for spark ignition engines. Such alcohols and oxygenated fuels from biorefinery have superior advantages over conventional gasoline including high oxygenation, lean flammability and octane number on one side and lower C/H ratio, heating value and boiling point as well [4].

Typically, a biorefinery consists of biochemical, chemical and thermo-chemical processes running side-by-side. Therefore, biodiesel glycerol processing using biorefinery is expected to ensure only useful products are produced in such a manner that pollutants, waste and losses are limited, in what is referred to as an *atom economy model*. In so doing, modern biorefineries are designed to accommodate all feedstocks and produce wide variety of products. Since glycerol is said to have contained economically viable molecules and compounds such as waxes, dyes, flavonoids, volatile fatty acids and polyphenols with cosmetics and semi-chemicals values [5] in addition to large fuels and fuels additives. According to Holm-Nielsen and Ehimen [6] the major considering factors during the design of an integrated biorefinery are the sources, type and composition of biomass, the techno-economic costs of the feedstocks, the conversion and integration technologies as well as the final energy recovery of the biorefinery. Water has characteristic properties during its transition to its critical point. Catalytic HTL has been explored to improve the yield and quality of the HTL products but with little or no impact on reducing the energy consumption of the process. In other to avert

some of these short comings, the use of Ionic Liquids [ILs] and their analogous Deep Eutectic Solvents [DESS] emerged as catalysts and co-solvents in LB processing technologies [7]. In nowadays green technology concept that gave birth to ionic liquids and in the latest, DESs, the application of DES in bio-oil production using HTL technology has not been explored. In spite of their reported selectivity, ease of synthesis and biodegradability, DESs have wide areas of application in chemical science and engineering.

In this research, the optimization of glycerol wastes materials into bio-oil and its fuels characterization will be investigated using deep eutectic solvents both as catalysts and temperature reducing solvent in HTL technology. This will help in reducing the cost of the technology in addition to other additional advantages expected to be discovered in this research. As such, the subcritical co-liquefaction of crude glycerol was conducted at varying liquefaction temperatures (250°C-350°C) and catalysts loading concentration (1% and 5% wt) of the slurry.

2. MATERIALS AND METHODS

2.1 MATERIALS

The glycerol was obtained from transesterification process after biodiesel production from the centre for advanced studies and research in automotive engineering, Delhi technological university, India. Other chemical and reagents herein used were analytical grade chemicals except otherwise stated.

2.2 SYNTHESIS OF CHOLINE CHLORIDE-PTSA DES

For each DES, one mole of ChCl (139.63 g) was combined with different molar ratio of PTSA in the ratio 1:4. Other

reaction conditions are: temperature 120°C, reaction time 180 min, stirring speed of 750 rpm and initial pressure of 4.5 MPa.

2.3 HYDROTHERMAL LIQUEFACTION

The reactor used for liquefaction was a 100 mL capacity reactor unit as shown in figure 1. At the start, Nitrogen gas was severally passed into the reactor. HTL was conducted at 250°C for 10 min reaction time and stirring speed was 750 rpm. Other reaction conditions included the catalyst concentration of 3 wt% and biomass to water ratio was 1:10, while the initial pressure was 4.5 MPa. After reaction completion, the obtained products were separated and analyzed accordingly.

