



Fixed-bed catalytic and non-catalytic empty fruit bunch biomass pyrolysis



M. Auta^{a,b}, L.M. Ern^a, B.H. Hameed^{a,*}

^a School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia

^b Department of Chemical Engineering, Federal University of Technology, Minna, Nigeria

ARTICLE INFO

Article history:

Available online 12 February 2014

Keywords:

Pyrolysis
Catalyst
Adsorption
Biomass
Bio-oil

ABSTRACT

An attempt to the global clarion call to explore for an alternative source of environmentally friendly, renewable and cheaper energy (fuel) source than the conventional fossil fuel, was made in this study. This involved testing the effects of three catalysts (potassium carbonate K_2CO_3 , calcium hydroxide $Ca(OH)_2$ and magnesium oxide MgO) in the empty fruit bunch (EFB) pyrolysis on the product yields. The $Ca(OH)_2$ catalyzed EFB pyrolysis gave the maximum percentage yield (42.64%) of bio-oil. The maximum bio-oil percentage yield from the $Ca(OH)_2$ catalyzed EFB pyrolysis was obtained at pyrolysis temperature of 600 °C, sweeping gas flow rate of 200 mL/min and using 10 wt.% of the catalyst. The GC–MS analysis of the $Ca(OH)_2$ catalyzed EFB pyrolysis showed an increase (10.68%) in the desirable phenolic content and a reduction (35.21%) in the undesirable acidic components of the bio-oils when compared with the phenolic (16.74%) and acidic (42.88%) components of non catalyzed EFB pyrolysis bio-oil. This study has revealed that the quantity and quality of bio-oils can be improved using $Ca(OH)_2$ catalyzed biomass pyrolysis.

© 2014 Published by Elsevier B.V.

1. Introduction

In a quest to meet the global energy challenge maintaining a sustainable serene environment, potentials of renewable biomass materials are being investigated as an alternative energy resource and for possible conversion to useful chemicals [1]. The clean environmentally friendly energy resource from biomass (cellulose and hemicellulose structures, extractives, inorganics and lignin) via pyrolysis is an embodiment of majorly bio-liquids, gases and char [2]. Products yield and composition of the pyrolysis is a function of biomass precursor, particle size, reactor type, heating rate, temperature, type of catalyst, catalyst impregnation, sweeping gas and its flow rate [3].

Pyrolysis of biomass is a wholesome approach of valorizing agricultural wastes as the resulting products are entirely useful. It involves deoxygenation reactions (decarboxylation, deoxygenation, decarbonylation) and removal of nitrogen (NH_3) and sulphur (H_2S) [4]. Biomass is composed of cellulose and hemicellulose structures, extractives, inorganics, lignin and heteroatoms (nitrogen, sulfur, hydrogen, oxygen) which vary in different materials [5]. The sulphur and nitrogen content in biomass is lower than that

found in fossil feed stock while it has higher oxygen and hydrogen content [6,7]. Among heteroatoms present in biomass, elimination of oxygen is of utmost importance as it high presence affects thermal value of bio-oils produced, enhances corrosivity and acidity and lessens stability of oxidation [8]. Biomass pyrolysis gaseous products are as valuable as the bio-oils and chars, ways of optimally harnessing them are being embarked upon [1,9]. The char obtained can be used for preparation of activated carbon and as briquettes due to its high calorific value [10]. Bio-oil is a dark brown, highly oxygenated, corrosive, viscous, complex chemicals and organic liquid used as substitute synthetic fuel [11]. It has high calorific value and can be used as additive for refined petroleum feedstocks, thermal power stations, gas turbines and can be converted to useful chemicals with ease [12–14].

The quality and quantity of bio-oil from biomass pyrolysis has been investigated by the use of suitable catalyst. Catalyst is used to selectively determine the product and subsequently the desired application. Copper catalyst has been used to enhance devolatilization at low temperatures with reduction in the formation of char residue [15]. To selectively target a product of pyrolysis process, slow heating and gas sweeping in a fixed-bed was used to channel pyrolysis of pine wood for bio-oils production [16]. Magnesium oxide catalyst was used to improve quality of bio-oils produced at the expense of the percentage oils yield, but the char and gases products were increased [17]. Also reported is deoxygenation

* Corresponding author. Tel.: +60 6405996422; fax: +60 45941013.
E-mail address: chbassim@eng.usm.my (B.H. Hameed).

(hydroxyl and methoxy group elimination) in situ pyro-catalytic process which was used to improve quality of bio-oil produced from empty fruit bunch and oil palm frond [18].

