Comparative Study of H-ZSM 5 Zeolite and Graphite Nanofiber (GNF) in Catalytic Pyrolysis of Oil Palm Fronds (OPF)

Cheah Kin Wai[1], Suzana Yusup[1*], Nur Suriawanie Muda[1], Nazratul Zaheera Abdul Kapor[1]

[1]Biomass Processing Centre, Centre of Biofuel and Biochemical, Mission Oriented Research, Chemical Engineering Department, Universiti Teknologi PETRONAS, Bandar Seri Iskandar Tronoh, Perak 32610, Malaysia

Abstract

In keeping an eye on the goal of a sustainable chemical and energy industry, bio-oil produced from biomass fast pyrolysis liquefaction has aroused great interests and attentions among various stakeholders. In present paper, carbon based catalyst, Graphite Nanofiber (GNF) was employed to investigate and evaluate its potential in thermal pyrolysis of Oil Palm Frond (OPF). The pyrolysis was carried out in a semi batch reactor which was externally heated by an electrical vertical split tube furnace. 15g of OFP biomass with 1.5g of catalysts is thermally decomposed at two distinct temperatures of 573K and 773K, producing a solid char residue and a liquefied vapour product after passing through a condenser. Comparative study of both catalyst performances in thermal pyrolysis of OPF was conducted in term of selectivity and conversion. Between Zeolite ZSM-5 and GNF, GNF catalysts achieved a better conversion performance in transforming a total of 66.57 wt% and 72.40 wt% of biomass into vapour and liquid products at 573K and 773K respectively. On the other hand, H-ZSM 5 Zeolite catalyst yields the highest selectivity of 64.33 wt% toward condensable vapour components at 773K with a remarkably high bio-oil yield of 45.71 wt%. Such superior results strengthened the fact of H-ZSM 5 Zeolite catalysts being the more effective catalyst than GNF in catalytic pyrolysis of OPF.

Key words: Catalytic Pyrolysis, Oil Palm Fronds, Bio-Oil, Graphite Nanofiber, H-ZSM 5 Zeolite

1. Introduction

Energy is the backbone of all human activities, ranges from domestic household usage to heavy industrial applications. The accomplishment of civilization so far have been mainly achieved through efficient and extensive harnessing of various forms of energy within the constraints of the planet's limited natural resources available. However, the rapid growing world population and inevitable human innate's aspirations for sustainable economic development have placed enormous demands on fossil fuel stock supply, which in turns resulted in escalating tensions associated with fossil fuel shortage and environmental consequences of an ever increasing consumption of non-renewable resources. Thus, the paramount global challenge in the new century would be exploring and developing new renewable energy as alternative source in order to renovate the energy sources structure as well as keeping sustainable development safe.

Thermo conversion of biomass is one of the leading near-term options for renewable fuel production and the resultant product, biomass derived fuels could be a promising prospective energy source of tomorrow due to its excellent reproducibility, resource universality and benign environmental protection [11,26]. Being the most abundant and largest renewable energy resource available in the world, lingo-cellulosic biomass materials are the ideal sustainable feedstock in producing such fuels with its low content of sulphur, nitrogen and ash. Unlike fossil fuels, photosynthesis in biomass plants harnesses the energy of sunlight and transforms atmosphere carbon to organic compounds and gaseous oxygen, whereas return it as it is decomposed. Hence, utilization of biomass as alternative energy resource promotes a closed carbon cycle with zero net emission of CO_2 in the atmosphere. Of the thermochemical technologies available up today, fast pyrolysis has been widely recognized as one of the most feasible and viable routes to renewable liquid fuels, chemicals and derived products. It involves thermal cracking of organic matrix as liquids and gaseous fuels under oxygen free atmosphere and moderate temperatures from 573K to 873K, yielding a dark brown free flowing liquid with a distinctive smoky smell, commonly known as bio-oil or pyrolysis oil [2]. The liquid product is readily served as a substitute for fuel oil in many static applications However, subsequent upgrading of the liquid fuel is mandatory and essential for further employment as transportation fuel or other chemical commodities due to its high acidity, moisture and oxygen content.