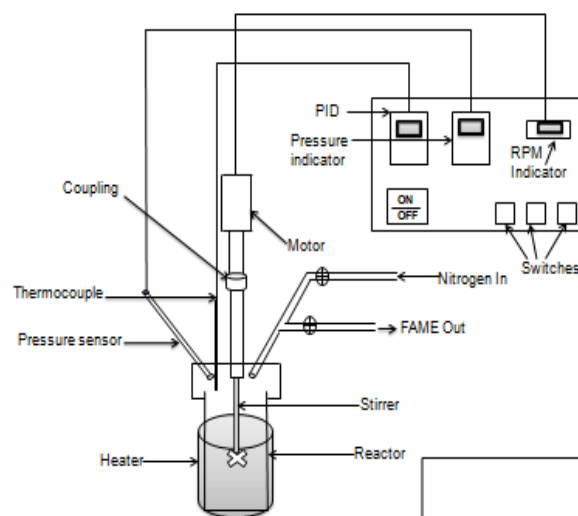


Fig. 1. Schematic reactor diagram for HTL of bio-crude glycerol

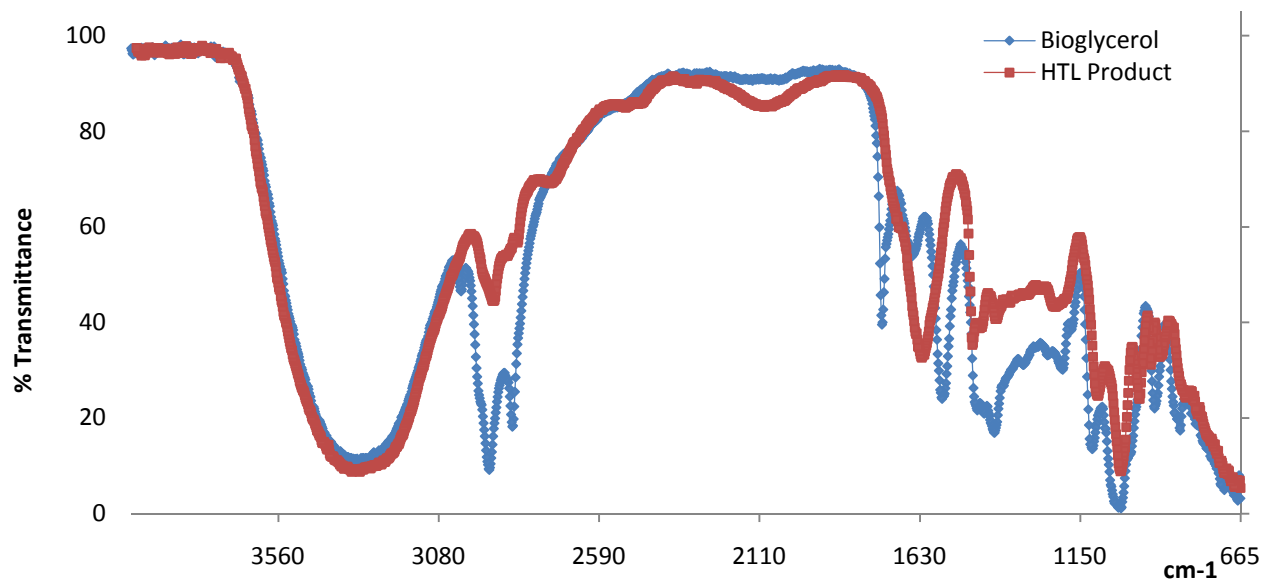


Fig. 2. FTIR spectrum of glycerol and its HTL product

3. RESULTS AND DISCUSSION

Waste biodiesel glycerol is an industrial source of different energy compounds and chemicals. Functional group analysis indicated the predominance abundance of oxygenated compounds in the liquefied product.

The results indicated the reduced oxygenation of compounds. Aromatic compounds in the form of monosaturated C-H bend within absorption range less than 1000 cm^{-1} and alcohols (1° , 2° and 3°) just slightly above that at $1035\text{-}1260\text{ cm}^{-1}$ respectively.

Notably, reduced absorption in the HTL product suggested the conversion of the alcohols. This was confirmed by the broad absorption beyond 3000 cm^{-1} . Correspondingly, absorption at 1630 cm^{-1} could be due to amides. At 250°C and above, amides and ethers are resulting from the decomposition of the lipids composition in the glycerol from the biodiesel production. The HTL product did not show significant absorption within the carboxylic acid range

(2500 cm^{-1} through 3500 cm^{-1}). Characteristic furanic compounds absorption owing to the presence of C=O stretching at $1710\text{-}1720\text{ cm}^{-1}$ could be found in the HTL product, which are facilitated by the acidity of the catalysts as reported by Zhuo et al., [8].

