

Production and Characterization of Biopolyols from Crude Glycerol Based Liquefaction Process

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ABSTRACT

The feasibility of using palm kernel cake and crude glycerol in liquefaction process to produce bio polyol was investigated in this study. The identified parameters for liquefaction conditions were reaction temperature, reaction time, biomass loading and acid loading. The optimal liquefaction conditions for bio polyol production were determined to be 10%(w/w) biomass loading, 1%(w/w) acid loading, and reaction temperature at 160°C for 90min. The optimal condition yielded 83 % biomass conversion with hydroxyl and acid numbers of 552 mg KOH/g and 0.56 mg KOH/g respectively. Result shows that palm kernel cake and crude glycerol can be used as an alternative raw material and liquefaction solvent to the production of bio polyol.

Keywords: Biomass, Biopolyols, Crude Glycerol, Liquefaction, Solvent.

1.0 INTRODUCTION

Bio polyols are polyol that contains two or more hydroxyl group in the molecule derived from biological material from living organism instead of petroleum-based material. The two major feedstock used are vegetable oils and lignocellulosic biomass [13]. Lignocellulosic biomass is considered as the most abundant renewable biomass feedstock in the world, it can be wood or agricultural residue disposed from agricultural industrial. The main structural that made up for lignocellulosic biomass are cellulose, hemicelluloses and lignin which are enriched with functionalized hydroxyl group that is favourable in converting to bio polyols [16]. Palm kernel cake is an abundant waste from oil palm industries. About 1.9 million tons of palm kernel cake is left over annually by oil extraction process from oil palm industry in 2003/2004 in Malaysia [17]. Therefore, the large quantities of palm kernel cake discarded made it inexpensive and suitable as the alternative source for bio polyol production. Bio polyols by liquefaction process are produced from a series of solvolysis and hydroxyalkylation reactions between liquefaction solvent and the functionalized group of the lignocellulosic biomass [14]. In the recent years, many studies of production of bio polyols with lignocellulosic biomass through liquefaction process are done which include: wheat straw [2], wood [9] and cornstalks [3]. The studies however uses high amount of petroleum-derived solvents, such as ethylene glycol and ethylene carbonate [6] as the liquefaction solvent. Substitute solvent that can be used to replace the petroleum-derived solvent is crude glycerol [13]. By replacing the petroleum-derived solvent, it can reduce the price hike for petroleum as well as the price for polyurethane and environmental pollution issue that was due to crude oil expedition and processing for the solvent. Crude glycerol is a by-product produced by biodiesel production process, it is estimated that 10kg of biodiesel can produce 1kg of crude glycerol as the by-product [4]. Crude glycerol is inexpensive, low value by-product due to the present of impurities such as free fatty acids, fatty acid methyl esters and soaps [5]. The crude glycerol

considers as a waste and it needs higher purification cost before selling, which it becomes a financial issue for biodiesel industry. Therefore, replacing the petroleum-derived solvent with crude glycerol in the liquefaction process of lignocellulosic biomass is able to reduce the production cost of bio polyol and polyurethane foams. Besides, crude glycerol as the solvent can contribute to the current issue on crude glycerol glut and disposal matter for biodiesel industry [6]. In this study, the feasibility of using palm kernel cake and crude glycerol for liquefaction process to produce bio polyol was investigated. Then, characterization study of the bio polyol synthesized from the liquefaction process was also carried out.

2.0 METHODOLOGY

2.1 Material

Palm kernel cake was obtained from Union Laboratories Sdn Bhd (Butterworth, Malaysia). Crude glycerol was obtained from Sime Darby Biodiesel Sdn. Bhd. (Malaysia) and contains approximately 80% glycerol, 0.35% oil, 9.6% methanol and 4.88% water. All chemicals used were in Analytical Reagent (AR) grade and were used without further purification.

2.2 Liquefaction Process

1000 ml three neck flask was used under atmospheric pressure with continuous constant stirring. Pre-weighed palm kernel cake (5-20% loading) was weighed. 58.75 gram of liquefaction solvents crude glycerol was measured and poured into the beaker containing palm kernel cake. 98% concentrated sulphuric acid (1-5% loading) was measured and poured into the beaker containing the palm kernel cake and crude glycerol. The mixture was mixed well in the beaker and poured into the flask. The flask then was placed in the heating mantle and connected with a glass Graham condenser. Heating mantle temperature was set to a desired temperature and conducted at a reaction time

(45–180 min). Once the reaction was completed, the flask was immediately removed and quenched in tap water in the sink to cool down [6].