Virtually any types of biomass materials can be incorporated into the pyrolysis process. It could be forestry biomass [26], agricultural residues [23], energy crops [19] or even food wastes [1]. Among the diverse agriculture crops available in Malaysia,

*Corresponding author.
E-mail address : drsuzana_yusuf@petronas.com.my

oil palm (Elaeis guineensis) is one of the most versatile and productive oil producing crops widely grown in many tropical climatic regions of Southeast Asia, particulary in Malaysia and Indonesia. With national government's policy on crop diversification as well as intensification, accelerated growth in palm oil industry makes Malaysia as the world's largest producer and exporter of palm oil today followed by Thailand and Indonesia, contributing over 49.5 % of world production and 64.5% of world exports. In line with the unprecedented growth of the palm oil industry, voluminous quantity of palm biomass waste is generated every year. For every tonne of palm oil produced from a fresh fruit bunch, approximately 1 tonne of empty fruit bunch (EFB), 0.7 tonne of palm fibers, 0.3 t of palm kernels and 0.3 tonne of palm shells are yielded, which amounts of a total of palm biomass of 2.3 tonnes [6]. A total of 24 million tons of frond biomass is annually produced and left rotting between the rows of palm trees, mainly for soil conservation, erosison control and ultimtaley the long term benefits fo nutrient recycling [6]. Exploitation of such abundant biomass resource as feedstock has a bright potential in producing a sustainably renewable energy source due to its vast availability and sustainability in Malaysia as well as low raw material cost and high production efficiency of biomass-derived oil. The motivation of using OPF into wealth is further strengthened by the facts that biomass contitutes up to 90% of the palm oil production , while oil is only 10% [6].

Despite the abundant OPF waste available in Malaysia, little research works have been attempted on using OPF as the pyrolysis feedstock in producing bio-fuel, specifically bio-oil. Therefore, the present author attempted on using OPF as the feedstock in thermal pyrolysis process with the hope of improving the yield of bio-oil produced from conventional biomass resources. In addition, studies on the the use of Zeolite H–ZSM 5 catalysts for biomass pyrolysis have often been conducted and published with a number of underlying objectives. Zeolite H-ZSM 5 catalyts have been demonstrated to be effective in producing high quanlity of liquid products during the pyrolysis reactions [10]. However, there are still plenty rooms for further exploration on others potential new catalysts in improving the production of bio-oil. GNF is one of the carbon allotropes that has a wide range of applications in electronics, energy storage, catalysis and gas sorption, but still has not been used as a catalyst in bio oil production in any previous study. The lightweight and stable carbon based materials possess high surface area and flexible functionality which offer a great scope in studying the performance of the carbon based catalyst in thermal pyrolysis of biomass. Thus, this paper mainly focuses in the use of an innovative OPF biomass resource in catalytic pyrolysis and the comprehensive comparison between Zeolite ZSM-5, a conventional pyrolysis catalyst and GNF, a scarcely studies pyrolysis catalyst.

2. Experimental

With Zeolite H-ZSM 5 as reference catalyst, the primary aim of present study is to investigate the applicability of GNF as a carbon based catalyst in producing high yield of pyrolysis oil through catalytic pyrolysis of OPF. The catalyst performances at two pyrolysis temperatures: 573K and 773K were assessed, evaluated and compared in terms of product conversion and selectivity. Identification of phenolic compounds present within the oil was performed under Gas Chromatographic coupled with Mass Spectrometry (GC-MS). In additional, the relationships of reaction temperatures, catalyst pore structure and catalyst acidity on the product yields were examined and discussed as well.

2.1 Feedstock Preparation and Characterization

Raw OPF was obtained from FELCRA Berhad Nasaruddin, Bota, Perak, Malaysia. Prior to the experiment, the biomass samples were grinded and sieved to give desired particles size of < 300µm before they were dried in the oven at 1050C for 24 hour. The lignin cellulosic contents of OPF were determined by using Thermogravimetric analyzer EXSTAR TG/DTA 6300, covering the studies of fixed carbon, ash content, moisture content, and volatile matter. The ultimate analysis for the elemental composition of carbon, hydrogen, nitrogen and sulphur were determined under CHNS Analyzer, LECO (Model 932) based on ASTM D5291 standard. Elemental analysis results were used to calculate the oxygen contents and the high heating value was measured using IKA C5000 Bomb Calorimeter. The dried OPF properties are listed in Table 1:

Table 1 Characteristic of OPF

Proximate Analysis (wt%)		**Ultimate Analysis (wt%)**	
Moisture	5.3	Carbon, C	43.6
Volatile Matter	72.13	Hydrogen, H	4.76
Fixed Carbon	19.52	Oxygen, O	50.56
Ash	3.05	Nitrogen, N	0.52
High Heating Value, HHV (MJ/Kg)	18.11	Sulphur, S	0.57

2.2 Catalyst Preparation and Characterization

The catalysts employed in this work were GNF and Zeolite H-ZSM 5 supplied by Platinum Green Chemical Sdn.Bhd and Zeolyst International respectively. The calcination of the samples was performed by heating the catalysts in a quartz tube furnace reactor under N2 flow at 773K for 5 hours. From running down of the N2 adsorption-desorption isotherms, Brunauer–Emmett–Teller (BET) specific surface area and

microspore volume of as-prepared samples were determined at 77K by using Surface Area Analyser Micromeritics ASAP 2021. Morphology and particle size of the porous samples were observed under Field Emission Scanning Electron Microscopy (FESEM, Zeiss Supra 55VP) analyser.

2.3 Experimental Setup and Configuration

Figure 1 illustrates the overall set up of the catalytic pyrolysis experiment. The setup consists of a semi-batch reactor which is externally heated by an electrical vertical split tube furnace and the pyrolyzer unit is equipped together with a liquid collecting unit. A total of 15g of OPF biomass with constant particle size of < 300µm is placed into the borosilicate tube, along with 1 wt% of catalyst loadings sandwiched in between two layers of glass wool. In order to measure in-situ feedstock temperature, the thermocouple set is introduced into the borosilicate tube and connected to the furnace heating system. Before heating up the pyrolyser unit, the pyrolyzer unit is purged with inert nitrogen gas at a flow rate of 500 mL/min for 5 minutes (Rahman, et al., 2014). Nitrogen flow is then lowered to 60mL/min once the furnace heating system started. Throughout the study, the heating rate are kept constant at 20 °C/min. Overall, the OFP biomass is thermally decomposed at two distinct temperatures of 573K and 773K with an interval of 30 minutes in each run. Consequently, a solid black char residue and a liquefied vapour are formed after the thermochemical conversion. After the completion of each run, the reactor is left to cool down to room temperature with the presence of nitrogen flow before performing the product analysis.

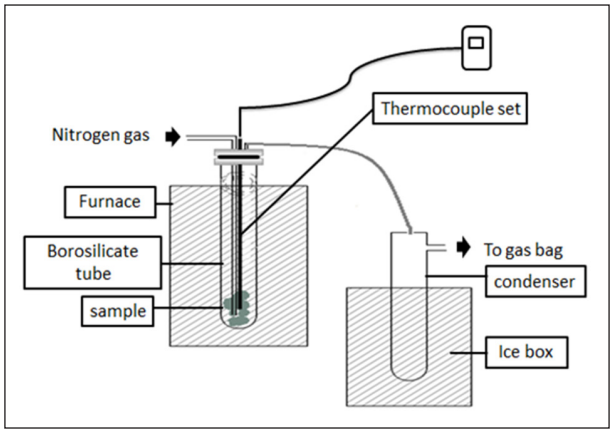

Figure 1 Semi Batch Reactor - Vertical Tube Furnace

2.4 Bio-Oil and Char Residue Yields Analysis

All product yields were reported on dry basic and each yield is basically averaged at two experiment replicates to ensure the reproducibility of the results obtained. The weight of bio-oil was computed by the weight difference of condenser before and after each run, similar to the weight of char residue formed. Comprehensive evaluation of the catalyst performance in thermal pyrolysis of OPF at two reaction temperatures was conducted in term of selectivity and conversion. Furthermore, the chemical compositions of bio-oil samples were analysed with an *Agilent 7890A GC model Clarus 500* (60m X 0.25mm ID, 0.25µm film thickness). Helium gas was employed as a carrier gas at a constant flow of 1.5mL/min. The dilution solvent used was methanol and the dilution rate was 1:5. About 1µL of diluted liquid bio-oil was injected into the column. The initial column temperature, 313K, was maintained isothermally for approximately 10 minutes. Thereafter, the temperature was subsequently raised to 348K at 0.90 °C/min, until the final temperature reached 393K. Finally, the final temperature of 473K was achieved with a very steep 10 °C/min ramp. The inlet pressure of the column was 135kPa and the scanning range was 10-300 amu.