Like many parts of the world, Malaysia has abundance of biomass materials. It is the second largest world producer of palm oil which has quantum of mesocarp fiber, kernels, shell, empty fruit bunch (EFB) and palm oil mill effluent (POME) from the oil production [19]. Processing of palm oil generate about 4 tons of empty fruit bunch from every ton of palm oil produced and this biomass can be converted to high energy bio-oil through pyrolysis [18]. There are ample reports on pyrolysis of empty fruit bunch [18,20–22], palm oil shell and their fibers [9] in the literature.

This study is aimed at investigating a suitable empty fruit bunch (EFB) pyrolysis catalyst for quantitative and qualitative product yield. It involved testing the efficiency of potassium carbonate, calcium hydroxide and magnesium oxide as pyrolysis catalyst. Effects of pyrolysis temperature, catalyst/EFB furnace loading pattern, sweeping gas flow rate and weight percent of catalyst on the products yield were evaluated.

2. Materials and methods

2.1. Materials

Empty fruit bunch (EFB) biomass obtained locally from Nibong Tebal, Malaysia was used for this study. The EFB was dried at 110 °C for 6 h and then sieved to 0.2–0.5 mm after grinding.

An analytical grade potassium carbonate (K_2CO_3) used in this study was obtained from Fluka Chemika, Switzerland while calcium hydroxide ($Ca(OH)_2$) and magnesium oxide (MgO) were obtained from R & M Chemicals. These chemical compounds were used as catalyst for pyrolysis activities investigation and their choice was informed by the fact that they belong to alkali and alkali earth metals groups which have been found to catalyze de-oxygenation especially de-carboxylation [23]. Merck Chemical company Germany supplied n-hexane used for the study without further purification.

2.2. Thermal gravimetric analysis of the EFB

The proximate analysis of the EFB was conducted using thermal gravimetric analysis (TGA) with the aid of TGA analyzer (Perkin Elmer STA6000). The analysis was carried out by heating 5.65 mg EFB to 900 °C at 10 °C/min under nitrogen inert atmosphere (20 mL/min). The moisture content of the EFB was evaluated around 105 °C, while the volatile components and fixed carbon under purged nitrogen gas and oxygen atmosphere, respectively were determined.

2.3. Fixed-bed EFB biomass pyrolysis

The pyrolysis experiment of EFB was carried out in an inert fixed-bed reactor under continuous 99.99% pure nitrogen flow (sweeping gas). In the electric furnace compartment of the fixed-bed, the bottom of the pyrolysis chamber tubular reactor was connected to a stainless steel tube and a round bottom flask which served as the bio-oil collector (figure not shown). The pyrolysis of the EFB was carried out catalytically using K_2CO_3 , $Ca(OH)_2$ and MgO separately as catalyst. In each case, 2 g of the EFB was loaded into the tubular reactor and the product was weighed after the experiment [20,28]. Inertness of the furnace chamber was maintained by a constant flow of nitrogen gas at 200 mL/min. Effect of temperature on the EFB pyrolysis was studied at various conditions of 400, 500 and 600 °C for 10 min. By gravity, the liquid phase (bio-oil) product was collected in the round bottom flask maintained at <5 °C in an ice cubes bath. The bio-oil collection was carried

out during and after pyrolysis until the furnace temperature was <50 °C.

The catalyzed pyrolysis experiment was carried out in two patterns. In the first arrangement, 5 wt.% catalyst (K_2CO_3 , $Ca(OH)_2$ and MgO) was mixed with 2 g of dried EFB before placing in the tubular reactor. While the 5 wt.% catalyst was placed in the reactor and then the EFB was introduced on top of it in the second arrangement. The premixed catalyst/biomass and separately placed catalyst/biomass pattern were tagged CBM and CB, respectively. The catalytic and non-catalytic pyrolysis products (bio-oil, char and gas) were determined in weight percent as follows: ratio of desired char product (g) to EFB feed (g) gave the char yield; ratio of desired liquid product (g) to EFB feed (g) gave the liquid oil yield; ratio of difference between EFB feed (g) and total yield of liquid oil and char to EFB feed (g) gave the gas yield [21].

2.4. Investigation of the suitable catalyst for the EFB pyrolysis

A measure of 2 g EFB and 5 wt.% catalyst (K_2CO_3 , $Ca(OH)_2$ and MgO) were mixed and then placed in the furnace and a heating rate set at 10 °C/min to dwell at 600 °C. Inert atmosphere in the furnace was maintained by constant 200 mL/min nitrogen gas flow during heating, dwelling and cooling period of the pyrolysis. At the end of the experiment, the resulting bio-oil was analyzed by gas chromatograph–mass spectrometry (GC–MS) analysis.

2.5. Effect of operating factors on the $Ca(OH)_2$ catalyzed EFB product yield

Three operating factors namely: pyrolysis temperature, catalyst loading and nitrogen gas flow rate were investigated.

