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Liquefaction of Oil Palm Biomass Using Polyhydric Alcohol as a Solvent

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Abstract: *Lignocellulosic biomass is mainly composed of cellulose, hemicellulose and lignin, which typically contains two or more hydroxyl groups per molecule. The liquefaction process is a convenient and effective technology for converting lignocellulose into liquid products and polyhydric alcohols with appropriate molecular weight are usually used as liquefaction solvent. In this study, palm mesocarp pressed fiber was subjected to a liquefaction process with polyhydric alcohol (polyethylene glycol and glycerol). The effects of various liquefaction conditions, such as liquefaction temperature, liquid ratio (liquefaction solvents/fiber) and catalyst content on the residue content were investigated. Solubilization of fiber was higher using crude glycerol as liquefaction solvent without adding any catalyst which obtained 49.34 % of residue content. Low residue content showed that degradation of hemicelluloses and reduction of lignin had occurred. Acidic catalyst added to pure glycerol exhibited greater influence than liquid ratio and liquefaction temperature which the lowest residue content of 22.38% was obtained compared to other parameters. Analyses of residue content by Fourier transform-infrared (FTIR) and thermogravimetric analysis (TGA) was complemented to each other which found the residue content consisted of un-dissolved cellulose, some lignin and their derivatives.*

Keywords: *liquefaction, polyhydric alcohol, crude glycerol, mesocarp*

I. Introduction

At present, most of the world's production of palm oil comes from South-East Asia. Malaysia is the second largest contributor and exporter in the palm oil industry. The oil palm industry generates large volume of lignocellulosic biomass from the oil extraction process. Solid biomass such as oil palm mesocarp pressed fiber an attractive feedstock because it is an abundant, renewable source, rich with various carbohydrate sugars and other useful chemical compounds that can be converted into a range of value-added products [1,2] . Currently, they are used as boiler fuel and research should be carried out to find other uses for any excess palm-pressed fiber [2].

Generally, lignocellulosic biomass consists of three main groups of polymers that are cellulose, hemicellulose and lignin. These compounds are also major components in oil palm biomass. Celluloses and hemicelluloses are polysaccharides of the desired carbohydrate sugar. Numbers of research and development activities were previously done in order to exploit biomass content potential and transform it into higher valued compounds [3,4,5]. This biomass resource can be converted to higher value products several methods such as gasification, pyrolysis and liquefaction. Alkaline pre-treatment has been identified as one of the best chemical pre-treatment methods for delignification of lignocellulosic biomass. This method is efficient if agricultural waste being used rather than the wood materials. Due to alkaline nature of crude glycerol, it is predicted that it can be used as a cooking solvent in lignocellulosic pre-treatment or liquefaction process [5].

Liquefaction using low boiling point solvent such as ethanol shows high volatility and flammability which not suitable to be use in high pressure operation and temperature. As a non-flammable compound polyhydric alcohol in particular glycerol is attractive for organosolv pretreatment, in fact, glycerol has been used as co-solvent for biomass liquefaction in previous work [5,6]. There are several advantages when crude glycerol is used as a cooking solvent. (1). Low solvent cost as crude glycerol is a byproduct of biodiesel and oleochemical industry. (2). The pretreatment can be performed under atmospheric pressure. (3) Glycerol can easily penetrate the fiber tissue due to its polar structure and (4). The drawback of its energy-recovery can be solved by converting it into polymers /resin. Therefore, this research aimed to investigate the feasibility of using crude glycerol as pretreatment solvent to enhance enzymatic hydrolysis of oil palm biomass. ~~The p~~

Up to now, utilizations of polyhydric alcohol as a liquefaction solvent have been investigated only for a few wood species and agricultural residues. On the other hand, a huge amount of palm mesocarp pressed fiber produced from the extraction of oil still remain unused and could be employed as a raw material in this study. Based on the above considerations, the objective of this research was to liquefy palm mesocarp pressed fiber using polyhydric alcohol, (PEG with different molecular weights and glycerol with different purities) as the liquefying solvent and evaluate the characteristic of insoluble residue using FTIR and TGA. Besides, the effect of liquefaction conditions such as liquefaction temperature, liquid ratio (liquefaction solvent/fiber) and catalyst content on the percentage of residue were also investigated.