With reference to Rahman et al [23], the percentage of char and liquid product yields were defined as:

$$Y_{Solid/Liquid} = \frac{W_{Solid\,/\,Liquid}}{W_{DriedOPF}} \times 100\% \qquad \text{Eq.1}$$

While selectivity and conversion of product yields were defined as [25]:

$$S_{Liquid} = \frac{W_{Liquid}}{W_{DriedOPF} - W_{Char}} \times 100\% \qquad \text{Eq.2}$$

$$C = \frac{W_{DriedOPF} - W_{Char}}{W_{DriedOPF}} \times 100\% \qquad \text{Eq.3}$$

3. Results and Discussion

3.1 Catalyst Characterization

Figure 2 illustrates the microstructural and morphologies of GNF and Zeolite H-ZSM 5 catalysts under TEM imaging. From Figure 2(A) and 2(D), both catalyst materials exhibits the same morphology structures as one-dimensional lines with nano-scale interplanal spacing were found in a regular arrangement on the catalyst surfaces. The coffin shape like zeolite crystals exhibit its rows of lattice reflection lines resulting from the regular atomic structure within the crystal, whereas the graphite plane layers of GNF fibers are stacked at a certain angle with respect to the axis of the hollow fiber and resulting fibers with exposed edge planes along the entire interior and exterior surfaces of the nanofibers. The GNF microstructure can be identified as "stacked cup" or "herringbone structure" which is in good agreement with the findings obtained by

Klein, et al. [13]. In additional, GNF samples have a hollow core coated with a cylindrical graphide like morphology layer, along the longitudinal axis of fiber, as depicts in Figure 2(C). In terms of the physiochemical properties, despite the same lattice structures, Zeolite H-ZSM 5 exhibits a higher surface area of 400m^2/g and a smaller pore volume of 0.125 cm^3/g in constrast to GNF catalyst with surface area of 173.3262 m^2/g and pore volume of 0.422 cm^3/g.

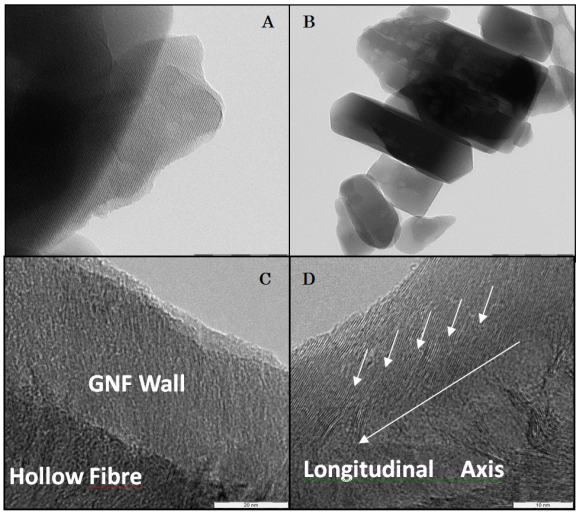

Figure 2 A) TEM image of Zeolite H-ZSM 5 at 50nm, (B) TEM image of Zeolite H-ZSM 5 at 100nm, (C) TEM image of GNF at 20nm, (D) TEM image of the GNF structure at 10nm

3.2 Effect of Temperatures on H ZSM-5 & GNF Catalytic Pyrolysis Yields

A preliminary analysis on the relationship between pyrolysis temperature and responding product yields was performed to evaluate the performance behaviour of both catalysts. The dependence of the product yields on the pyrolysis temperatures are presented in Figure 3 and 4, where it can be observed that more condensable liquid and gas products were yielded at high temperature, regardless of the type of catalysts. When the reaction temperature elevated from 573K to 773K, the liquid product yields increased slightly from 40.5 wt% to 45.7 wt% and from 41.3 wt% to 45.3 wt% for H-ZSM 5 and GNF catalysts respectively. Such results adequately agreed with many pyrolysis studies reported by Ates & b [3], Bunches [5], Rahman, et al. [22] and Sukiran, et al. [24]. At high temperature, more heat energy is being transferred into the inner core of the biomass structure which reduces the temperature gradient of the biomass particles and resulting in improved decomposition efficiency and better production of liquid yields.