2.3 Determination of Biomass Conversion

2 grams of bio polyol sample was weighed and 30 ml of ethanol was measured and added to the bio polyol. Then the mixture was centrifuged at 5000 rpm for 20 minutes to separate the solid residue by centrifugation. After the removal of supernatant, centrifugation separation was carried out again and it was similar as the method described above. After that, the solid residue was rinsed with 50 ml of de-ionized water in the centrifuge tube and shaken at 30°C for 10 minutes to remove sulphates formed in the liquefaction process when sulphuric acid is added. The dissolved mixture was then vacuum-filtered with a filtering crucible with filter paper. The residue obtained was then sent to a drying oven at 105°C for 24 hours [6]. Finally, the dried residue was weighed to determine the biomass conversion ratio.

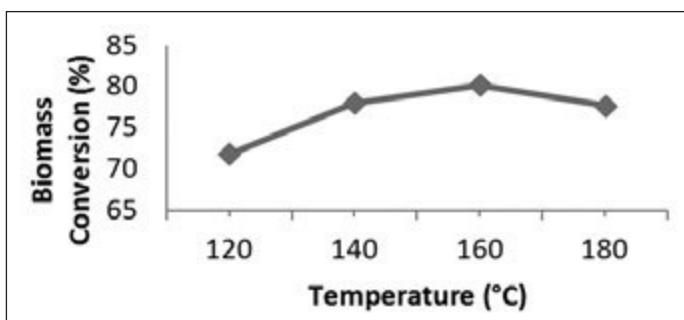
2.4 Determination of Hydroxyl and Acid Number of Bio Polyol

The hydroxyl number and acid number of bio polyol sample were determined by ASTM D4274-05D and ASTM D4662-08 respectively. For the hydroxyl number, 2 grams of bio polyol was weighed. 25 ml of the prepared esterification reagent was accurately pipette added into a 250 ml flask with the bio polyol. The flask was capped with aluminium foil and placed into a water bath which maintained at 98 ± 2 °C for 15 minutes. After that, the flask was cooled down to room temperature. The mixture was then sent for titration by using 0.5N NaOH solution. 0.5N NaOH was poured into burette and titrated slowly into the mixture until the pH reached neutral, which it was further determined by using a digital pH meter. For acid number, similarly, 2 grams of bio polyol was weighed. 50 ml of ethanol was measured and mixed with bio polyol in a 250 ml flask. Then titration method was carried out again but instead of 0.5N NaOH, 0.1N NaOH was used and poured into the burette. NaOH solution is titrated drop by drop into the mixture until the pH reached neutral and it was further determined by digital pH meter.

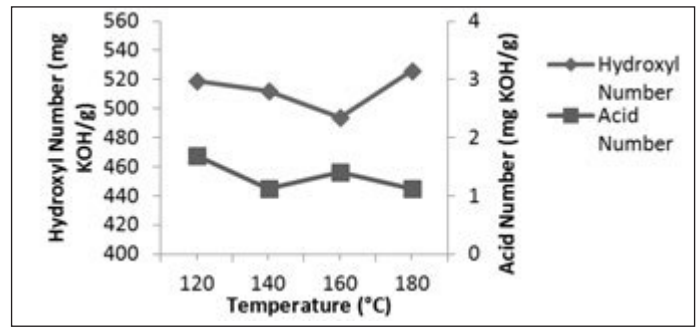
3.0 RESULT AND DISCUSSIONS

3.1 Effects of Reaction Temperature

As shown in Figure 1a, the biomass conversion increased from 71% to 80% as the reaction temperature increased from 120 to 160°C, this indicates the increased in reaction temperature will increase the acceleration of liquefaction reactions. However, the biomass conversion decreased from 80% to 77% as the reaction



