Effect of Crystallization Temperature on the In-situ Valorization of Physic Nut (*Jatropha curcus* L.) Wastes using Synthetic HZSM-5 Catalyst

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Abstract. Physic nut waste is selected as the biomass feedstock for fast pyrolysis as it is available in large amounts from biodiesel production in Thailand. The volatile matter and fixed carbon contents are 73.8% and 13.6% while ash contents are 5.8%. Carbon is the main element with 49.03 wt%. The oxygen content of 39.0 wt% is considerably high which could directly convert to the oxygenated pyrolysis liquid products. To decrease oxygenated compounds, HZSM-5 was used as a catalyst to upgrade pyrolytic products from fast pyrolysis using analytical pyrolysis-GC/MS method. The HZSM-5 catalyst was successfully synthesized by hydrothermal method at 160 - 180°C for 24h. The particle size, surface area,

and pore diameter were 11.25 – 15.52 μm , 567-582 m^2/g , and 21.78-26.11 $\text{\AA}$, respectively. The pyrolysis was performed at 500°C with the Jatropha wastes to catalyst ratio of 1:1 to 1:10. The presence of HZSM-5 contributed to eliminate the undesirable oxygenated compounds such as acids and ketones which could alleviate problem regarding acidity and instability in bio-oil. In addition, it enhanced significantly the yields of desirable hydrocarbon compounds. The increase in catalyst contents had an effect on the enhancement of hydrocarbons yields, and tended to promote deoxygenation and denitrogenation. At moderate biomass to catalyst ratio (1:5), HZSM-5 synthesized at 170°C contributed to improve the hydrocarbon yields of 95%, including mainly toluene and xylene, which are valuable products because of their high heating value properties.

Key-words. Fast pyrolysis, Physic nut waste, HZSM-5 zeolite, Py-GC/MS

1. Introduction

Due to the scarcity of fossil fuel resources in the present and the increasing emissions of combustion-generated pollutants, alternative and renewable energy including wind power, solar power, hydrogen production, fuel cell and biomass have been paid much attention (Maher and Bressler, 2007). Among renewable energy, biomass is expected to be a renewable source in the near future because of its clean energy and the potential of biomass-derived fuel to replace fossil fuel. Biomass can be converted to a variety of fuels and chemicals by different techniques such as mechanical, biological, and thermal processes. Fast pyrolysis, the thermal decomposition process with a rapid heating rate, short residence time and the absence of oxygen, is one of the most effective methods to convert solid biomass to obtain high liquid yields of 70-80% (dry basis) as well as permanent gases and solid char. The main product

from fast pyrolysis is liquid product known as bio-oil (Bridgwater, 2012; Oasmaa and Czernik, 1999).

Physic nut waste, or *Jatropha curcus L.* (JCL), a small tree or large shrub, is one of the most promising biomass sources for bio-diesel production because of its interesting features such as non-edible and drought-resistant plant, easy propagation, and gives high oil contents (Achten et al., 2008; Koh et al., 2011; Pandey et al., 2012). After oil extraction process, the Physic nut wastes are the by-products which caused the disposal and environmental management problems. The idea to utilize this waste as a biomass feedstock in pyrolysis application should be a good option to resolve these problems and moreover, create added value to this waste.

As-received bio-oil can be directly applied in many static applications such as boilers, industrial klins, and gas turbines (Bridgwater, 2012; Oasmaa et al., 2010). However, bio-oils show poor fuel properties compared to petroleum fuels including low heating value, incompatibility with conventional fuel, high viscosity, chemical instability and acidity. These poor fuel propertied resulted from oxygen-rich compounds derived from depolymerization and fragmentation reactions of cellulose, hemicelluloses and lignin such as water, acids, ketones, aldehydes, phenolics, sugars (Bridgwater, 2012; Oasmaa and Czernik, 1999). To upgrade bio-oil in transport fuel applications, catalytic cracking technologies by using zeolites such as ZSM-5, H-Y, Mordenite, Ferrierite, H-Beta, SAPO-34, USY on pyrolysis vapors are of interest in order to reduce the oxygen contents via dehydration, decarboxylation, and decarbonylation reactions and also increase hydrocarbon yields in bio-oils. Among zeolite catalysts, HZSM-5 with three-dimensional, having intersection channel system involving sinusoidal ($5.3 \times 5.6 \text{ \AA}$) and straight ($5.2 \times 5.7 \text{ \AA}$) channels revealed more effective for promoting the deoxygenation of pyrolysis products and increasing aromatic yields because of its unique characteristics such as acid property, shape selectivity, high

thermal stability. (Aho et al., 2008; Carlson et al., 2009; French and Czernik, 2010; Mihalcik et al., 2011; Mochizuki et al., 2013; Murata et al., 2012; Vichaphund et al., 2013; Vichaphund et al., 2014).

In addition, a few researchers suggested that ZSM-5 catalyst has the advantage of long life time and can be regenerated after pyrolyzed in fluidized bed reactor. Aho et al. proved that the spent zeolites including H-Beta, H-Y, H-ZSM5, and H-MOR were successfully regenerated at 450°C for 2 h without the changing structure of zeolites [Aho et al., 2008]. Carlson et al. studied the life time and regeneration of ZSM-5. They found that the catalyst could be applied in pyrolysis process for 10 times-regeneration cycles and was regenerated at 600°C in air atmosphere for 3 h. After characterization, the ZSM-5 structure after 10 reaction/regeneration cycles showed slightly change in the intensity of XRD peak at a small angle, $2\theta = 8$ [Carlson et al., 2011].