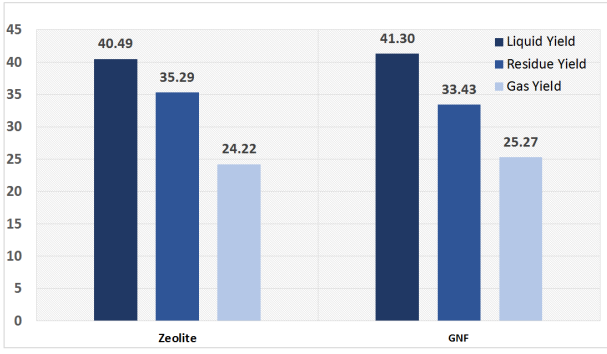

Figure 3 Liquid, Residue & Gas Yields of Zeolite H-ZSM 5 & GNF Catalytic Pyrolysis at 573K

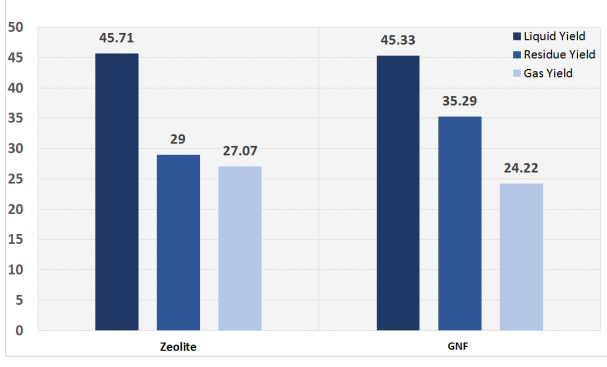

Figure 4 Liquid, Residue & Gas Yields of Zeolite H-ZSM 5 & GNF Catalytic Pyrolysis at 773K

However, it is noticeable that for both catalyst materials, the liquid product yield is relatively low at the temperature of 300 °C and this could be attributed to partial decomposition of the solid fraction within the biomass structures. When the pyrolysis products of the organic matters start forming at low temperature, the decomposition mechanisms of the biomass structure are still in partial, which is consistent with the high char yield obtained at such low temperature [3]. Furthermore, the decrease in char yield with an increase in pyrolysis temperature could either be due to greater primary biomass decomposition or through secondary cracking of pyrolysis oil into gaseous products. Increment of temperature has made the rate of thermal cracking reaction of the pyrolysis vapors becomes faster, thus resulting in the rapid release of non-condensable compounds such as carbon dioxide and carbon monoxide. This elucidated on the sudden sharp increment in the gas yields from 573Kto 773K.

In the context of liquid product yields, the present author revealed that GNF catalytic pyrolysis yielded a greater quantity of liquid products at low temperature, while high pyrolysis temperature is more favourable in Zeolite H-ZSM 5 catalytic pyrolysis for producing high liquid product yield. Furthermore,

catalytic pyrolysis of OPF using Zeolite H-ZSM 5 generates lesser gas yield as compared to GNF catalysts. However, the latter offers better biomass decomposition efficiency which leads to lower char residue yields. In overall, Zeolite H-ZSM 5 catalyst yielded the highest quantity of liquid product with the yield percentage of 45.71 wt% at pyrolysis temperature of 773K. Such high liquid yields can be explained by high porosity and surface area available on the catalyst surface which reduces diffusion limited transfer and provides effective chemical adsorption as well as reactant conversion [16].