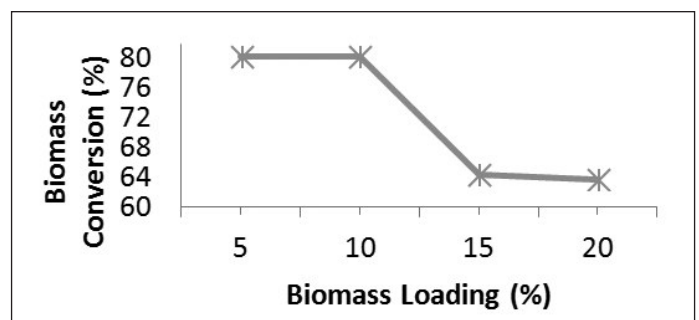
(a)



(b)

Figure 1: Effect of reaction temperature on biomass conversion (a), acid and hydroxyl number (b). (reaction time: 90min; sulphuric acid loading: 3%; biomass loading: 10%)

temperature further increased from 160 to 180°C. The decreased in biomass conversion is caused by the thermal decomposition of the palm kernel cake. From the differential thermogravimetric analysis results, above 200°C the decomposition of biomass occurred [7]. During the liquefaction reaction carried out at 180°C, it was observed that the temperature reading fluctuated between 170 - 220°C. The unstable temperature reading was mainly caused by the decomposition of biomass. Thus, the biomass conversion for 180°C decreased. In Fig. 1b, it shows the changes of hydroxyl and acid numbers of bio polyol. The hydroxyl number decreased from approximately 518 mg KOH/g to 493 mg KOH/g as the reaction temperature increased from 120 to 160°C and the hydroxyl number increased from 493 mg KOH/g to 525 mg KOH/g when temperature was further increased to 180°C. A series of reactions: condensation/dehydration of liquefaction solvents or thermal oxidative reaction can be occurred which decrease the substance containing hydroxyl group [11]. Thus, the hydroxyl number of bio polyol decreased as the reaction temperature increased. For acid number, it was less than 2mg KOH/g for all reaction temperature ranged from 120 to 180°C. It shows a slight decreased in value as the temperature increases. This could be due to the impurities present in the crude glycerol such as methanol, fatty acids, soap and glycerol. The impurities can react with each other by reaction such as: transesterification, esterification and etherification which consume the acidic compounds during the liquefaction reaction [6]. Thus, increasing hydroxyl number was noticed as the acid number decreased (Fig. 1b). Further increase of temperature from 160°C to 180°C showed the increase of hydroxyl number, decrease of acid number and the decrease of biomass conversion as well, this may cause by the recondensation reaction among the biomass derivatives and crude glycerol [13]. The reaction converted the substance back to its original formed and increased the percentage of insoluble residues which can be insoluble cellulose, lignin or lignin derivatives [15]. Thus, it increased the hydroxyl number and decreased the acid number.



(a)

3.2 Effects of Biomass Loading

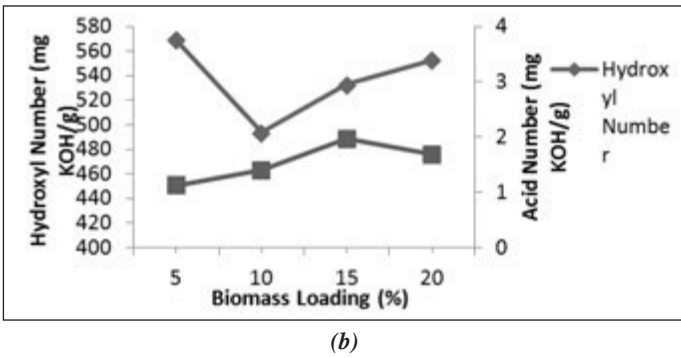


Figure 2: Effect of biomass loading on biomass conversion (a), acid and hydroxyl number (b). (reaction time: 90min; sulphuric acid loading: 3%; temperature: 160°C)