II. Research Methodology

Materials

Crude glycerol was obtained from a biodiesel plant in Malaysia and the main composition of crude glycerol was as follows (% wt): glycerol 79.30 %, water 6.69 %, soap 16.20 %, methanol 7.30 % and oil 0.97 %. Polyethylene glycol (PEG) (400, 300, 200) and 98 % sulfuric acid (H_2SO_4) were purchased from R&M Chemical. Glycerol and 99.9% sodium hydroxide (NaOH) pellet were obtained from Systerm ChemAR. Potassium hydoxide (KOH) was purchased from HmbG Chemical. All the reagents used were of technical grades. Palm mesocarp pressed fiber was obtained from Palm Oil Mill Technology Center (POMTEC), Labu, Malaysia. Palm mesocarp pressed fiber was washed with hot water, and then dried in an oven at 105 °C overnight before being used for liquefaction process. The fiber was then ground to average size of 250-600 micrometer and stored in a sealed plastic bag at room temperature (RT).

Determination of viscosity

The viscosity of PEG (200, 300 and 400) and glycerol were determined using a viscometer (Anton Paar GmbH, Germany) equipped with a small sample adapter, temperature probe and temperature control unit. Viscosity was determined at the following conditions, temperature: 20 °C, rotational speeds: 60 rpm and spindle size: TL7.

Liquefaction process

In this work, the effect of the various solvents used (PEG 200, PEG 300, PEG 400, pure glycerol, treated glycerol and crude glycerol) were studied. Liquefaction temperatures used were at 100, 120, 150 and 180 °C with constant reaction time (60 min). Solid to liquid weight ratio were studied at 1:3, 1:4, 1:5 and 1:6 with 5.0g of dry fiber in 15g, 20g, 25g and 30g of solvent, respectively. The catalyst loading (NaOH/KOH/H_2SO_4) applied in the liquefaction process were weight percentages based on the net weight of solvent used.

The liquefaction process studied was according to Hu et al. [7]. The liquefaction process was carried out in a 250 mL three neck flask, equipped with stirrer, condenser and thermometer with constant stirring. The mixture of fiber with liquefaction solvents and catalyst was placed into the flask and then heated to the desired reaction temperature using a temperature-controlled heating mantle. Subsequently, the temperature was held constant to conduct the reaction for a predetermined reaction time (60 min), after which, the flask was immediately removed from the heating mantle. The volatiles evaporated during the liquefaction process were recovered by a glass Graham condenser connected to the flask. The product mixture was then filtered with ethanol and rinsed with distilled water. The diluted resultant was filtered using Whatman No. 4 filter paper to separate the insoluble residue and liquid fraction. The insoluble residue fraction was then dried in an oven at 105 °C overnight. The insoluble residue content lignocellulosic material was calculated according to Hassan et al. [5] by equation 1:

$$\text{RC, \%} = (W_r / W_o) \times 100 \qquad \text{(equation 1)}$$

Where RC is the residue content; Wr is the oven–dried weight of the residue after filtration and Wo is the weight of the initial fiber.

Determination of holocellulose

Fiber (4.0 g) was mixed with 154.0 mL of distilled water, 6.0 mL of sodium chlorite ($NaClO_2$) with 25% concentration (v/ v) and 0.5 mL of acetic acid (CH_3COOH). The mixture was then heated on a heating plate at a temperature of 70–80 °C and stirred with a magnetic bar. After 60 minutes, in the same quantity as distilled water, acetic acid and sodium chlorite were added. This process is repeated every 60 minutes for 4 hours. Next, the sample was cooled by immersion in ice at 0 °C and filtered. The samples were rinsed with distilled water until reaching neutral pH. Lastly, the filtrate was rinse using acetone. Then the sample was dried in an oven at 105 °C overnight. Holocellulose is determined as in equation 2.

Holocellulose (%) = final mass (g)/initial mass (g) x 100% (equation 2)

Determination of lignin

Fiber (0.5 g) was mix with 10 mL of 72 % (v/v) sulfuric acid. The mixture was stirred evenly for 2 hours. The temperature should be maintained consistently at 20 ° C by adding ice around the beaker. Then, the mixture was transferred into a flask continued by adding 300 mL of distilled water to dilute sulfuric acid to 4 %. The solution was boiled for 4 hours and the result was then filtered. The residue left over from the filtration result is counted as insoluble lignin. Percentage of lignin is determined as in equation 3.

