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Effect of reaction conditions on the catalytic esterification of bio-oil

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Abstract– Studies of bio-oil upgrading via esterification of palm shell bio-oil and alcohols employing acid catalysts were carried out in this work. The effects of esterification conditions on reaction conversion and product quality were investigated. Results indicated that esterification reaction using solid acid catalyst of Amberlyst15 enabled the conversion of organic acids in the bio-oil to esters and could also reduce certain amount of active aldehydes. The utilization of H_2SO_4 liquid catalyst was found to give higher conversion at the same reaction condition. Furthermore, higher reaction conversion to esters was achievable under conditions of higher temperature, longer reaction time, higher amounts of catalyst and alcohol and the use of shorter hydrocarbon chain of alcohol. Bio-oils, after being subjected to esterification, gave moderate heating value of 23-25 MJ/kg and improved fuel properties of decreased density, viscosity, carbon residue content, ash content, pour point and acidity.

Key words: Pyrolysis, Bio-oil, Upgrading, Esterification, Acid Catalysts

INTRODUCTION

Bio-oil from biomass pyrolysis possesses certain disadvantages of corrosiveness, low heating value, high viscosity and ageing characteristic, thus making crude bio-oil unsuitable for its direct use as an alternative fuel [1]. These problems arise from the presence of a large number of chemicals (from short chain organic compounds to long chain oligomeric species). In particular, the oxygenated compounds in bio-oil such as phenols, sugars, acetaldehyde, esters, ethers and carboxylic acids can undergo various chemical reactions, leading to the deterioration of bio-oil properties during storage. Various processes such as hot-vapor filtration, catalytic hydrotreating and catalytic cracking have been applied to chemically improve the bio-oil properties [2]. However, catalytic upgrading processes give low yield of the upgraded oils and could produce undesirable products of coke deposit on the catalyst surface, giving high costs of product recovery [3]. In addition, the bio-oil treated via hot-vapor filtration process at an elevated temperature (~400-420 °C) could accelerate polymerization reactions, thereby increasing the rates of particle growth and agglomeration [4]. As a result of these limitations, a more simple alternative approach based on the esterification of organic acids in bio-oil with an alcohol was adopted in this work to explore its effectiveness in improving certain bio-oil fuel properties.

Esterification reaction is an upgrading method that can convert carboxylic acids in bio-oil to esters ($R\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH + R'\text{-}OH \rightleftharpoons R\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}R' + H_2O$). It is not only able to reduce corrosiveness of the bio-oil but can also prohibit some reactions catalyzed by these acids, for example, the reactions of oligomers or polymer formation (homopolymerization of aldehydes, phenol/aldehyde polymerizations, etc.) [4]. This treatment could be an attractive method for improving bio-oil properties due to its ease of operation, low investment cost and avoiding secondary reactions that may occur at high operating temperatures. Although limited studies on bio-oil upgrading by esterification reaction have been reported thus far, this upgrading technique is still the topic of recent interest. Doshi et al. [5] upgraded the bio-oil derived from fast pyrolysis of sewage sludge via esterification using H_2SO_4 as a liquid acid catalyst. It was found that odor of the treated oil was improved from an extremely annoying level to a not annoying level (ASTM D1833-87) with about four times reduction in viscosity and up to 9% increasing in heating value. However, using solid catalyst in place of H_2SO_4 to reduce corrosion problem was also proposed. It is noted that increasing amount of alcohol for the esterification reaction can reduce heating value of the upgraded oil and therefore alcohol separation by fractional distillation would be needed in this process. Later, several researchers improved the process by using various types of solid acid catalyst and/or recovery of the alcohol by distillation [6-8]. Junming et al. [6] reported that density and acidity were reduced (1.16 to about 0.93 g/cm^3 for density and pH from 2.82 to 6.21) and the gross calorific value increased from 14.3 to 23 MJ/kg using ethanol as a reactant and SO_4^{2-}/ZrO_2 as a catalyst at the reaction temperature of 55-77 °C. Mahfud et al. [7] treated the bio-oil with a higher boiling point alcohol of n-butanol in the presence of a solid acid catalyst of Nafion SAC13 at 50-80 °C under reduced pressure of less than 10 kPa. The results indicated that the upgraded oil properties were improved, particularly the heating value and viscosity but the acidity was still close to that of the raw bio-oil. In studying the effect of catalyst type, Zhang et al. [8] used solid acid catalyst $40SiO_2/TiO_2\text{-}SO_4^{2-}$ and solid base catalyst $30K_2CO_3/Al_2O_3$-NaOH to compare their effectiveness. It was found that acidity of the bio-oil was lowered by the use of both catalysts but the solid acid catalyst was capable of converting volatile and nonvolatile organic acids into more esters. However, the strong acidification of solid acid catalyst tended to intensify the acidity of bio-oil.