Furanic compounds are the intermediate products from the decarboxylation of fatty acids into pyrrolide according to Gai et al., [9]. It was reported that bio-crude glycerol could be converted into different alkyl alcohols, acetaldehydes, and formaldehyde [10]. Liquefaction indicated unchanged transition of monohydric sugars as well as saturated fatty acids (palmitic acid and stearic acid) on one hand and the thermal degradation of polymeric sugars, unstable compound such as acetol and unsaturated fatty acids. Increasing catalyst concentration (from 1% to 5 % wt) improved the conversion of refined biocrude production via catalytic C=O dehydration. However, total conversion was economically lower than 24.67% at the maximum. Fig. 3 shows the proposed schematic compounds transition with increasing reaction temperature from 250°C to 350°C .

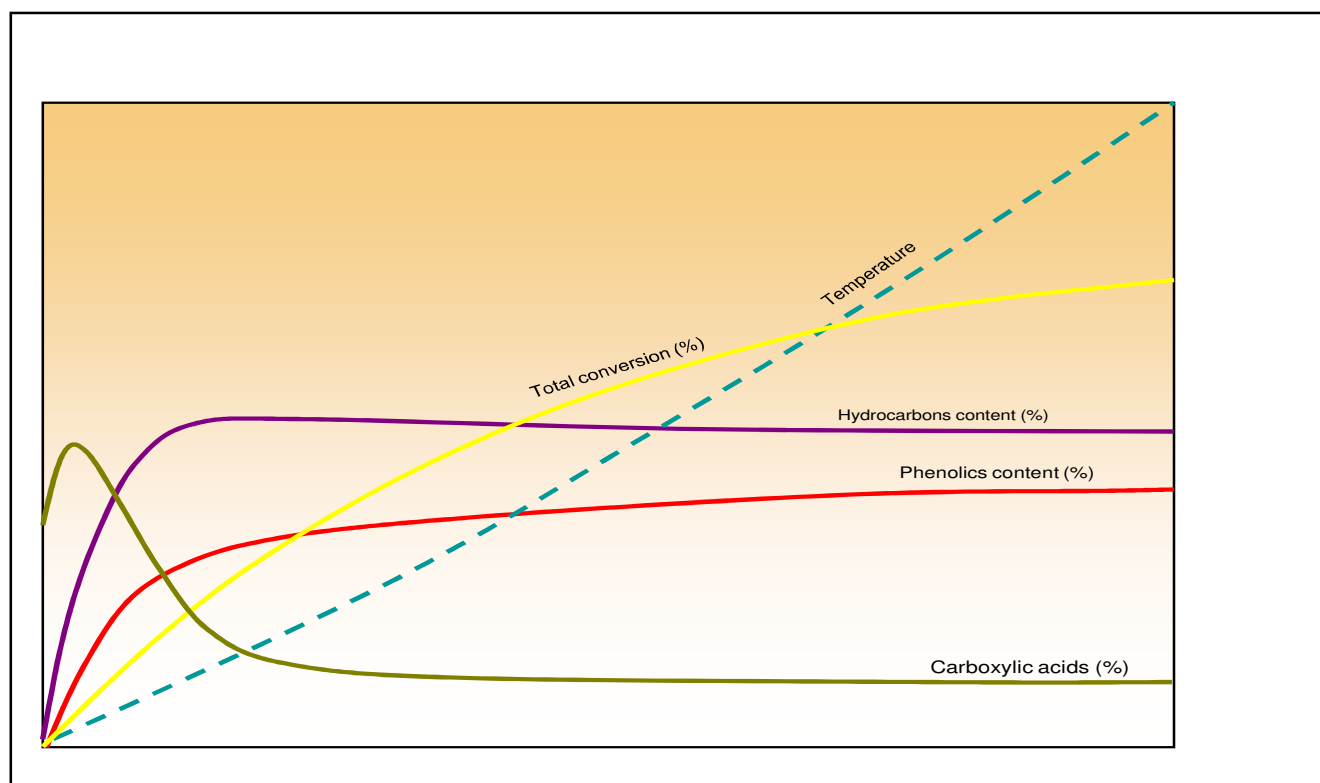


Fig. 3. Schematic compounds transition during HTL of biodiesel glycerol

This concept could perfectly fit into the biorefining concept in biomass pretreatment and fuels conversion. It could be deduced that the major oxygenated compounds present are carboxylic acids, aromatic compounds and alkyl alcohols to mention but a few. Interestingly, at 300°C , biocrude glycerol is thermally decomposed into lower alkane, aldehydes and