Lignin (%) = final mass (g) /initial mass (g) x 100% (equation 3)

Analyses of the insoluble residues

Fourier-Transform Infrared (FTIR)

Insoluble residues were ground into fine form before the analysis was conducted. Infrared spectra of the insoluble residue were investigated by using Fourier Transform Infrared Spectroscopy Perkin Elmer model Frontier. The spectrum was recorded from 4000 cm^{-1} to 700 cm^{-1}. The aim of the analysis was to identify the functional groups of the raw material and then compare any structural changes after the liquefaction process.

Thermogravimetric analysis (TGA)

Insoluble residues were ground into fine form before analysis was conducted. The thermal behavior of insoluble residue was studied by using a thermogravimetric analyzer, model Perkin Elmer Pyris 6. Scans were recorded from 30 °C to 850 °C at a heating rate of 20 °C/min under a nitrogen gas.

III. Results And Discussions

Effect of solvent on the residue content

In the liquefaction process, most studies have focused on the effect of solvent used in order to break up the chemical backbone at the lignocellulosic related fragment. Therefore, in this study we examined the effect of solvent on the percentage of the remaining residue (not dissolved) after the liquefaction process. PEG and glycerol were chosen as a liquefaction solvent for solubilization of palm mesocarp pressed fiber. ~~In this study,~~ The solubilization of mesocarp pressed fiber displayed different trends depending on the molecular weight and purity of the solvent used (Figure 1). The lowest residue content indicated the highest solubilization.

Overall, all PEG with different molecular weights (200, 300 and 400) used gave better solubilization compared with using pure and treated glycerol. Besides, solubilization of fiber was more effective in the lower molecular weight of PEG (PEG 200) which obtained 64.42 % of residue content followed by PEG 300 (67.37%) and PEG 400 (70.05%). As PEG molecular weight increased, the viscosity steadily rose from 60 to 120 mPa.s. As shown in Figure 1, the viscosity of PEG increase from PEG 200 to PEG 400 followed by pure glycerol (viscosity of treated and crude glycerol are not shown due to extremely high viscosities at room temperature). Pure glycerol alone is not preferred because its high viscosity led to more difficulty to disperse the fiber. Jin et al. [12] investigated the effect of different molecular weights of PEG (400, 600 and 1000) as the main liquefaction solvent to liquefy enzymatic hydrolysis lignin. They found that liquefaction efficiency was highest at the smallest molecular weight of PEG.

However, the use of crude glycerol with high viscosity gave the lowest residue content at 49.32 % compared to pure glycerol at 70.05 %, treated glycerol at 70.71 % and also all PEG used in this study. Higher solubilization using crude glycerol in this study was due to the presence of impurities (water 6.69 %, soap 16.20 % and methanol 7.30 %) which could act as base-catalytic to improve the liquefaction process. Although crude glycerol had a very high viscosity, but as a non-flammable, non-volatile compound with high boiling point, crude glycerol is still suitable for the liquefaction process due to the compositional difference of this solvent from other solvents mentioned above.

In their latest study, Todaka et al. [8] proposed that alkalinity from soap played a vital role in glycerol penetration into the sample. Another study by Hu et al. [7], solubilization of fiber require both alkalinity and surfactant activity for a successful liquefaction process. Sodium soap in crude glycerol reacts as surfactant and provides base condition to disperse the decomposition of lignin and hemicellulose in glycerol. Additionally, the amount of soap concentration in the glycerol also attribute to the increment of the solubilization process. Thus, a comparison was made with a previous study by Sun & Chen [9]. Sun & Chen [9] reported that the crude glycerol used in their study which was composed of less than 5% soap could not effectively remove lignin from lignocellulosic biomass of wheat straw, thus low solubilization of fiber was obtained. As mentioned by Todaka et al. [8], solubilization of fiber sample required 10 to 20% of soap in glycerol to be suitable and resulted in the minimum residual content. This is due to the high concentration of salt which decreases the intermolecular bonding in fiber hence allowing the hydrogen bond to bind more with glycerol [7]. Thus, in this study, a soap or salt concentration of 16.20 % in crude glycerol was suitable to be used as solvent for the liquefaction process.