Fig. 2a shows the biomass conversion at 5% and 10% were similar and approximately 80%; however, further increases the biomass loading to 15% and 20% resulted in sharp decreases in the biomass conversion at approximately 64% and 63%. This indicates that the liquefaction efficiency decreased with the increased biomass loading and resulted in the decrease of biomass conversion. This could be the recondensation reaction occurred by the liquefied components as high concentration of raw material tends to recondense [1]. Furthermore, the amount of liquefaction solvent may not be sufficient to completely liquefy the high amount of palm kernel cake and caused low biomass conversion [8]. In Fig. 2b, it shows the hydroxyl number decreased from 569 mg KOH/g to 493 mg KOH/g as the biomass loading increases from 5% to 10%. Further increase the biomass loading to 20%, it shows an increase to 552 mg KOH/g. As explained above, condensation/dehydration of liquefaction solvents or thermal oxidative reaction can be occurred which decrease the substance containing hydroxyl group and the recondensation reaction tends to recondense back to its original formed which caused the increase in hydroxyl number. Besides, acid number increased from 1.1 mg KOH/g to 2 mg KOH/g as biomass loading increased from 5% to 15% but it decreased to 1.6 mg KOH/g as the biomass loading was further increased to 20%. The increase of acid number may due to the acid substance formation during the liquefaction process which increases the acid number in the bio polyol [10].

3.3 Effects of Sulphuric Acid Loading

In Fig. 3a, it shows the biomass conversion decreased slightly from 83% to 80% as sulphuric acid loading increased from 1% to 3% and a sharp decreased in biomass conversion from 80% to 56% and 51% respectively as sulphuric acid loading further increased to 4% and 5%. The increase in acid loading had resulted

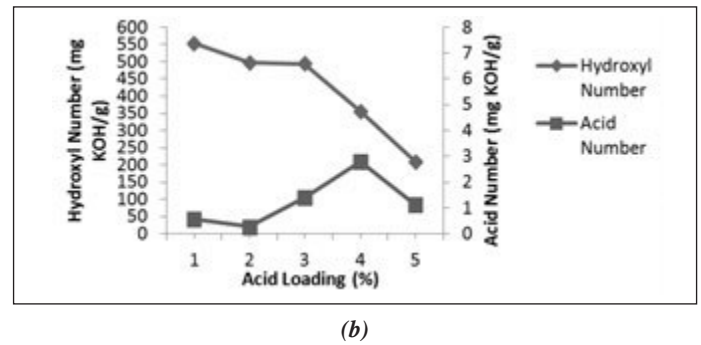
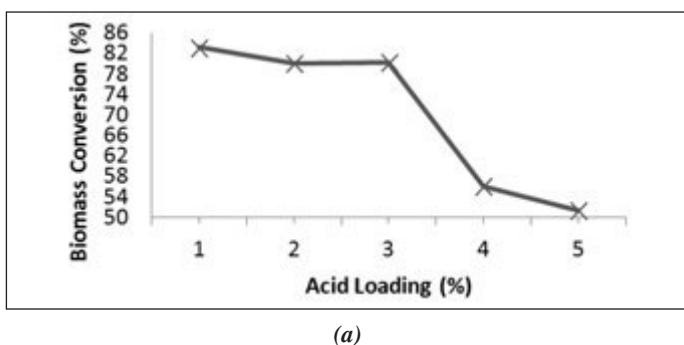


Figure 3: Effect of sulphuric acid loading on biomass conversion (a), acid and hydroxyl number (b). (reaction time: 90min; biomass loading: 10%; temperature: 160°C)

in the decrease of biomass conversion was due to the decrease of alkalinity of liquefaction solvent. Crude glycerols contain alkaline catalyst residue (KOH or NaOH) which are left from the biodiesel production. The alkaline catalyst residue will be neutralized by the sulphuric acid and this decreases the alkalinity of crude glycerol as the acid loading increases [6]. In Fig. 3b, the acid number of bio polyol increased approximately from 0.28 mg KOH/g to 2.8 mg KOH/g as the acid loading increased from 1% to 4%, and decreased to 1.1 mg KOH/g as it further increased to acid loading of 5%. Moreover, the hydroxyl number of bio polyol decreased from 552 mg KOH/g to 208 mg KOH/g as the acid loading increased from 1% to 5%. From acid loading of 1% to 4%, the acid number and hydroxyl number observed were in inverse condition, this is due to the consumption of hydroxyl group by acids [6]. High concentration of sulphuric acid can promote the recondensation reaction where it consumed the hydroxyl groups and decreased the hydroxyl number [12]. Thus, an increase in acid loading will decrease the hydroxyl number of bio polyol.