In conclusion, it is logical to infer that the esterification process

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has improved certain properties of bio-oil. It should be noted that there are a number of important parameters such as catalyst type and esterification conditions that can affect the effectiveness of bio-oil upgrading. Moreover, the complex compositions of bio-oil itself could be responsible for the occurrence of side reactions that may influence the properties of the upgraded oil. Thus, a detailed study of bio-oil upgrading by esterification for a selected bio-oil was carried out in this work.

EXPERIMENTAL

1. Materials

The oil sample used for esterification study in this work was the oil phase separated from the aqueous phase by centrifuging (3,000 rpm for 20 min) the raw bio-oil derived from the batch pyrolysis of palm shell in a fixed-bed reactor under the following pyrolysis conditions: average palm shell size of 2.03 mm, pyrolysis temperature of 700 °C, heating rate of 20 °C/min and nitrogen flow of 200 cm^3/min [9]. The yield of oil phase after being separated from the raw oil was found to be 57% by weight. Two types of alcohol including methanol (99.9%) and ethanol (99.8%) were employed for the esterification study and were purchased from Carlo Erba Reagents Group. There are two types of catalysts used including solid acid catalyst of Amberlyst15 and liquid catalyst of 96% sulfuric acid (H_2SO_4). They were acquired from Acros Organics Group and Carlo Erba Reagents Group, respectively. The Amberlyst15 catalyst is the dry type of sulfonic acid cation-exchange resin (H^+ ~4.7 meq/g), which is a macroreticular polymeric resin of crosslinked styrene divinybenzene copolymers.

2. Esterification Reaction

Fourteen test conditions as detailed in Table 1 were used to investigate the effect of process variables on the esterification of bio-oil from palm shell. The bio-oil sample and alcohol were mixed according to the required mole ratio of alcohol and carboxylic acid in the bio-oil, and the catalyst was added on a weight percent of bio-oil. It was found from a preliminary experimentation that 1 g of bio-oil

Table 1. Experimental conditions for studying esterification of bio-oil and alcohols and results of reaction conversion

Run No.	Parameters studied	Base conditions	Parameter values	Percent conversion	pH
1	Reaction temperature (°C)	- 3.25 : 1 mole ratio of methanol to carboxylic acids in bio-oil - Reaction time of 24 hr - 5 wt% Amberlyst15 catalyst	25	34.96	3.15
2			50	58.71	3.22
3			60	73.39	3.31
4	Reaction time (hr)	- 3.25 : 1 mole ratio of methanol to carboxylic acids in bio-oil - Reaction temperature of 60 °C - 5 wt% Amberlyst15 catalyst	1	37.77	3.02
5			5	62.46	2.98
6			12	70.58	3.20
3			24	73.39	3.31
7	Catalyst loading (wt% of Amberlyst15)	- 3.25 : 1 mole ratio of methanol to carboxylic acids in bio-oil - Reaction temperature of 60 °C - Reaction time of 24 hr	0	13.13	4.32
3			5	73.39	3.31
8			15	78.64	2.74
9			30	86.87	1.81
3	Catalyst type	- 3.25 : 1 mole ratio of methanol to carboxylic acids in bio-oil - Reaction temperature of 60 °C - Reaction time of 24 hr	5 wt% of fresh Amberlyst15	73.39	3.31
10			5 wt% of H_2SO_4	93.75	-
11			5 wt% of used Amberlyst15	66.73	3.48
3	Mole ratio of methanol to carboxylic acids in bio-oil	- Reaction temperature of 60 °C - Reaction time of 24 hr - 5 wt% Amberlyst15 catalyst	3.25 : 1	73.39	3.31
12			6.50 : 1	75.81	4.31
3	Alcohol type	- 3.25 : 1 mole ratio of alcohol to carboxylic acids in bio-oil - Reaction temperature of 60 °C - Reaction time of 24 hr - 5 wt% Amberlyst15 catalyst	Methanol	73.39	3.31
13			Ethanol	54.80	3.42
14	Addition of molecular sieve 3A	- 3.25 : 1 mole ratio of methanol to carboxylic acids in bio-oil - Reaction temperature of 60 °C - Reaction time of 24 hr - 5 wt% Amberlyst15 catalyst	20 wt% of molecular sieve 3A	40.58	3.11

Table 2. Oxygenated compounds of palm shell bio-oil derived at pyrolysis temperature of 700 °C