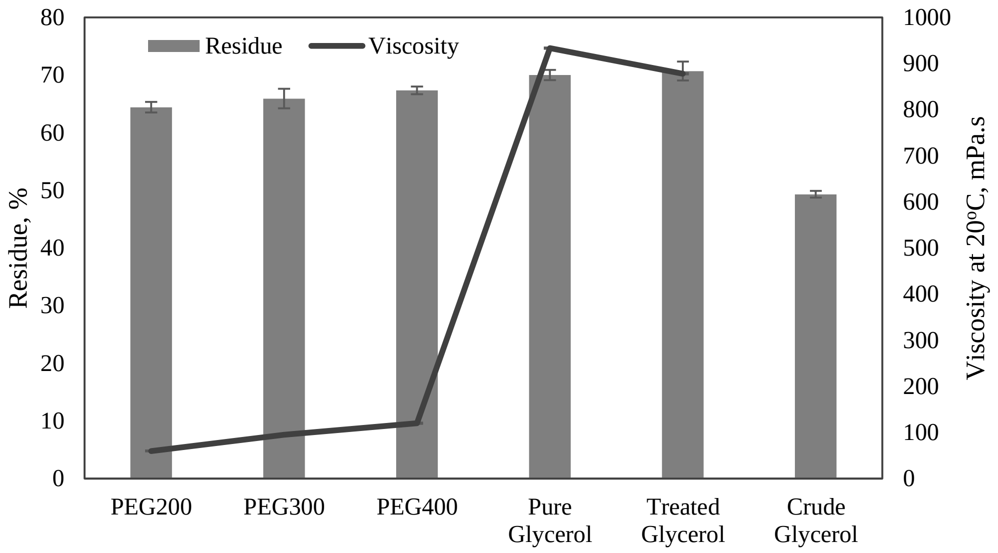

Figure 1. Effect of molecular weight of PEG and purity of glycerol on the residue content. Liquefaction condition: time, 1 h; temperature, 150 °C.

Effect of catalyst on the residue content

Another possibility to improve the liquefaction process might be the application of a catalyst. Figure 2 shows the effect of 2% (w/w) addition of the catalyst (NaOH, KOH and H_2SO_4) by weight of pure glycerol on the residue content. The liquefaction experiment was carried out at a constant temperature of 150 °C for 60 min (Figure 2). Overall, the result shows that the use of catalyst can substantially increase the extent of liquefaction compared to that without a catalyst.

In the literature, H_2SO_4 is a well-known catalyst for biomass liquefaction process [7, 11, 12]. Wang et al. [14] compared the effect of acid catalyst (hydrochloric, phosphoric and sulfuric acids) on wheat straw liquefaction and found that H_2SO_4 exhibited the best catalytic ability which resulted in minimum residue content. Hence, in this study H_2SO_4 was selected to represent the acids group. In our finding, H_2SO_4 showed the lowest residue content at 22.38% compared to alkali catalyst, NaOH (53.93%) and KOH (61.17%). Similarly, to Hu et al. [15], the slow liquefaction rate was observed in the alkaline-catalyzed process compared to the acid-catalyzed. This could be explained by the recalcitrant of the crystalline cellulose and ability of acid to penetrate into the fiber as well as diffusion of decomposed components of fiber into the liquefaction solvents [14]. Thus, H_2SO_4 has proven to be the most effective catalyst in reducing residue content compared to alkaline catalyst. However, when comparing alkaline catalysts, NaOH is more effective than KOH.