3.3 Influence of Catalysts on Product Compositions

The composition of Zeolite ZSM-5 and GNF catalytic pyrolysis liquids are presented in Table 2. Due to the multiplicity of pyrolysis liquid products, only dominant organic compounds with percentage quantified area greater than 1% are incorporated into the present analysis. In general, the most representative organic compounds in pyrolysis bio-oil are classified into 9 functional groups: alcohols, ketones, phenols, esters, acids, aldehydes, ether, aromatics hydrocarbon and amines. Among the functional groups identified, aldehydes and phenols components constitutes principally in the liquid products at both pyrolysis temperatures and catalyst materials. The formation of phenolic compounds is mainly derived from secondary catalytic cracking of lignin derived compounds, which the C-O and C-C bonds are cracked at the acid sites of the catalysts [19]. Domination of such organic compounds in the liquid products accords with the earlier observations of Lai & Idris [14] where the encrusted lignocellulosic polymer of OFP biomass are rich in lignin components. It is further supported by the finding of Patwardhan, et al., [21], where high amounts of phenols, phenol derivatives and aldehydes are formed during pyrolysis of lignin and hemicellulose.

As can be seen from Table 2, catalytic pyrolysis using Zeolite ZSM-5 yielded a more diverse organic product distribution than GNF catalysts. Such superior cracking ability is mainly attributed to its high acidity property together with its specific shape and size selectivity, which theoretically increase the propensity of the catalyst in cracking reactions and resulting a higher extent of organic compounds. This finding corroborates with the previous studies of Aho, et al. [2], Atutxa, et al. [4], Horne & Williams [8] and Lappas et al. [15], in which high acidity zeolites are highly effective in promoting cracking reaction during catalytic pyrolysis reactions due to the presence of strong Brönsted and Lewis acid sites. Reactions such as cracking, dimerization, cyclization and dehydrocyclization typically takes places by donating protons to pyrolytic substrates at the acid sites of the catalysts [9]. Another reason behind such trend can be linked to its high specific surface area which promotes enhanced substrate access and improved diffusion, resulting in better product yields and quality.

On the other hand, the present authors revealed that the catalytic effects of GNF only slightly affected by the pyrolysis temperature as the composition of the liquid products formed does not varied much at both low and high temperatures, despite its high pore volumes. It could conceivably be hypothesised that the large pore volume potentially resulted in far less contact with incoming pyrolytic substrates and leads shapes selectivity becomes a non-issues [18]. Essentially, it offers significantly less cracking reactions to occur as pyrolytics products can be channelling through the catalyst freely with minimum contacts. Furthermore, the narrow product distribution range of GNF catalytic pyrolysis suggested that thermal pyrolysis could be the only pyrolysis reaction step as the neutral functionality of carbon based catalysts does not promote desirable cracking reactions on the organic matters as compared to Zeolite ZSM-5. In the context of aromatic production, the use of Zeolite ZSM-5 catalysts only resulted a small production of aromatic contents, which is surprisingly lower than the typical concentration values reported in the literature [7,9,16]. However, it can be seen that Zeolite ZSM-5 has a more pronounced effect in aromatization reaction as it forms a relatively strong aromatization of liquid products in contrast to GNF. Marcilla, et al. [17] reported that the high aromatization reactions could be attributed to the numerous Brönsted acid sites available within its structure, where intense cracking reactions take place.

Table 2 GC-MS Analysis of Pyrolysis Liquid Products

Group	GC-MS Peak Area (%)			
	Zeolite – 573K	Zeolite – 773K	GNF – 573K	GNF – 773K
Alcohols	3.49	2.4	0	8.06
Ketones	19.9	20.98	11.38	13.3
Phenols	19.72	40.05	37.99	37.18
Esters	9.91	1.96	0	0
Acids	0	1.88	0	0
Aldehydes	30.31	17.29	15.41	15.32
Ether	8.32	3.79	6.21	4.58
Aromatics	1.2	3.02	0	0
Amines	2.93	6.88	0	0
Total	98.60	98.25	70.99	78.44

3.4 Catalyst Performances Evaluation

Of H-ZSM 5 Zeolite and GNF, GNF catalysts achieved a better conversion performance in transforming a total of 66.57 wt% and 72.40 wt% of OPF into non-condensable vapour products and liquefy bio-oil at 573K and 773K respectively. On the other hand, H-ZSM 5 Zeolite catalyst yields the highest selectivity of 64.33 wt% toward condensable vapour components at 773K

with a remarkably high bio-oil yield of 45.71 wt%. In overall, it can be concluded that GNF catalyst has an excellent capability in converting organic matters into liquid and gaseous products, whereas Zeolite H-ZSM 5 owns a higher selectivity towards condensable vapour components which resulting in better liquid product yields.