alkyl alcohols which could be converted into lighter gaseous products at high temperature decomposition [11].

The total reducing sugars (TRS) were determined by using DNS method and presented in Fig. 4(a). At different HTL temperature, TRS reduction was observed, specifically when DES was used in small concentrations (1-2 % v/v).

High TRS are suitable for biofuels production via fermentation process. Although the TRS was significantly low. High TRS are only expected for highly cellulosic and hemicelluloses feedstocks. In contrast, the percentage total acid number (mg KOH/g) varied significantly with increasing HTL temperature. Fig. 4(b) presents the changes in the TAN with increasing HTL temperature. High TAN

suggests low liquefaction, since acids and acidic compounds are largely present in the aqueous phase. Increasing temperature lowered the TAN by ensuring complete conversion of the acids into compounds with lower pH and correspondingly higher heating values. Compounds such as ether, esters and alkyl alcohols are much better fuels than acids [7].

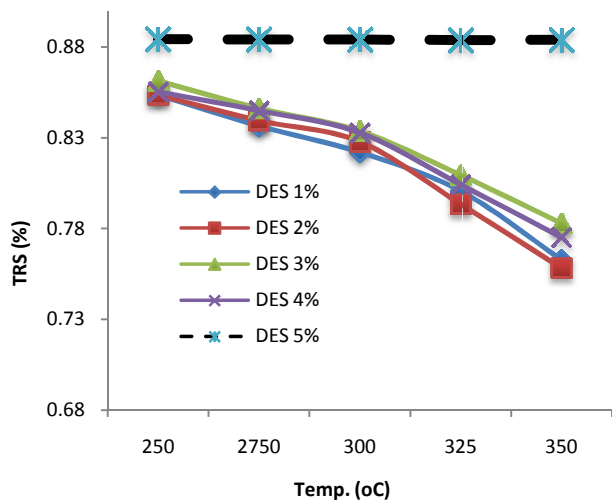


Fig. 4(a). Effect of HTL temperature on TRS

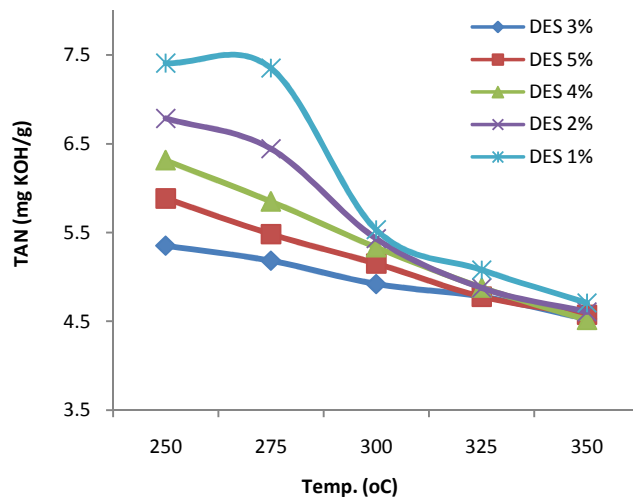
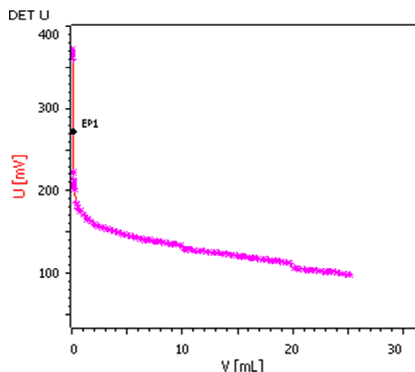
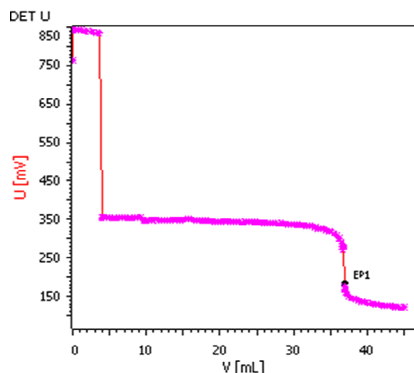