The CBM method (pre-mixing of 2 g of EFB with 5 wt.% catalyst) of pyrolysis furnace loading using $Ca(OH)_2$ was applied at fixed nitrogen gas flow rate of 200 mL/min and heating rate of 10 °C/min to investigate effect of pyrolysis temperature (500, 550 and 600 °C) on the EFB products yield.

At a fixed pyrolysis temperature of 600 °C, 10 °C/min, dwelling time of 10 min and 200 mL/min N_2 , the CBM pyrolysis furnace loading method with different $Ca(OH)_2$ weight percent of 5, 10 and 15 influence on product yield was investigated.

The effect of variation of sweeping gas flow rate (100, 200 and 300 mL/min) on the EFB pyrolysis product yield was studied at fixed furnace conditions of 600 °C for 10 min, 10 °C/min and 5 wt.% $Ca(OH)_2$ catalyst.

2.6. The EFB gas chromatograph–mass spectrometry bio-oil analysis

The bio-oil analysis was conducted with gas chromatograph–mass spectrometry (GC–MS) analyzer (Perkin Elmer Clarus 600) equipped with a HP-5MS capillary column (30 mm × 0.25 mm × 0.25 μm) and mass selectivity (MS) detector. Helium was used as a carrier gas at a constant flow rate of 1 mL/min. The initial oven temperature was operated at 65 °C for 2 min and then ramped at 10 min⁻¹ up to 280, and held for 25 min. The injection temperature was held at 250 with a volume of 1 L. Identification of the GC–MS peaks were based on the NIST MS Search 2.0 libraries.

3. Results and discussion

3.1. Characterization of the palm empty fruit bunch (EFB) biomass

The EFB proximate analysis was studied using thermo gravimetric analysis (TGA) technique which is invaluable in the study of

carbonaceous materials thermal behavior [24]. The TGA of the EFB was carried out between 25 and 900 °C under nitrogen gas atmosphere. An initial weight loss was observed at temperature above 100 °C which was attributed to vaporization of retentate physically absorbed water (moisture). The main pyrolysis reactions which are depolymerization, decarbonylation and cracking were believed to have taken place at the devolatilization temperature range of 200–400 °C [18,25]. The proximate analysis of the EFB gave a moisture content, volatile matter, ash and char of 9.58, 76.10, 7.20 and 7.12 wt.%, respectively. This is comparable with proximate analysis results of EFB used by other researchers [26].

3.2. Effect of temperatures on product yield from non-catalytic pyrolysis

The fixed bed pyrolysis furnace temperature was varied from 400 to 600 °C to study the variation effect on products yield of the EFB. The percentage of the various non-catalytic pyrolysis products obtained are presented in Fig. 1.

The amount of solid (char) was found to be decreasing with increase in pyrolysis temperature while the gaseous products increased concurrently with temperature. The highest percentage obtained of the char at 400 °C was 33.26% whereas 35.40% was obtained at 600 °C. The char and gaseous products yield obtained was in accordance with the expected trend [22,27,28]. Secondary cracking of volatiles of pyrolysis often enhances the yield of gaseous product and some gas products that are non-condensable may also be formed by decomposition of char at elevated temperatures [20]. Decrease in char and increase in gas yield as the pyrolysis temperature increases have also been observed by previous researchers [26]. The oil yield was 31.34% at the pyrolysis temperature of 400 and attended a maximum yield of 49.67% at 600 °C. Greater primary decomposition of feedstock and secondary decomposition of char as the temperature increased may have enhanced the bio-oil yield [29].

3.3. Effect of the EFB catalyst loading pattern on bio-oil yield

The fixed-bed pyrolysis tubular reactor was loaded in two patterns: placing of the catalyst at the bottom of the reactor before introducing the EFB (CB) and pre-mixing of the catalyst and EFB (CBM) before loading into the reactor. At constant sweeping gas flow rate of 200 mL/min, 600 °C pyrolysis temperature and 5 wt.% K₂CO₃ catalyst, variance of percentage product yield was observed between the CB and CBM tubular reactor loading pattern as shown in Table 1. The char, liquid and gas products yield for the CBM pattern were approximately the same (33 wt.%) while a great variation of similar products yield was observed with the CB tubular furnace loading pattern. However, the weight percent yield of bio-oil (33 wt.%) was about the same for both CB and CBM arrangements.