Chemical	Chemical concentration in palm shell bio-oil (wt%)
1,4-Doxane-2,3-diol	0.762
Furfural	0.227
3-Furanmethanol	0.038
2-Methyl-2-cyclopenten-1-one	0.092
Cyclohexanone	0.083
Benzaldehyde	0.083
2,5,Dihydro-3,5-dimethyl-2-furanone	0.037
2-Hydroxy-3-methyl-1-cyclopentene-1-one	0.204
3-Ethyl-2-hydroxy-2-cyclopenten-1-one	0.054
1,2,4-Trimethoxybenzene	0.939
Verapamil	0.151
Total of ethers, ketones and aldehydes	2.670
Benzoic acid	0.719
Decanoic acid (Capric acid)	0.549
Dodecanoic acid (Lauric acid)	3.429
Tetradecanoic acid (Myristic acid)	1.348
Hexadecanoic acid (Palmitic acid)	4.127
(9Z)-Octadecenoic acid (Oleic acid)	1.947
Octadecanoic acid (Stearic acid)	0.514
Total of acids	12.633
Benzyl alcohol	0.089
Phenol	9.045
2-Methyl-phenol, (o-Cresol)	0.372
4-Methyl-phenol, (p-Cresol)	0.711
2-Methoxy-phenol, (Guaiacol)	1.380
3,4-Dimethyl phenol	0.169
2-Methoxy-4-methyl-phenol	1.451
1,2-Benzenediol	0.606
4-Ethyl-4-methoxy-phenol	1.355
4-Methyl-1,2-benzenediol	0.279
2,6 Dimethoxy-phenol (Syringol)	1.770
2-Methoxy-4-(1-propenyl)-phenol	0.363
2-Methoxy-6-(2-propenyl)-phenol	0.316
Methylparaben	0.309
2,5-Bis(1,-dimethylethyl)-phenol	0.058
2,6-Dimethoxy-4-(2-propenyl)-phenol	0.363
2,4,6-Tris(1,1 dimethyl ethyl)-phenol	0.061
2,2'-Methylene bis(6-1,1-dimethyl ethyl)-4-methyl-phenol	0.349
2,4-Bis(dimethylbenzyl)-6-t-butyphenol	1.704
Total of alcohols and phenols	20.750
Total of esters	15.314
Total of unknown	4.270
Total oxygenated compounds	55.637

contains acid content of 4.80 mmol/g oil based on the titration result as outlined in Section 3.2. Table 2 gives the analysis of oxygenated fraction of bio-oil, showing the composition of organic acids in the test bio-oil [9]. The resultant mixture reaction was carried out to upgrade the bio-oil under a controlled temperature condition using a water bath (P Selecta, Unitronic) shaken at 50 rpm for the desired reaction time.

3. Product Analysis

^{1}H NMR and volumetric titration were used to identify and quantify the derived ester product, respectively, after upgrading the bio-oil by esterification.

3-1. ^{1}H NMR

The occurrence and progression of esterification reaction were ascertained by analyzing the ^{1}H NMR spectra of reaction products at a frequency of 300 MHz using a Varian Inova-300 NMR spectrometer. Samples were prepared for analysis by diluting 10 μL of the upgraded bio-oils in 990 μL of 99.8% deuterated chloroform, $CDCl_3$ (Wilmad-LabGlass, SP Industries Inc). Tetramethylsilane, TMS, (99.7%, Merck Group) was also added into the sample solutions for use as an internal standard (chemical shift at 0 ppm). In addition, the NMR analysis of a mixture of raw bio-oil and methanol without added catalyst was also carried out. The derived NMR spectrum was used as a blank test information for analyzing NMR results of the upgraded bio-oils.

3-2. Volumetric Titration

To determine the extent of esterification in terms of reaction conversion, the concentration of carboxylic acids in the bio-oil must be known. This information can be obtained by titrating the bio-oil with a strong base of KOH, the technique of which is commonly used for determining the acid number of bio-oils, biodiesel, petroleum products and lubricants according to ASTM D664-07 [10-15]. However, to apply this analyzing method for bio-oil, a few considerations should be noted. Firstly, the titrant KOH can also react with phenol and its derivatives containing in the bio-oil [16]. Secondly, to calculate reaction conversion we need to know the amount of total carboxylic acids in the raw bio-oil (at the initial time of reaction) and this can be derived by titrating the raw bio-oil with $NaHCO_3$ since $NaHCO_3$ does not react with phenol. Finally, there is a possibility of proton releasing from the catalyst which can as well react with KOH. To account for this effect, 5 g of water was mixed with the catalyst under the same condition as that used for bio-oil esterification and the water was titrated with KOH to determine its acid content. Based on these considerations, the percent conversion of carboxylic acids in the bio-oil (X) can be estimated from the volume of titrants used according to the following equation,

$$X = \frac{V_{KOH\text{-}raw} - (V_{KOH\text{-}up} - V_{KOH\text{-}cat})}{V_{NaHCO_3\text{-}raw}} \times 100 \quad (1)$$

where $V_{KOH\text{-}raw}$ represents the volume of 0.1 M KOH titrated with the mixture of raw bio-oil and alcohol without catalyst added, $V_{KOH\text{-}up}$ is the volume of 0.1 M KOH titrated with the upgraded bio-oil after esterification, $V_{KOH\text{-}cat}$ is the volume of 0.1 M KOH titrated with water after contacting with the catalyst and $V_{NaHCO_3\text{-}raw}$ is the volume of 0.1 M $NaHCO_3$ titrated with the mixture of raw bio-oil and alcohol. The nominator term in Eq. (1) is proportional to the amount of carboxylic acids converted by the reaction, assuming that the concentration of phenols in the solution remains unchanged throughout the course of esterification reaction.