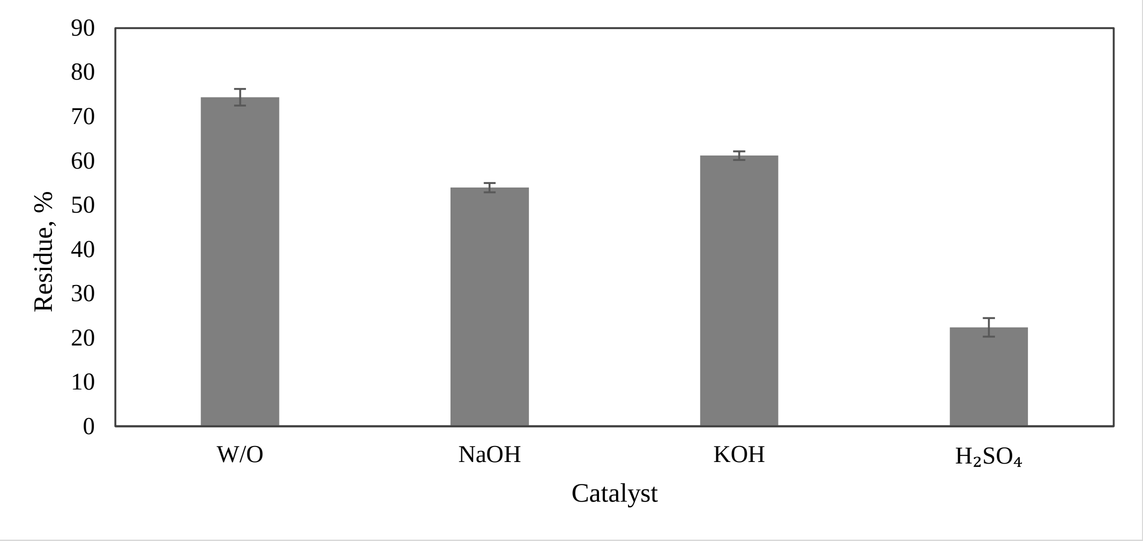

Figure 2. Effect of catalyst on the residue content. Liquefaction conditions: time, 1 h; temperature, 150°C, fiber:solvent ratio, 1:5 and catalyst concentration, 2% (w/w) in pure glycerol. W/O: without catalyst concentration.

Effect of solvent ratio on the residue content

To investigate the influence of the liquefaction solvent ratio on the amount of residue remaining, a set of experiments was conducted at different weight ratios (w/w) of fiber to solvents at 1:3, 1:4, 1:5 and 1:6. Figure 3 shows the residue content decreased as the amount of liquefying solvent increased for crude glycerol. This may be ascribed to excess liquefying solvent which allows proper stirring of the reaction, and thus more penetration into lignocellulosic material components which resulted in the fragmentation of macromolecule chains [15]. Besides, the formation of hydrogen bonding between lignocelluloses with solvent cause an increment of solubilization in the liquid part, thus reducing the residue content. However, solvent ratios which are too high are not recommended as the work up procedure for treated fiber might be complicated.

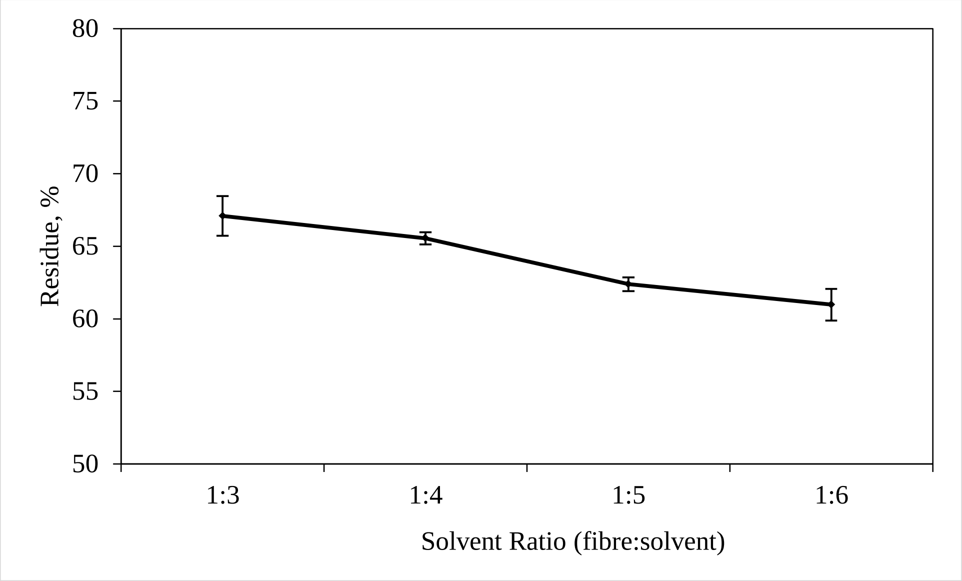

Figure 3. Effect of solvent ratio on the residue content. Liquefaction conditions: time, 1 h; temperature, 150 °C using crude glycerol

Effect of temperature on the residue content

Liquefaction of mesocarp pressed fiber using crude glycerol at four different reaction temperatures are shown in Figure 4. Results show the residue content decreased as the temperature in the reaction increased. It was indicated that increasing temperature could accelerate the liquefaction reaction. These results could be attributed to the susceptible component such as lignin and hemicellulose [16].

According to Demirbas [16], ether and glycosidic linkages of the fiber could break down easily and degradation occurred at higher temperature. However, at liquefaction temperatures above 150 °C, the solid content remained almost unchanged and slightly decreased at 180 °C. A similar trend was also observed by Zhang et al. [18]. They found that, the percentage residue was very high at the lowest temperature of 130 °C, but decreased as temperature increased to 150 °C. However, further increase in temperature to 170 °C did not decrease the residue content significantly. Hassan et al. [19] also reported that liquefaction temperatures >150 °C are not necessary due to the slight decrease in the amount of residue.