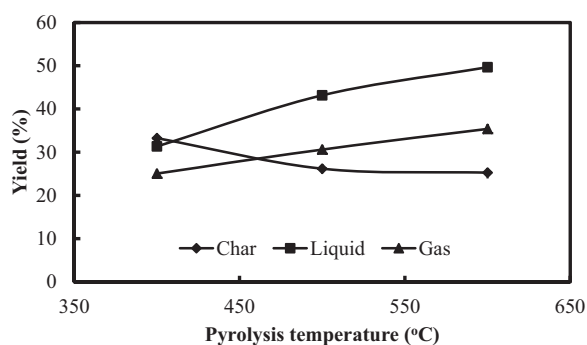


Fig. 1. Effect of temperature on product yields for non-catalytic EFB pyrolysis (200 mL/min N₂ gas flow rate, 10 min dwelling time).

Table 1
Effect of catalyst/EFB pyrolysis reactor loading pattern on products yield.

Product (wt.%)	Catalyst loading pattern	
	CBM	CB
Char	33.02	23.01
Liquid	33.52	33.44
Gas	33.46	43.55

The CBM produced an excellent rigid char matrix and reduced the burnt off or conversion of the EFB to gaseous products [30,31]. The rigid char that may have been formed and probable conversion of the gaseous products to liquid products informed the choice of CB pattern of tubular reactor loading in subsequent experiments.

3.4. Comparison of EFB products yield between non-catalytic and catalytic pyrolysis

The use of 5 wt.% K₂CO₃, Ca(OH)₂ and MgO as catalyst for the EFB pyrolysis at similar operating conditions of 200 mL/min sweeping gas flow rate, 600 °C pyrolysis temperature as the non-catalytic pyrolysis, gave various percentage of products as presented in Fig. 2.

The gas yield was determined by the difference between the amount of feed sample and the sum of the amount of liquid and char products obtained. The three catalysts gave higher percentage of gas products when compared with the non-catalytic pyrolysis gas product yield. But the weight percent char yield of the K₂CO₃ and Ca(OH)₂ catalyzed pyrolysis was reduced while a slight increase of same was observed with the MgO catalyzed process. Catalytic pyrolysis of the EFB was majorly decomposition of cellulose, hemicelluloses and lignin components of the biomass which is in accordance with reports by previous researchers that used similar catalysts for pyrolysis and obtained higher gaseous products with K₂CO₃ giving greater effect [17,28,32].

The Ca(OH)₂ catalyzed pyrolysis gave higher yield of liquid (bio-oil) compared with the K₂CO₃ and MgO pyrolysis as can be seen in Fig. 2. The use of Ca(OH)₂ as catalyst was found to increase the yield of bio oil during pine wood pyrolysis and the following reaction pattern was proposed [28]:



Eqs. (1–5) represents possible reactions that occurred in the tubular reactor during the EFB pyrolysis using the three catalysts. The reactions were characterized with release of gaseous products as the decomposition of the biomass progressed. The equations of

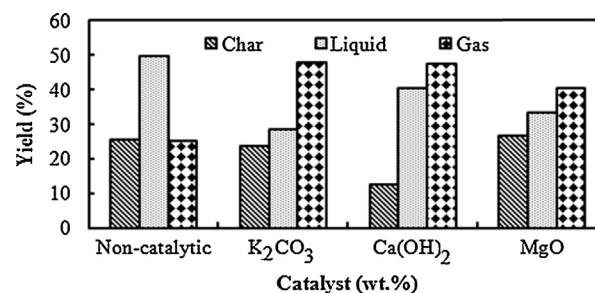


Fig. 2. Percentage yield of non-catalytic and catalytic EFB pyrolysis (5 wt.% catalyst, 200 mL/min N₂, 600 °C pyrolysis temperature for 10 min).

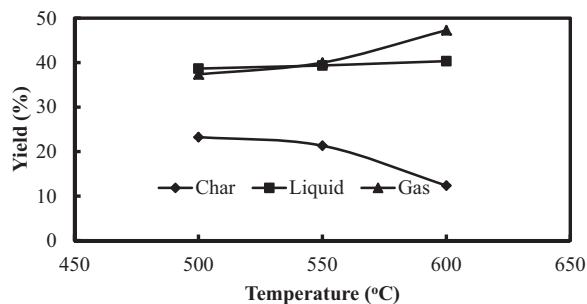


Fig. 3. Effect of temperature on Ca(OH)₂ catalyzed EFB products yield at N₂ flow rate of 200 mL/min and 5 wt.% of the catalyst with a dwelling time of 10 min.

reaction (1)–(3) showed that Ca(OH)₂ catalyzed pyrolysis decomposed further, giving rise to cumulative yield of CO and CO₂ which was slightly larger than each yield of K₂CO₃ and MgO catalyzed pyrolysis. The use of Ca(OH)₂ promoted water gas reaction which revealed how it further promoted decomposition of the biomass [33,34].