3-3. Fuel Properties

The separated oil phase of bio-oil from palm shell pyrolysis, two

alcohols (methanol and ethanol) and four samples of upgraded bio-oil products (Run No. 3, 7, 12 and 13 in Table 1) were characterized for their basic fuel properties including calorific value (ASTM D240-92), density (Gay-Lussac bottle), viscosity (ASTM D445-96), pH (744 pH meter, Metrohm), carbon residue (ASTM D524-97), ash content (ASTM D482-95), flash point (ASTM D93-97) and pour point (ASTM D97-96a). The upgraded bio-oils after esterification were characterized without an attempt to remove the remaining unreacted alcohol because the presence of alcohol in bio-oil can help stabilize the bio-oil properties [4].

RESULTS AND DISCUSSION

1. Raw Material Characterization

Results on chemical structures of the test bio-oil analyzed by ^{1}H NMR technique are shown in Fig. 1(a). The chemical structures can be identified as follows: chemical shift at 9.4-10.0 ppm is the groups of aldehydes, at 6.4-8.4 ppm is aromatics, at 5.0-6.4 ppm represents proton of aqueous solution left in the bio-oil, at 3.0-5.0 ppm is esters, alcohols or ethers, at 2.0-3.0 ppm is ketones, acids or alkynes and at 0.8-2.0 ppm is saturated alkanes. Fig. 1(b) shows the results from the analysis of the original unreacted bio-oil and alcohol mixture. Comparing Figs. 1(a) and 1(b), it is seen that the proton peak in aqueous solution (at chemical shift 5-6.4 ppm) no longer exists for the unreacted bio-oil/methanol mixture. The effect of proton in aqueous solution and that from hydroxyl group of methanol may alter the hydrogen's electronic environments such that the original proton peak may be shifted and appears as part of the broad peak (chemical shift 3.6-5 ppm) as observed in Fig. 1(b). To validate this hypothesis, it may be necessary to prepare bio-oil/methanol mixtures with differing methanol compositions and NMR analysis performed to detect any positional variation of the proton peak. The unreacted bio-oil/methanol mixture was analyzed with ^{1}H NMR in order to compare the spectra results with those of the upgraded bio-oils. If an ester group exists in the solution, NMR analysis should show a sharp narrow peak at the chemical shift in the vicinity of 3.6-5.0 ppm as previously stated. However, at the same range of chemical shift, an unreacted mixture of bio-oil and methanol shows a rather broad peak of NMR spectra as displayed in Fig. 1(b). The broad peak nature of NMR spectra of pure methanol as shown in Fig. 1(c) undoubtedly contributes to the broad peak appearance of the unreacted bio-oil and alcohol mixture, as mentioned earlier.

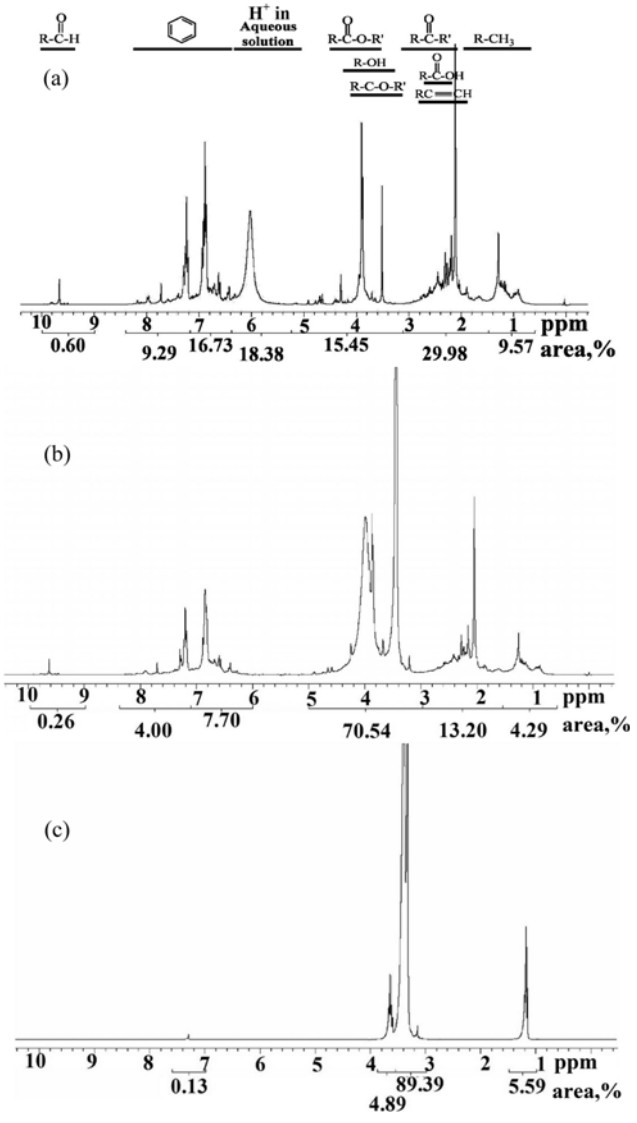

Fig. 1. ^{1}H NMR spectra of (a) palm shell bio-oil (b) mixture of palm shell bio-oil and methanol (unreacted) with 3.25 : 1 mole ratio of methanol to carboxylic acids in bio-oil and (c) pure methanol.