Todaka et al. [8] studied different types of biomasses and found that the temperature requirement of the treatment depends on the type of biomass used. Delignification for hardwoods and gramineous plant occurred above 170 ˚C and 150 ˚C, respectively, whereas for softwoods delignification occurred above 200 ˚C. In this study, the mesocarp fiber can be categorized into the gramineous group based on the results obtained. Besides lignin removal, the treatment also preserved the cellulose. The increase in temperature in this study does not show thermal decomposition of cellulose despite the increase of lignin removal. In this study, only hemicellulose decomposition was recorded and removed during treatment. Table 1 shows the changes in the holocellulose and lignin compositions of samples after treatment by crude glycerol at various temperature. The lignin contents of treated samples decreased from 31.30% in the raw sample to 17.32% in the sample treated at 180^{o}C, whereas holocellulose content increased from 65.45% in the raw sample to 77.32% in the sample treated at 180^{o}C.

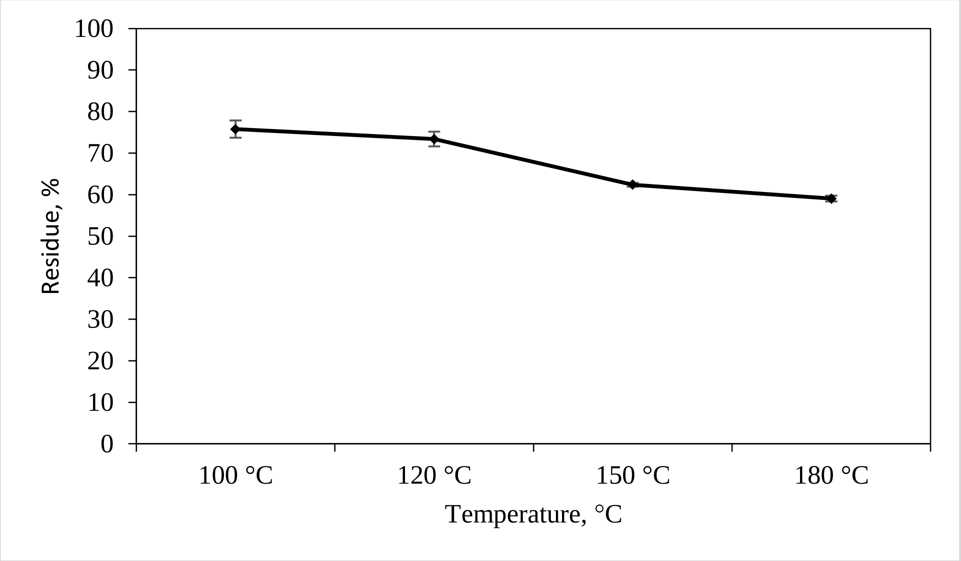

Figure 4. Effect of temperature on the residue content. Liquefaction conditions: time, 1 h; ratio solid: liquid, 1:5 using crude glycerol

Table 1. Chemical composition of treated fiber at different temperature

Temperature, °C	[a]Holocellulose, %	[a]Lignin, %
Untreated	65.45 ± 0.00	31.30 ± 0.40
100	69.22 ± 0.73	27.80 ± 1.69
120	74.48 ± 0.78	24.07 ± 1.56
150	75.69 ± 1.78	19.83 ± 1.22
180	77.32 ± 0.55	17.32 ± 0.48

[a] liquefaction conditions: time, 1 h; solid/liquid, 1:5 in crude glycerol

Fourier-Transform Infrared (FTIR)

The raw fiber and liquefied residue were characterized using FTIR spectroscopy. The purpose of this analysis was to determine the functional groups of the liquefied residue. To show the existence of hemicellulose and lignin removal in palm fiber, spectrum for raw fiber and liquefied residue were compared. The IR spectra obtained for the raw material differed from that liquefied residue, while the spectra of the liquefied residue using PEG, pure glycerol and crude glycerol were quite similar. Figure 5 shows FTIR spectra of the raw fiber and the liquefied residue after liquefaction process using pure glycerol and PEG. The liquefaction conditions used were a temperature of 150 °C in 60 min of reaction time. From the results, the most significant changes were observed at wave numbers of 1737 cm^{-1}, 1607-1594 cm^{-1}, 1509 cm^{-1} and 1234 cm^{-1}.