3.5. Effect of temperature on Ca(OH)₂ catalyst pyrolysis

A temperature variation of 500, 550 and 600 °C were used at constant sweeping gas flow rate of 200 mL/min and 5 wt.% Ca(OH)₂ to determine the effect on the yield of EFB pyrolysis products. The result of the temperature effect on the Ca(OH)₂ is shown in Fig. 3.

The char yield was found to decrease with subsequent increase in temperature from 500 to 600 °C. The trend was due to decomposition of the EFB and secondary decomposition of residues char as the temperature was increased. This is similar to observations made by previous researchers in the investigation of the effect of temperature on EFB pyrolysis char yield [20]. The bio-oil (38–40 wt.%) and gaseous (37–47 wt.%) products yield increased with temperature increase as can be seen presented in Fig. 3. This was attributed to secondary decomposition activities [35]. The slightly higher percentage of gaseous products was attributed to water gas shift reaction products of Ca(OH)₂ catalyzed pyrolysis previously mentioned in Section 3.4 [28,33].

3.6. Effect of Ca(OH)₂ amount on EFB pyrolysis products yield

As presented in Fig. 4, the effect of Ca(OH)₂ ratio (5, 10 and 15 wt.%) on the EFB products yield was evaluated at constant fixed-bed pyrolysis furnace temperature of 600 °C, for 10 min, and sweeping gas flow rate of 200 mL/min.

It was observed that an increase in the Ca(OH)₂ ratio from 5 to 15 wt.% increased the char yield from 12% to 20% and decreased the gas yield by 8% from 47 wt.%. While a 2.3 wt.% decrease bio-oil yield was noted with 10–15 wt.% amount of the catalyst ratio used. The release of water molecules formed during conversion of

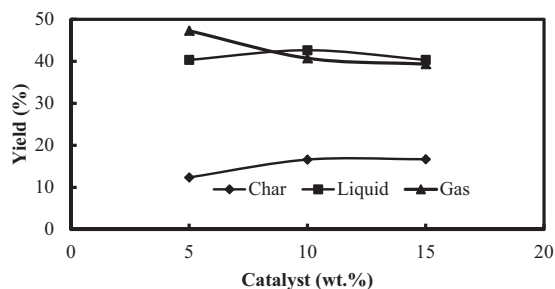


Fig. 4. Effect of Ca(OH)₂ amount on the EFB pyrolyzed products yield (600 °C, 200 mL/min).

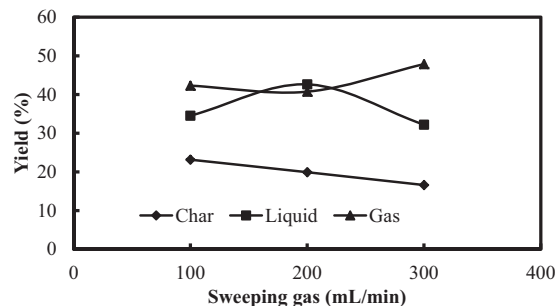


Fig. 5. Effect of sweeping gas flow on Ca(OH)₂ catalyzed EFB pyrolysis products yield (pyrolysis temperature of 600 °C for 10 min, 5 wt.% catalyst).

Ca(OH)₂ to CaCO₃ may have enhanced the yield of char with subsequent addition of the calcium hydroxide catalyst during pyrolysis. The decrease of the bio-oil yield as the catalyst ratio was increased to 15% after its initial increase (5–10 wt.%), revealed that 10 wt.% was the optimum amount of the Ca(OH)₂ that gave highest yield of the oil. This is similar to report on use of alumina catalyst for pyrolysis of herb residue industrial waste that had highest bio-oil yield between catalyst ratio range of 0–20% [36]. The slight decrease of gas yield with increase in the catalyst ratio showed that further increase of Ca(OH)₂ used did not promote conversion of char residue and bio oil formed by secondary decomposition to gaseous products. This is similar to report on EFB pyrolysis gas product yield with the addition of boric oxide catalyst [18].

3.7. Effect of sweeping gas flow rate on product yields

The sweeping gas influence on the EFB pyrolysis product yield was investigated by varying the N₂ flow rates of 100, 200 and 300 mL/min as other conditions such as catalyst ratio (5 wt.%) and fixed-bed pyrolysis furnace temperature (600 °C for 10 min) were fixed. The result of the sweeping gas effect on the Ca(OH)₂ catalyzed EFB pyrolysis is shown in Fig. 5.