2. Effect of Esterification Conditions on Reaction Conversion

The effects of esterification conditions including reaction temperature, reaction time, catalyst loading, catalyst type, alcohol type and alcohol to carboxylic acids mole ratio on the reaction conversion were investigated. ^{1}H NMR is the technique used to identify the existence of ester groups produced from the esterification reaction for which the NMR spectra occur at the chemical shift of 3.6-5.0 ppm. Titration of bio-oil with KOH and $NaHCO_3$ was also used to quantify the amount of acids left in the upgraded bio-oils, thus enabling the estimation of percent conversion of acids to esters by Eq. (1).

The effect of reaction temperature was investigated by studying esterification of the bio-oil and methanol under the following conditions: 3.25 : 1 mole ratio of methanol to carboxylic acids in bio-oil, reaction temperature varying from 25-60 °C, 5 wt% Amberlyst15 solid catalyst and reaction time of 24 hrs. The results presented in Table 1 indicate that the conversion increased approximately linearly with increasing reaction temperature and the highest temperature studied gave the highest esterification conversion of about 73%. Also as Fig. 2 shows, the sharpness of esters spectra at chemical shift 3.6-5.0 ppm is progressively increasing with increasing reaction temperature from 25 to 60 °C. These results correspond to the increased conversion of acids in the bio-oil to esters with increasing reaction temperature, as indicated in Table 1.

For the effect of reaction time, Table 1 and Fig. 3 show that longer reaction time gave increased esterification conversion for the conditions of 3.25 : 1 mole ratio of methanol to carboxylic acids in bio-oil, 5 wt% of Amberlyst15 and reaction temperature of 60 °C. The percent conversion increased sharply for the first 1 hr of reaction time to about 40%, followed by a slow increase and started to attain a constant value (equilibrium) after about 12 hrs. The relationship

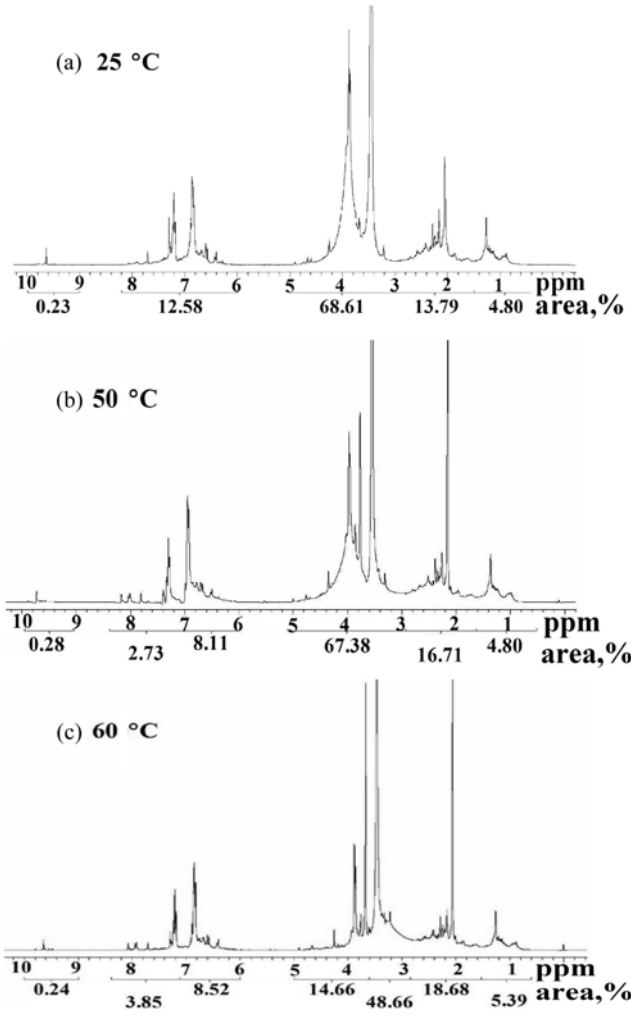

Fig. 2. Effect of reaction temperature on ^{1}H NMR spectra of the upgraded bio-oils (a) 25 °C, (b) 50 °C and (c) 60 °C (Run no. 1, 2 and 3 of Table 1).