3.4 Effects of Reaction Time

Referring to Fig. 4a, the biomass conversion increased from

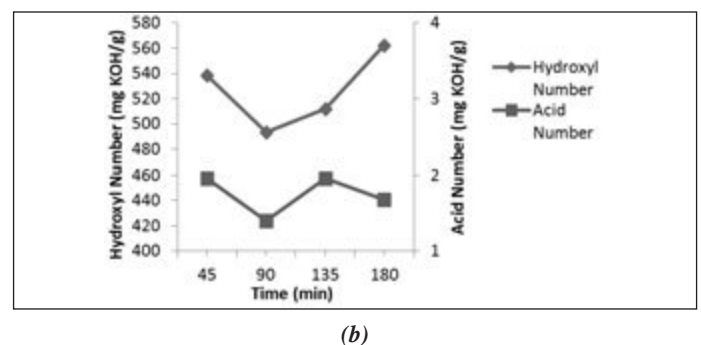
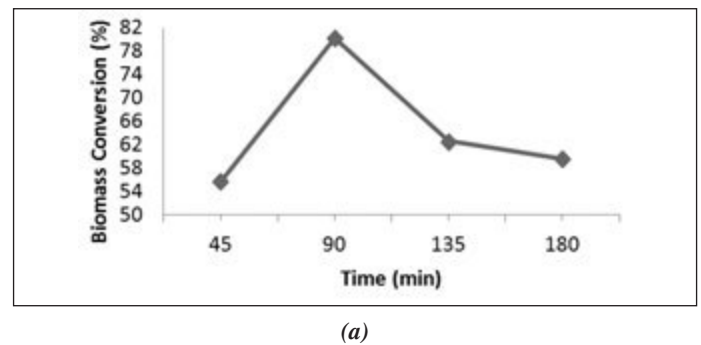


Figure 4: Effect of reaction time on biomass conversion (a), acid and hydroxyl number (b). (sulphuric acid loading: 3%; biomass loading: 10%; temperature: 160°C)

approximately 55% to 80% as the reaction time increased from 45min to 90min and it decreased to 62% and 59% as the reaction time was further increased to 135min to 180min respectively. As the reaction time increased after 90min, re-polymerization reactions of the liquefied components occurred and caused the rate of liquefaction process to decrease and produced high amount of biomass residue that was not converted to bio polyol [1]. In Fig. 4b, it shows the hydroxyl number decreased from 538 mg KOH/g to 493 mg KOH/g as the reaction time increased from 45min to 90min and it increased to 562 mg KOH/g when there was a further increase in reaction time to 180min. As for acid number, the trend at 45min to 135min is similar to hydroxyl number, acid number decreased from approximately 2 mg KOH/g to 1.4 mg KOH/g from 45min to 90min and increased back to 2 mg KOH/g from 90min to 135min. However, further increase the time to 180min decreases the acid number to 1.6 mg KOH/g. As mentioned above, condensation/dehydration of liquefaction solvents or thermal oxidative reaction occurred had decreased the substance containing hydroxyl group and decreased the hydroxyl number of bio polyol. Similar to other observation, the recondensation reaction among the biomass derivatives and crude glycerol tends to recondense the biomass into insoluble residue and caused the biomass conversion to decrease, increased the hydroxyl group and decreased the acid number as the derivatives recondensed in the bio polyol formed.

4.0 CONCLUSION

Palm kernel cake was successfully liquefied using crude glycerol as the liquefaction solvent and sulphuric acid as the catalyst. The liquefaction conditions were identified with the parameters: reaction temperature, reaction time, biomass loading and acid loading. The optimal biomass conversion achieved was 83% at the conditions: 160°C reaction temperature, 10% biomass loading, 1% acid loading and 90min of reaction time, and the hydroxyl number and acid numbers were about 552 mg KOH/g and 0.56 mg KOH/g respectively. Bio polyol synthesized through liquefaction can be done by using palm kernel cake and crude glycerol from biodiesel production which can be an alternative source instead of purified glycerol to reduce the cost and increase the productivity. Furthermore, the hydroxyl number obtained which below 600 mg KOH/g if favorable for the synthesis of PU foam. Hence, it is proven that crude glycerol can be applied as liquefaction solvent to produce bio polyol. ■

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PROFILES



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