The gas yield slightly decreased as sweeping gas flow rate was increased from 100 to 200 mL/min and then increased with further flow rate elevation to 300 mL/min which was directly opposite to the pattern observed for the bio-oil product yield. However at 200 mL/min sweeping gas flow rate, bio-oil product yield was higher (42 wt.%) which signified optimum flow rate that enhanced the Ca(OH)₂ EFB pyrolysis catalytic activities. Similarly, previous researchers observed that higher sweeping gas flow rate (>150 mL/min) favored gaseous product yield as against bio-oil yield that was found to be decreasing when the flow rate was exceeded [35].

3.8. The GC–MS analysis of the EFB pyrolyzed bio-oils

Gas chromatograph–mass spectrometry has been used in recent times for characterization of complex and heterogeneous bio-oil samples (polymers/copolymers) to augment the challenges often faced with the traditional gas chromatograph during analysis [37,38]. The bio-oils of both the non-catalytic and catalytic pyrolysis GC–MS analysis captures the desirable products (alcohols, aromatic and aliphatic hydrocarbons), high added value chemicals (furan and phenols) and undesirable products (acids, aldehydes, ketones, esters, ethers and other oxygenates) [39]. The GC–MS analysis was focused on similar components present in both the EFB non-catalytic and Ca(OH)₂ catalyzed pyrolysis bio-oils for comparison.

The two important quantitative data generated from GC–MS analysis are the peak area and retention time. The EFB pyrolysis bio-oil GC–MS quantitative data for non-catalytic and catalytic processes are presented in Table 2. The results revealed that

Table 2
Relative proportions (area %) of similar main pyrolysis compounds in bio-oils.

Name of compound	Formula	Peak area (%)		Retention time (min)	
		Bio-oil A*	Bio-oil B**	Bio-oil A*	Bio-oil B**
4-Pyrone	C ₅ H ₄ O ₂	1.838	2.999	5.444	5.189
Phenol	C ₆ H ₆ O	7.585	14.601	5.954	5.564
1,3-Methyl-1,2-cyclopentanediol	C ₆ H ₈ O ₂	1.344	2.496	6.439	5.984
1,2,3-Butanetriol	C ₄ H ₁₀ O ₃	4.233	6.841	7.960	7.230
Phenol, 2-methoxy-4-methyl-	C ₈ H ₁₀ O ₂	0.363	0.319	9.371	8.445
1,2-Benzenediol	C ₆ H ₆ O ₂	1.404	2.423	10.601	9.311
Phenol, 2,6-dimethoxy-	C ₈ H ₁₀ O ₃	6.020	7.381	12.222	10.741
Benzenemethanol, 3-hydroxy-5-methoxy-	C ₈ H ₁₀ O ₃	0.269	0.477	12.567	11.041
Phenol, 4-methoxy-3-(methoxymethyl)-	C ₉ H ₁₂ O ₃	0.690	1.342	13.717	11.962
9-Ethoxy-10-oxatricyclo[7.2.1.0(1,6)]dodecan-11-one	C ₁₃ H ₂₀ O ₃	0.430	0.509	15.088	13.072
Phenol, 2,6-dimethoxy-4-(2-propenyl)-	C ₁₁ H ₁₄ O ₃	0.410	0.875	17.589	15.078
Thiophene, 2-isobutyl-5-isopentyl-	C ₁₃ H ₂₂ S	1.220	1.257	18.479	15.798
Oleic acid	C ₁₈ H ₃₄ O ₂	42.885	7.675	33.111	24.612
Total area		68.691	49.195		

A* is non-catalyzed pyrolysis bio-oil, B** is Ca(OH)₂ catalyzed pyrolysis bio-oil.

there was significant difference between non-catalytic and catalytic pyrolysis GC–MS length of time between the bio-oil injection and elution of individual components or the target component peak (retention time); also the amount of electronic charge measured over a certain period by the detector (peak area). The main components identified in the EFB bio-oils were phenolic compounds and their derivatives which were approximately 16.74% and 27.42% for non-catalytic and catalytic biomass pyrolysis oils products, respectively. The high value added phenolic chemicals of important commercial value are compounds consisting of phenols, methoxyphenols eugenols and alkylphenols which are common components found in biomass pyrolysis bio-oils [40]. Also detected were oleic acid, 9-octadecenoic (C₁₈H₃₄O₂) with 18 carbon atoms which had peak area of 42.88% in non-catalytic and 7.67% in Ca(OH)₂ catalyzed EFB pyrolysis bio-oils. The presence of acids though could serve as source for chemical feedstock when harnessed but causes corrosion effects and a hindrance for use in transportation sector which is detrimental to the bio-oil quality [41]. The GC–MS bio-oil analysis showed that the use of Ca(OH)₂ catalyst for the EFB pyrolysis had significant effect by its influence on reduction of undesirable acidic component in the oil and its enhancement of decomposition of the biomass to yield more desirable phenolic compounds [39]. This result is similar to report by previous researchers on use of Ca(OH)₂ as catalyst for pine wood pyrolysis in fixed-bed that observed complete disappearance of acid groups of the emergent bio-oil which was attributed to the catalyst neutralization ability of the carboxylic groups in hemicelluloses [28].