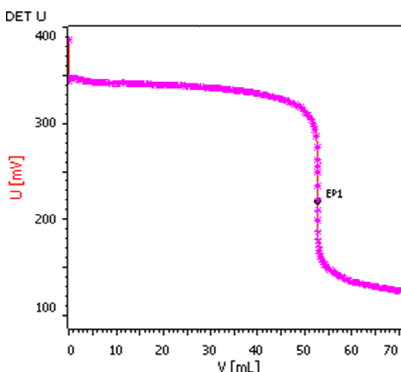
Fig. 4(b). Effect of HTL temperature on TAN



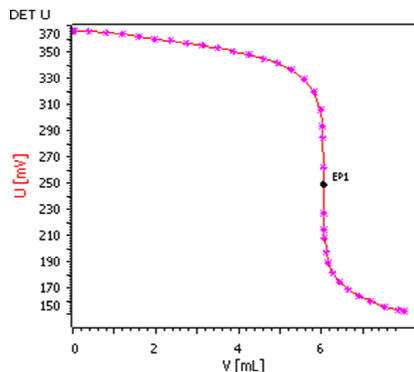
Iodine value of Bio-glycerol



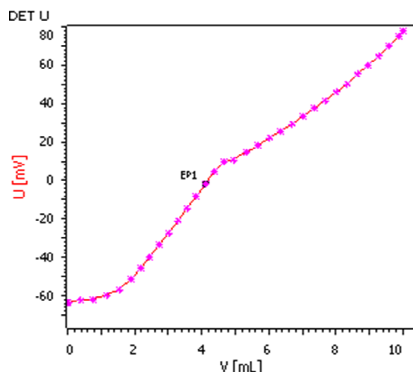
Peroxide values Bio-glycerol



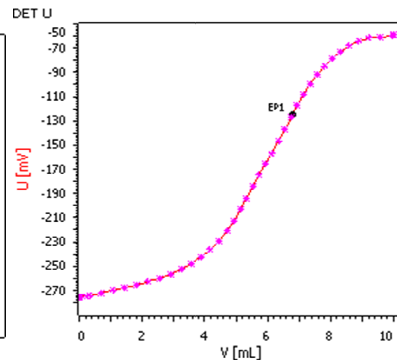
Peroxide values By-products



Iodine value of By-product



Saponification values Bio-glycerol



Saponification values By-product

Fig. 5. Properties of products and glycerol

Additional properties investigated including the saponification and the peroxide values showed variation in the properties of biodiesel glycerol and the HTL product at 300°C. Fig. 5 showed selected properties of the products. It was obvious that the liquefaction was responsible for the drop in iodine value resulting from complete hydrolysis of acidic components of the waste glycerol. In addition, saponification value is equally reduced.

4. CONCLUSIONS

The paper herein discussed the transition of different compounds and molecules with increasing HTL temperature. Varying the HTL temperature from 250°C to 350°C showed the variations in the chemical composition of the products at different stages. Results suggested the dominant compounds at lower temperatures are acidic and high molecular weight compounds. Increasing temperature showed the production of lower molecular weight compounds such as esters and ethers. Properties of the products tested showed some variations in TAN, while TRS showed marginal changes. It is suggested that crude biodiesel glycerol could be incorporated into HTL of other biomass.

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