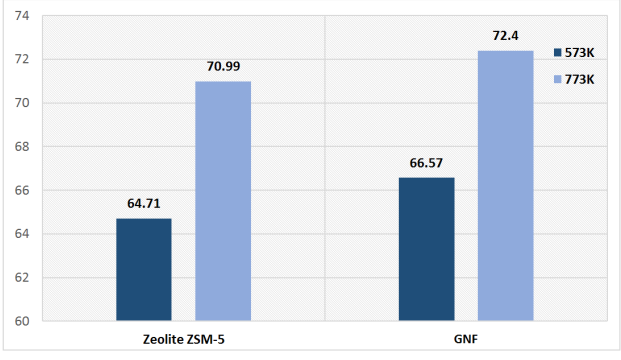

Figure 5 Biomass Conversion of Zeolite H-ZSM 5 & GNF at 573K & 773K

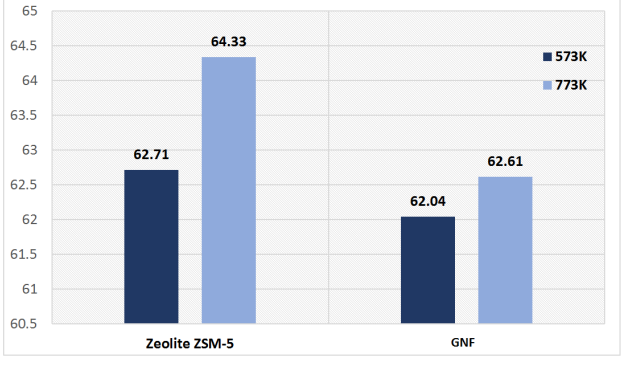

Figure 6 Zeolite H-ZSM 5 & GNF Catalyst Selectivity toward Condensable Organic components at 573K &773K

4. Conclusions

A comparative study between Zeolite ZSM-5 and GNF catalytic pyrolysis of Oil Palm Fronds (OPF) has been conducted in terms of biomass conversion and selectivity. Despite the low selectivity of GNF catalysts towards condensable gaseous components, Graphite Nanofiber (GNF) demonstrated relatively good biomass conversion performance at low temperature which is desirable from the prospective of energy efficiency. However, catalytic pyrolysis of Oil Palm Fronds using Zeolite H-ZSM 5 exhibits excellent conversion capability and higher selectivity towards condensable organic components at high temperature which ensuing in remarkably high production of liquid bio-oil yields.

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References

[1] Ahmed, I. & Gupta, A., 2010. Pyrolysis and gasification of food waste: Syngas characteristics and char gasification kinetics. *Applied Energy*, 87(1), pp. 101-108.

[2] Aho, A. et al., 2007. Fast pyrolysis of biomass for bio-oil with ionic liquid and microwave radiation. *Chemical Engineering Part B Process Safety and Environmental Protection,* 2007(85), pp. 473-480.

[3] Ates, F. & b, M. A. I., 2009. Influence of temperature and alumina catalyst on pyrolysis of corncob. Fuel, Volume 88, pp. 1991-1997.

[4] Atutxa, A. et al., 2005. Kinetic description of the catalytic pyrolysis of biomass in a conical spouted bed reactor. *Energy Fuel,* Volume 19, pp. 765-774.

[5] Bunches, B.-o. f. P. o. O. P. E. F., 2009. Mohamad Azri Sukiran; Chow Mee Chin; Nor Kartini Abu Bakar. *American Journal of Applied Sciences,* 5(6), pp. 869-875.

[6] Chang, S. H., 2014. An overview of empty fruit bunch from oil palm as feedstock for bio-oil production. *Biomass & Bioenergy,* Volume 62, pp. 174-181.

[7] Fostera, A. J. et al., 2012. Optimizing the aromatic yield and distribution from catalytic fast pyrolysis of biomass over ZSM-5. *Applied Catalysis A: General*, 423-424(2), pp. 154-161.

[8] Horne, P. & Williams, P., 1996. Upgrading of biomass-derived pyrolytic vapors over zeolite ZSM-5 catalyst: effect of catalyst dilution on product yields. *Fuel*, Volume 75, pp. 1043-1050.