4. Conclusion

Three catalysts (K₂CO₃, Ca(OH)₂ and MgO) applicability in the pyrolysis of palm oil empty fruit bunch (EFB) was investigated and Ca(OH)₂ catalyzed pyrolysis showed greater effect in improving the quantity of the targeted bio-oil product. This study involved evaluation of the fixed-bed operating factors impact on the product yield which include pyrolysis temperature, sweeping gas (N₂) flow rate and Ca(OH)₂ catalyst weight percent. The maximum bio-oil yield of 42.64 wt.% was obtained at pyrolysis temperature of 600 °C, 10 wt.% Ca(OH)₂ and sweeping gas flow rate of 200 mL/min. The GC–MS analysis of the Ca(OH)₂ catalyzed EFB pyrolysis bio-oil revealed higher percentage (>10%) of desirable phenolic compounds and lower undesirable acidic groups (>35%) when compared with the non-catalyzed EFB pyrolysis bio-oil analysis.

Acknowledgements

The authors acknowledge the research grant provided by the Ministry of Higher Education, Malaysia under the

Exploratory Research Grant Scheme (ERGS) (Project code: ERGS/1/2012/TK05/USM/01/5) that resulted in this article.

References

- [1] S. Zuo, Z. Xiao, J. Yang, *Journal of Analytical and Applied Pyrolysis* 95 (2012) 236–240.
- [2] Q. Bu, H. Lei, A.H. Zacher, L. Wang, S. Ren, J. Liang, Y. Wei, Y. Liu, J. Tang, Q. Zhang, R. Ruan, *Bioresource Technology* 124 (2012) 470–477.
- [3] I.V. Babich, M. van der Hulst, L. Lefferts, J.A. Moulijn, P. O'Connor, K. Seshan, *Biomass and Bioenergy* 35 (2011) 3199–3207.
- [4] S. Bezegeanni, Z. Fang (Eds.), *InTech*, 2013, ISBN 978-953-51-1050-7, pp. 299–326, <http://dx.doi.org/10.5772/52649>, <http://www.intechopen.com/books/liquid-gaseous-and-solid-biofuels-conversion-techniques/catalytic-hydroprocessing-of-liquid-biomass-for-biofuels-production> (accessed 22.06.13).
- [5] R. Miranda, C. Sosa, D. Bustos, E. Carrillo, M. Rodríguez-Cantú, V.H. Montoya (Eds.), *InTech*, 2012, ISBN 978-953-51-0197-0, pp. 57–77, <http://www.intechopen.com/books/lignocellulosic-precursors-used-in-the-synthesis-of-activated-carbon-characterization-techniques-and-applications-in-the-wastewater-treatment/no-title-specified-4> (accessed 22.06.13).
- [6] J.P. Diebold, A Review of the Chemical and Physical Mechanisms of the Storage Stability of Fast Pyrolysis Bio-Oils. In: National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, Colorado 80401-3393, Midwest Research Institute, Battelle, U.S.A., 2000, pp. 1–59.
- [7] Y. Xu, X. Hu, W. Li, Y. Shi, S. Shaikat (Eds.), *InTech*, 2011, ISBN 978-953-307-491-7, pp. 197–223, <http://www.intechopen.com/books/progress-in-biomass-and-bioenergy-production-preparation-and-characterization-of-bio-oil-from-biomass> (accessed June, 2013).
- [8] E. Karimi, I.F. Teixeira, A. Gomez, E. de Resende, C. Gissane, J. Leitch, V. Jollet, I. Aigner, F. Berruti, C. Briens, P. Fransham, B. Hoff, N. Schrier, R.M. Lago, S.W. Kycia, R. Heck, M. Schlaf, *Applied Catalysis B: Environmental* 145 (2014) 187–196.
- [9] H. Yang, R. Yan, H. Chen, D.H. Lee, D.T. Liang, C. Zheng, *Fuel Processing Technology* 87 (2006) 935–942.
- [10] Z. Liu, F.-S. Zhang, J. Wu, *Fuel* 89 (2010) 510–514.
- [11] M.S. Abu Bakar, J.O. Titiloye, *Journal of Analytical and Applied Pyrolysis* 103 (2013) 362–368.
- [12] F.D.M. Mercader, M.J. Groeneveld, S.R.A. Kersten, N.W.J. Way, C.J. Schaverien, J.A. Hogendoorn, *Applied Catalysis B: Environmental* 96 (2010) 57–66.
- [13] A.V. Bridgwater, *Biomass and Bioenergy* 38 (2012) 68–94.
- [14] N. Thegarid, G. Fogassy, Y. Schuurman, C. Mirodatos, S. Stefanidis, E.F. Iliopoulou, K. Kalogiannis, A.A. Lappas, *Applied Catalysis B: Environmental* 145 (2014) 161–166.
- [15] J. Chattopadhyay, C. Kim, R. Kim, D. Pak, *Journal of Industrial and Engineering Chemistry* 15 (2009) 72–76.
- [16] Z. Wang, J. Cao, J. Wang, *Journal of Analytical and Applied Pyrolysis* 84 (2009) 179–184.
- [17] E. Pütün, *Energy* 35 (2010) 2761–2766.
- [18] X.Y. Lim, J.M. Andrésen, *Fuel Processing Technology* 92 (2011) 1796–1804.
- [19] M.K. Lam, K.T. Lee, *Biotechnology Advances* 29 (2011) 124–141.
- [20] M.A. Sukiran, C.M. Chin, N.K. Abu Bakar, *American Journal of Applied Sciences* 6 (2009) 869–875.
- [21] M. Misson, R. Haron, M.F. Kamaruddin, N.A. Amin, *Bioresource Technology* 100 (2009) 2867–2873.
- [22] N. Abdullah, H. Gerhauser, F. Sulaiman, *Fuel* 89 (2010) 2166–2169.
- [23] T.S. Nguyen, M. Zabeti, L. Lefferts, G. Brem, K. Seshan, *Biomass and Bioenergy* 48 (2013) 100–110.
- [24] B.B. Uzun, N. Sarioğlu, *Fuel Processing Technology* 90 (2009) 705–716.