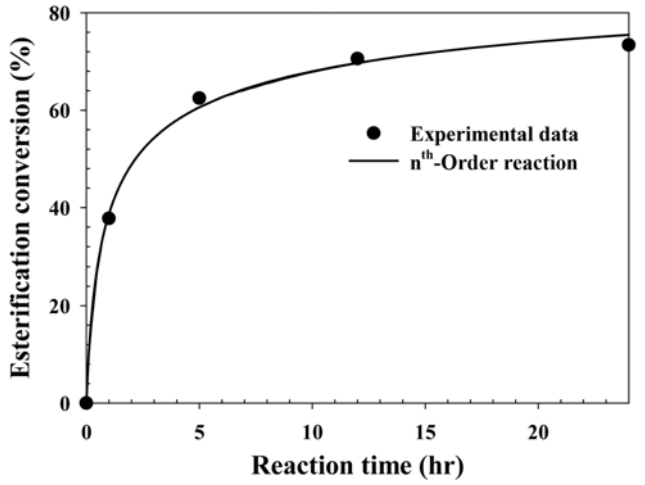

Fig. 3. Effect of reaction time on conversion of esterification reaction for esterification conditions of 3.25 : 1 mole ratio of methanol to carboxylic acids in bio-oil, 5 wt% of Amberlyst15 catalyst and reaction temperature of 60 °C (Run no. 4, 5, 6 and 3 of Table 1).

between percent conversion and reaction time can be best described by the nth-order reaction model which reads

$$X = 100\left[1-\left[\frac{1}{1+(n-1)ktC_{A0}^{(n-1)}}\right]^{\left(\frac{1}{n-1}\right)}\right], \quad n \neq 1 \tag{2}$$

where X is percent conversion of carboxylic acids in bio-oil, n is the reaction order, k is the reaction rate constant, t is reaction time and C_{A0} is the initial concentration of carboxylic acids in solution (3.154 mol/L). The best fitted values of n and k for this set of data are 4.23 and 0.0293 $(mol/L)^{-3.23}$ $(hr)^{-1}$, respectively. The esterification rate can be easily obtained by differentiating Eq. (2) with respect to time.

The effects of catalyst loading and catalyst type on the formation of ester products were investigated for the esterification conditions of 3.25 : 1 mole ratio of methanol to carboxylic acids in bio-oil, reaction temperature of 60 °C and reaction time of 24 hrs. Solid acid catalyst of Amberlyst15 was used for studying the effect of catalyst

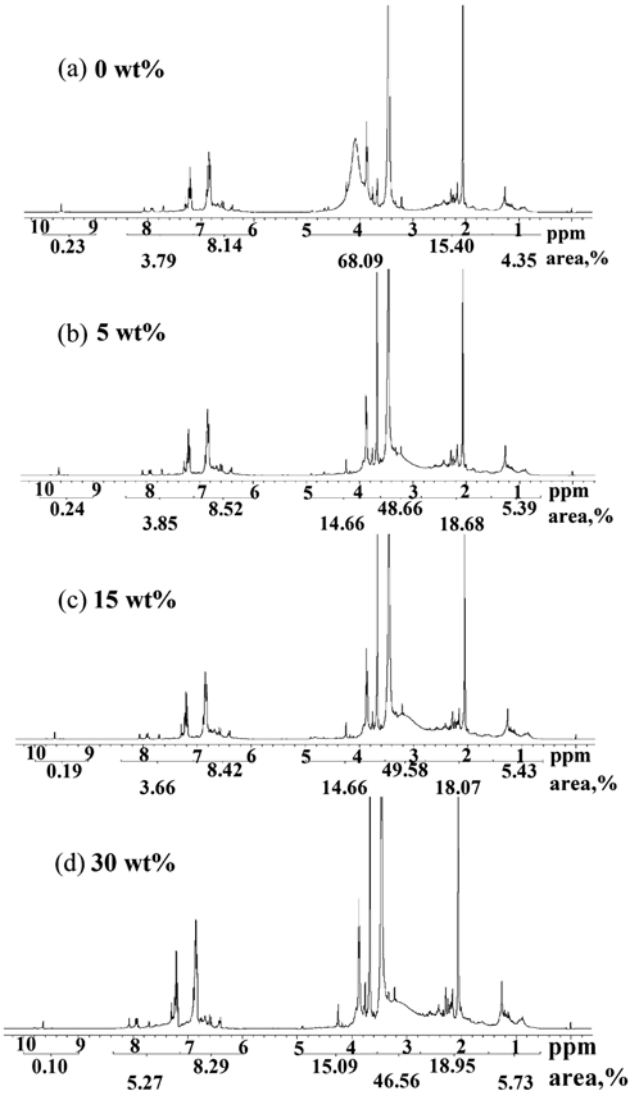

Fig. 4. Effect of catalyst loading of Amberlyst15 on ^{1}H NMR spectra of upgraded bio-oils (a) 0 wt%, (b) 5 wt% (c) 15 wt% and (d) 30 wt% (Run no. 7, 3, 8 and 9 of Table 1).