[9] Iliopouloua, E. et al., 2012. Catalytic upgrading of biomass pyrolysis vapors using transition metal-modified ZSM-5 zeolite. *Applied Catalysis B: Environmental,* 127(1), pp. 281-290.

[10] J.Mihalcik, D., A.Mullen, C. & A.Boateng, A., 2011. Screening acidic zeolitesfor catalytic fast pyrolysis of biomass and its components. *Journal of Analytical and Applied Physics,* Volume 92, pp. 224-232.

[11] Junming, X., Jianchun, J., Jie, C. & Yunjuan, S., 2010. Biofuel production from catalytic crackin of woody oils. *Bioresource Technology,* 101(14), pp. 5586-5591.

[12] Khalil, A. et al., 2006. Chemical composition,anatomy, lignin distribution, and cell wall structure of Malaysian plant fibers. *BioResources*, 2(1), pp. 220-232.

[13] Klein, K. L. et al., 2008. Surface characterization and functionalization of carbon nanofibers. *Journal of Applied Physics,* 103(6).

[14] Lai, L. W. & Idris, A., 2013. Discruption of Oil Palm Trunks and Fronds by Mircowave-Alkali Pretreatment. *BioResources*, 2(8), pp. 2792-2804.

[15] Lappas, A. et al., 2002. Biomass pyrolysis in a circulating fluid bed reactor for the production of fuels and chemicals. *Fuel*, Volume 81, pp. 2087-2095.

[16] Lópeza, A. et al., 2011. Catalytic pyrolysis of plastic wastes with two different types of catalysts: ZSM-5 zeolite and Red Mud. Applied Catalysis B: Environmental, Volume 104, pp. 211-219.

[17] Marcilla, A., Beltrán, M. I. & Navarro, R., 2009. Thermal and catalytic pyrolysis of polyethylene over HZSM5 and HUSY zeolites in a batch reactor under dynamic conditions. *Applied Catalysis B Environmental*, Volume 1, pp. 78-86.

[18] Mihalcik, D. J., Mullen, C. A. & Boateng, A. A., 2011. Screening acidic zeolites for catalytic fast pyrolysis of biomass and its components. *Journal of Analytical and Applied Pyrolysis*, 92(1), pp. 224-232.

[19] Mullen, C. A. & Boateng, A. A., 2008. Chemical Composition of Bio-oils Produced by Fast Pyrolysis of Two Energy Crops. *Energy & Fuels*, Volume 22, pp. 2104-2109.

[20] Pattiya, A., Titiloye, J. O. & Bridgwater, A., 2008. Fast pyrolysis of cassava rhizome in the presence of catalysts. *Journal of Analytical and Applied Pyrolysis,* 81(1), pp. 72-79.

[21] Patwardhan, P. R., Satrio, J. A., Brown, R. C. & Shanks, B. H., 2009. *Product Distribution From Fast Pyrolysis of Hemicellulose.* Houston, Texas: American Institute of Chemical Engineers.

[22] Rahman, A. A., Abdullah, N. & Sulaiman, F., 2014. Temperature effect on the characterisation of pyrolysis products from oil palm fronds. *Advance in Energy Engineering (AEE)*, Volume 2.

[23] S, M., Bakar, A. & Titiloye, J. O., 2013. Catalytic pyrolysis of rice husk for bio-oil production. *Journal of Analytical and Applied Pyrolysis*, Volume 103, pp. 362-368.

[24] Sukiran, M. A., Bakar, N. K. A. & Chin, C. M., 2009. Optimization of Pyrolysis of Oil Palm Empty Fruit Bunches. *Journal of Oil Palm Reseach*, Volume 21, pp. 653-658.

[25] Vi, D. K., Yusuf, S., Uemura, Y. & Nuruddin, M. F., 2013. Catalytic Pyrolysis of Rice Husk via Semi-batch Reactor using L9 Taguchi Orthoginal Array. Advanced Material Reseaches, *Engineering and Manufacturing Technologies in Industry*, Volume 787, pp. 184-189.

[26] Zhang, H., Zheng, J. & Xiao, R., 2013. Catalytic Pyrolysis of Willow Wood with Me/ZSM-5 (Me= Mg, K, Fe, Ga, Ni) to Produce Aromatics and Olefins. *Bioresources*, 4(8), pp. 5612-5621.