- [25] N. Prakash, T. Karunanithi, *Journal of Applied Sciences Research* 4 (2008) 1627–1636.
- [26] S.W. Kim, B.S. Koo, J.W. Ryu, J.S. Lee, C.J. Kim, D.H. Lee, G.R. Kim, S. Choi, *Fuel Processing Technology* 108 (2013) 118–124.
- [27] S. Sensoz, D. Angin, *Bioresource Technology* 99 (2008) 5492–5497.
- [28] Z. Wang, F. Wang, J. Cao, J. Wang, *Fuel Processing Technology* 91 (2010) 942–950.
- [29] I. Velghe, R. Carleer, J. Yperman, S. Schreurs, *Journal of Analytical and Applied Pyrolysis* 92 (2011) 366–375.
- [30] H. Deng, L. Yang, G. Tao, J. Dai, *Journal of Hazardous Materials* 166 (2009) 1514–1521.
- [31] W. Tongpoothorn, M. Sriuttha, P. Homchan, S. Chanthai, C. Ruangviriyachai, *Chemical Engineering Research and Design* 89 (2011) 335–340.
- [32] Z. Gökdağ, A. Sinağ, T. Yumak, *Biomass and Bioenergy* 34 (2010) 402–410.
- [33] I. Ahmed, A.K. Gupta, *Applied Energy* 86 (2009) 1732–1740.
- [34] O.O. James, A.M. Mesubi, T.C. Ako, S. Maity, *Fuel Processing Technology* 91 (2010) 136–144.
- [35] L. Zhou, H. Yang, H. Wu, M. Wang, D. Cheng, *Fuel Processing Technology* 106 (2013) 385–391.
- [36] P. Wang, S. Zhan, H. Yu, X. Xue, N. Hong, *Bioresource Technology* 101 (2010) 3236.
- [37] K.L. Sobeih, M. Baron, J. Gonzalez-Rodriguez, *Journal of Chromatography A* 1186 (2008) 51–66.
- [38] P. Kusch, M.A. Mohd (Eds.), InTech, 2012, ISBN 978-953-51-0298-4, pp. 343–363, <http://www.intechopen.com/books/advanced-gaschromatography-progress-in-agricultural-biomedical-and-industrial-applications/pyrolysis-gaschromatography-mass-spectrometry-of-polymeric-materials> (assessed 22.06.13).
- [39] E.F. Iliopoulou, S.D. Stefanidis, K.G. Kalogiannis, A. Delimitis, A.A. Lappas, K.S. Triantafyllidis, *Applied Catalysis B: Environmental* 127 (2012) 281–290.
- [40] F. Ates, M.J.A. Işıkdağ, *Energy and Fuels* 22 (2008) 1936–1943.
- [41] N.A.S. Amin, M. Misson, R. Haron, M.F.A. Kamaroddin, N. Wan, N.W. Omar, K.-G. Haw, *International Journal of Biomass and Renewables* 1 (2012) 6–14.