The broad band at about 3600-3000 cm^{-1} is the characteristic stretching of vibration of hydroxyl groups, which indicates the presence of OH groups. The peak at 2800-2800 cm^{-1} is the characteristic for C-H stretching of aliphatic CH_3, CH_2 and CH groups [11]. Absorption at 1737 cm^{-1} in the raw fiber is assigned to the characteristic carbonyl groups (C=O) in hemicellulose and/or lignin [21]. This band disappeared after the liquefaction process which could be due to the removal of hemicellulose. The peaks at 1607 cm^{-1} and 1509 cm^{-1} are indicative of the aromatic vibrations in bound lignin [22], which indicated that lignin was not completely removed. The transmittance peak at 1234 cm^{-1} also disappeared after liquefaction process. This wave length is associated with an acetyl group to the hemicellulose or likely to represent a network of groups carboxylic groups of ferulic and *p*-comeric acids in lignin [23]. These results suggested the removal of a large portion of hemicellulose. According to Wang et al. [22], hemicellulose easily broken down as it is in amorphous form and thermally less stable than cellulose and lignin. Besides that, a high temperature used during the liquefaction process causes more components of lignocellulose decomposition. Therefore, less vibration excitation produced by a particular functional group resulting in a decrease in the intensity of the absorption wavelength.

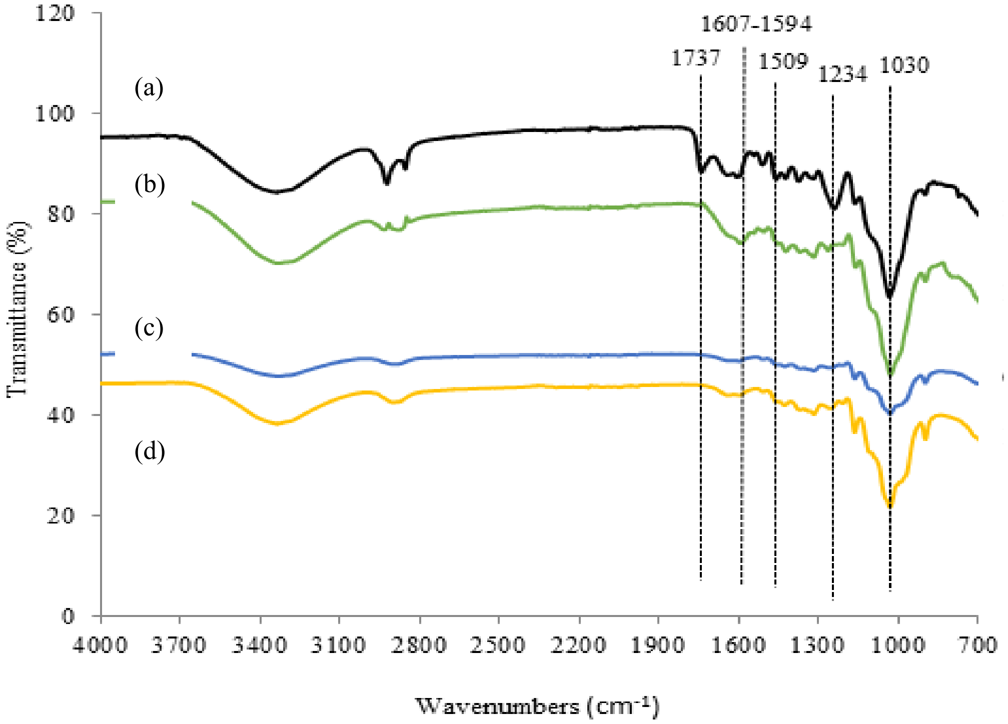

Figure 5. FTIR spectra of (a) raw fiber and liquefied residue treated by (b) pure glycerol, (c) crude glycerol and (d) PEG as liquefaction solvent. Liquefaction condition: time, 1h; temperature, 150 °C

Thermogravimetric Analysis (TGA)

Thermograms derivative curves (rate of weight loss) of the raw fiber and the liquefied residue are shown in Figure 6. Generally, they have three main curves indicating three main components in lignocellulose. The first peak in the temperature ranges from 250-300 °C is attributed to the degradation of hemicellulose. The second peak at 300-350 °C corresponds to α-cellulose and the next peak at 300-600 °C corresponds to lignin [24].