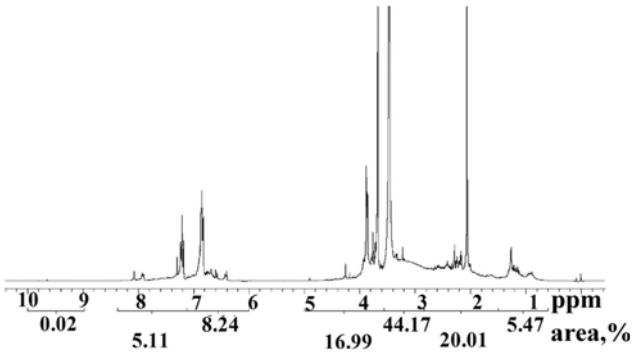

Fig. 5. ^{1}H NMR spectra of upgraded bio-oils using 5 wt% H_2SO_4 (Run no. 10 of Table 1).

loading, and the results are listed in Table 1 and shown in Fig. 4. It was discovered that the upgraded bio-oil without catalyst gave only 13.13% of esterification conversion and showed similar ^{1}H NMR spectra to those of the original unreacted bio-oil and alcohol mixture (compare Fig. 1(b) and Fig. 4(a)). However, the presence of only 5 wt% Amberlyst15 catalyst could provide almost a fivefold increase of conversion compared with the case of not using catalyst. However, increasing catalyst loading from 5 to 30 wt% gave rise to a mere 20% increasing of conversion. Qualitatively, it can be also observed from Fig. 4 that the clear sharp peaks of ^{1}H NMR spectra in the range of 3.6-5.0 ppm were obtained with the use of 5-30 wt% Amberlyst15.

On the effect of catalyst type, Table 1 indicates that the use of 5 wt% H_2SO_4 gave the maximum conversion of 93.75%, while 30 wt% Amberlyst15 gave lower conversion of 86.87%, even though the H^+ amount of 30 wt% Amberlyst15 is higher than that of 5 wt% H_2SO_4 (1.41 meq/g oil for 30 wt% Amberlyst15 versus 1.02 meq/g oil for 5 wt% H_2SO_4). This difference is probably attributed to mass transfer limitation inside the pores of Amberlyst15. For this case, the reactants must transport to hydrogen ion sites located in the macroreticular pore of Amberlyst15 catalyst, while H_2SO_4 catalyst can readily associate with the large molecules of fatty acids in the bulk of liquid phase. Furthermore, the spectra at chemical shift of 9.0-10.0 ppm (Fig. 5) indicate that aldehyde group almost disappeared (only 0.02% of area under the curve remaining at 9.4-10 ppm chemical shift) when 5 wt% of H_2SO_4 was used as the catalyst. Similarly, peak area reduction at this position was also observed when more than 15 wt% of Amberlyst15 was used (Fig. 4). Thus, apart from participating in the esterification reaction, the active H^+ of catalysts can also lower aldehyde contents possibly by inducing the side reaction of acetalization [4]. The formation of acetals via this reaction could contribute advantageous effects for both reducing aldehyde content and shifting away the formation of acetaldehyde hydrates to produce polymeric resins [4]. Furthermore, in this study the effectiveness of reused solid catalyst was compared to that of the fresh catalyst. It was found that the reuse of Amberlyst15 catalyst gave about 10% reduction in reaction conversion in comparison with the use of fresh catalyst (Table 1). It is possible that the used catalyst could contain lower amount of active H^+ because the released proton may have lost with the bio-oil during the first cycle of esterification upgrading. This is supported by the evidence from Table 1, which shows that the pH of the bio-oil upgraded by solid catalyst (Run No. 3) is lower than that derived from without using catalyst (Run No. 7). It should be also observed that the pH value decreased markedly with increasing amount of Amberlyst15 catalyst (Table 1). The high acid character of the upgraded bio-oil derived from using this solid acid catalyst still exists and is a significant problem inherent to this type of upgrading method. This characteristic was also reported when employing other types of solid acid catalysts such as Nafion SAC13 and $40SiO_2/TiO_2$-SO_4^2 [7,8].

The effects of alcohol content and alcohol type were investigated by studying esterification with 5 wt% of Amberlyst15 at 60 °C for 24 hrs. Generally, higher amount of alcohol can shift the esterification reaction in the forward direction to obtain higher conversion [17]. The results shown in Table 1 indicate that increasing alcohol content gave higher esterification conversion, but the conversion was increased by only 2.42% for a twofold increase of mole ratio of methanol to carboxylic acids. Thus, it may be inferred that the mole ratio of 3.25 : 1 of methanol to carboxylic acid is probably adequate to achieve reasonably high reaction conversion (~73%) under the condition tested. For the effect of alcohol type, Table 1 shows that the bio-oil upgraded using methanol exhibited much higher conversion of 73.39% compared with the use of ethanol which gave only 54.80% conversion. This may be ascribed to the effect of the size of alkyl group of alcohol on the reaction rate; higher active reagent of the shorter carbon-chain alcohol and greater solubility of this alcohol in the bio-oil could promote a faster reaction rate [18]. However, the esterification of bio-oil and ethanol could be operated at a higher temperature to attain higher esterification conversion. The work of Doshi et al. [5] showed that bio-oil derived from fast pyrolysis of sewage sludge via esterification with ethanol using H_2SO_4 produced faster reaction rate when the reaction temperature was increased from 50 to 75 °C.