From Figure 6, the initial peak loss between 30 to 100 °C was due to the moisture content present in the sample. It was observed that the raw fiber contained the highest amount of moisture content compared to the liquefied residue. The peak at around 294 °C which represents hemicellulose disappeared in the liquefied residue. In other words, the unstable hemicellulose ingredient was removed during liquefaction. According to Md. Yunos et al. [23], hemicellulose was the easier compound to be removed and was easily volatile at lower temperature due to their branches and consists of various saccharides that appear in a random organization. Complimentary to FTIR results, proved that the pretreatment process successfully removed of hemicellulose.

After the liquefaction process, peaks representing cellulose and lignin still existed at 330°C and 599°C, respectively. The presence of the lignin peak confirms that lignin has not been fully removed from the sample. Meanwhile, cellulose is more thermally stable than hemicellulose and more heat energy is needed to break down its crystalline structure and to cleave its macromolecules because of the hydrogen bonds that provide much of the binding energy for α-cellulose [25].

Lignin decomposes at a slower rate and covers a wide range of temperature. The broader degradation temperature range of lignin can be explained by the presence of various oxygen containing functional groups in its structure. These complex structures of lignin show various thermal degradation behaviours, since the scissions occur at different temperatures [2].

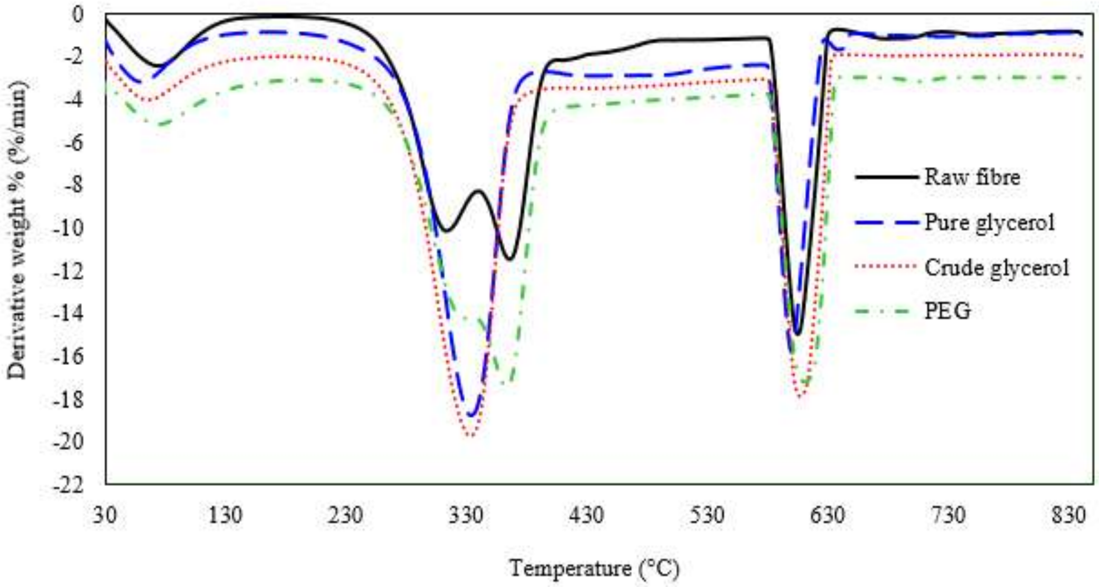

Figure 6. DTG analyses for raw fiber and liquefied fiber treated with pure glycerol, crude glycerol and PEG

IV. Conclusions

In this study, degradation of hemicellulose and lignin in mesocarp was affected by the viscosity of solvent to penetrate and break the bonding in lignocellulose materials to achieve low residue content. However, crude glycerol with high viscosity can be used as a liquefaction solvent due to the presence of various impurities, especially soap which could act as based catalyst. Besides, the effects of various liquefaction conditions found that the addition of the acidic catalyst into pure glycerol has a greater influence than the liquid ratio and temperature of liquefaction. FTIR analysis revealed successful elimination of hemicellulose and reduction of the lignin component which was complemented by TGA analysis. Results obtained from this study support the potential of producing value-added product (polyol) from crude glycerol and palm biomass. However, to ensure the success of this conversion, the contents of organic impurities in crude glycerol need to controlled at optimal levels. Both crude glycerol and palm biomass are low-cost renewable materials, their uses in producing value-added product and solvent may provide the benefit of cost-effectiveness and reduced carbon footprint

V. Acknowledgement

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