In addition, a certain amount of water can be produced from the esterification process; about 5.75 wt% of water was produced from the mixtures of 3.25 : 1 mole ratio of methanol to carboxylic acids in the bio-oil, calculated based on the stoichiometric amount of water produced from 100% conversion of acid in the raw bio-oil. To affect the increased conversion by shifting the reaction equilibrium, the addition of 20 wt% molecular sieve 3A into the original mixture to remove product water was also examined. However, it was found that adding molecular sieve 3A provided an adverse effect of giving much lower conversion than that derived from the case of not using molecular sieve 3A under the same reaction conditions (40.58% vs 73.39%). This may result from the possible adsorption of methanol molecules by molecular sieve 3A, thus giving less amount of alcohol available for the reaction. It was determined experimentally in this work that this adsorbent is capable of alcohol adsorption with the capacity of 0.3 ml methanol per gram of adsorbent.

3. Fuel Properties of Upgraded Bio-oils

Four upgraded bio-oil samples were selected for the measurement of their basic fuel properties and the results are summarized in Table 3. After esterification, the bio-oils gave heating value similar to that of the raw bio-oil. It was also observed that the use of different alcohol type showed a definitive effect on the heating value of the upgraded bio-oils. Relatively constant values of heating value in the range of 23.10-23.78 MJ/kg were obtained with methanol at different esterification conditions (Run No. 3, 7, and 12), whereas the upgraded bio-oil using ethanol (Run No. 13) gave slightly higher

Table 3. Fuel properties of raw bio-oil and upgraded bio-oils by esterification

Fuel properties	Methanol	Ethanol	Dewatered palm shell bio-oil	Upgraded oils of Run No.			
				3	7	12	13
Calorific value (MJ/kg)	22.62	28.73	25.55	23.78	23.73	23.10	25.40
Density at 25 °C (g/cm^3)	0.791	0.793	1.130	0.985	0.987	0.933	0.992
Viscosity at 40 °C (mm^2/s)	0.577	1.22	9.14	1.19	1.27	0.97	1.54
pH	6.63	6.58	2.92	3.31	4.32	4.21	3.42
Ramsbottom carbon residue (wt%)	0.019	0.021	6.35	4.31	4.56	2.93	4.74
Ash (wt%)	-	-	0.089	0.066	0.071	0.038	0.051
Flash point (°C)	11*	14*	88	35	35	22	28
Pour point (°C)	−98.0**	−114.0**	−18	<-20	<-20	<-20	<-20

Note: * flash point [19,20], ** freezing point [19,20]

value of 25.40 MJ/kg. The upgraded bio-oils improved certain fuel properties, i.e., giving lower values of viscosity, ash content, % carbon residue content and pour point. However, the presence of remaining alcohol solvent in the upgraded bio-oils gave unsatisfactory properties of lowering energy density and flash point. The upgraded oils, which have lower density, cause energy density to be less than that of the raw bio-oil (21.55-25.20 GJ/m^3 for the upgraded oils and 28.87 GJ/m^3 for the raw bio-oil) and their flash points being in the range 22-35 °C, indicating that the use of upgraded oils by esterification should require more attention to safety even at room temperature. In addition, the pH of upgraded oils was increased slightly compared with that of the raw oil. It is also noted that the upgraded oils derived from using Amberlyst15 catalyst (Run No. 3) showed lower pH values than that of the upgraded oils without addition of catalyst (Run No. 7) at the same esterification conditions. This is possibly caused by the release of active H^+ from Amberlyst15 catalyst into the bio-oils over the course of esterification reaction.

CONCLUSION

The upgrading of bio-oil (a separated oil phase of raw bio-oil from palm shell pyrolysis) by esterification process with acid catalysts showed that, under the conditions studied, maximum conversion of 93.75% was achievable by using 5 wt% of liquid H_2SO_4. Under the same conditions, maximum conversion of bio-oil upgraded by 30 wt% Amberlyst15 solid catalyst was about 86.87%. The higher reaction temperature, reaction time, mole ratio of methanol to acids and the use of smaller molecule of methanol gave higher esterification conversion. The kinetic and conversion of esterification reaction of palm shell bio-oil and methanol using Amberlyst15 catalyst can be well described by the n^{th}-order reaction scheme, giving the reaction order and reaction rate constant to be 4.23 and 0.0293 (mol/L)$^{-3.23}$ (hr)$^{-1}$, respectively. The treated bio-oils had similar heating values compared with that of the raw bio-oil (23.10-25.40 MJ/kg) and showed improved properties of lowering values of viscosity, carbon residue content, ash content and pour point and less acidity (increasing pH). In addition, the reduction of active chemicals such as acids and aldehydes should lessen the problem of ageing rate of the upgraded oil by prohibiting the reactions occurring and/or being catalyzed by these chemicals [4]. Amberlyst15 appears to be an effective catalyst for esterification reaction but it has a weak point of releasing active H^+ during esterification reaction, causing the lowering of pH value of the upgraded oil. Thus, a better catalyst with a characteristic of high proton affinity on the support should be a viable alternative for bio-oil upgrading by this simple process of esterification.

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