Hence, the aim of this work is to synthesize HZSM-5 zeolite by hydrothermal method and to investigate catalytic activity of the prepared catalysts for the conversion of physic nut waste to pyrolytic products. Catalytic fast pyrolysis was performed using analytical pyrolysis-GC/MS (Py-GC/MS) technique. This technique is the effective tool for the preliminary study involving catalytic activity and catalyst screening prior to scale up to the larger reactor system, where more quantity of physic nut waste could be fed and the effect of catalysts on bio-oil yield could be measured. The product distribution after HZSM-5 –catalyzed pyrolysis was discussed in terms of synthesis temperature and catalyst content to reveal the catalytic effects of the synthesized catalysts.

2. Material and methods

2.1 Biomass: Physic nut waste

Physic nut residues (*Jatropha* or *J. curcus L.*) used in this work was obtained from local plants that were left after extraction of oil from biodiesel production process from Chiang rai province, the northern part of Thailand. Prior to the test, this waste was dried at 60°C for 24 h, crushed with a grinder, and then sieved to particle size with equal or less than 125µm. The elemental, proximate and component analysis results of physic nut wastes are presented in Table 1. Physic nut wastes consisted of three main compositions including 59.20% cellulose, 18.00% hemicelluloses, and 22.80% lignin. The volatile matter and fixed carbon contents are 73.80% and 13.60% which are closed to those of wood while ash contents of 5.80% are higher than approximately 1% of wood. Carbon is the main element with 49.20 wt%. The hydrogen, nitrogen, and sulfur are 6.35, 4.47, and 1.10 wt%, respectively. The oxygen content of 39.60 wt% is considerably high which could convert directly to the oxygenated liquid products. Based on the ultimate analysis, the approximate chemical formula of the physic nut wastes can be written as $(C_{4.1}H_{6.4}O_{2.5}N_{0.3})_n$. The physic nut residue has acceptable heating value (LHV) of 18.8 MJ/kg (Czernik and Bridgwater, 2004; Oasmaa and Czernik, 1999).

2.2 Characterization of thermal degradation

The thermal degradation behavior of physic nut waste was conducted by using thermogravimetric analyzer (Mettler Toledo: TGA/SDTA 851). In each experiment, approximately 40-45 mg of samples were heated from 50°C to 1000°C with different heating rates of 10, 30, and 50°C/min in the presence of nitrogen gas with flow rate of 50 ml/min.

2.3 Catalyst synthesis and characterization

The reagents used in the synthesis of ZSM-5 zeolite were sodium metasilicate pentahydrate ($Na_2O_3Si \cdot 5H_2O$, $\geq 97\%$, Fluka), sodium aluminate ($NaAlO_2$, Al_2O_3 50-56%,

Sigma-Aldrich), tetrapropylammonium bromide (TPABr, 98%, Aldrich), ammonium chloride (NH_4Cl , $\geq 99.5\%$, Sigma-Aldrich). The compositions of reagents were in the following molar ratio: 40SiO_2 : 4TPABr : $41 \text{ Na}_2\text{O}:\text{Al}_2\text{O}_3$: $1882 \text{ H}_2\text{O}$. After mixing, the mixture solution was kept in a teflon lined stainless steel autoclave with the heat treatment in the range of $150\text{--}180^\circ\text{C}$ for 24h to crystallize zeolite. Then, the sample was filtered and washed by deionized water. The white powder was dried at 100°C overnight and calcined at 540°C for 5 h in air atmosphere to remove organic template. In order to obtain HZSM-5, the powder was converted to proton form by ion-exchange with 1 M NH_4Cl solution at 80°C for 8 h. After that, the sample was washed with deionized water to remove chloride ions, dried at 100°C overnight and then calcined at 540°C for 5 h in air atmosphere to obtain HZSM-5. Phase analysis of synthesized powder was confirmed by X-ray powder diffraction (XRD; PANalytical, X' Pert Pro) with 40kV, 45 mA, CuK_α radiation. The sample was scanned at 2θ from 5 to 60° with a step size of 0.02 . Microstructure was characterized by scanning electron microscope (SEM; JEOL, JSM-5410). The specific surface area and N_2 adsorption isotherms were measured by using a Quantachrome Autosorb-1. The hybrid nonlinear density functional theory (NLDFT) model describing N_2 absorption in micro/mesopores was used to calculate the pore size distribution.

2.4 Pyroprobe-GC/MS experiment

Pyrolysis experiment was carried out using a pyroprobe pyrolyzer (multi-functional pyrolyzer, PY-2020iD, Frontier Lab) with an auto-shot sampler AS-1020E interfaced to a gas chromatograph coupled to a mass selective detector (GCMS-QP2010, Shimadzu). Each experiment, catalysts were placed above 0.4 mg of physic nut waste to obtain the biomass to catalyst ratios of 1:1, 1:5 and 1:10. Then, the sample was pyrolyzed in the Pyroprobe batch reactor set at 500°C and hold for 30 s. The pyrolysis vapors were then flushed to and

identified by GC/MS. The column used was a 30 m $\times$ 0.25 mm Ultra alloy 5 (i.d., 0.25 μ m film thickness). Helium (99.999%) was used as a carrier gas with a column flow of 1.3 ml/min, and the split injector ratio was 1:50. During the analysis of the pyrolytic products, the oven temperature was started from 50°C (3 min) to 200°C (heating rate of 5°C/min) then to 350°C (heating rate of 10°C/min, hold 10 min). The injector and detector temperature was kept at 280°C, and the mass spectrometer was operated in EI mode at 70 eV. The mass spectra were obtained from m/z 20 to 800 with the scan speed of 625 amu/s. Identification of chromatographic peaks was achieved according to the NIST and Wiley mass spectrum library. The product yield (%) of pyrolytic products was calculated by the peak area % detected from GC/MS. Noncondensable gases and the solids left after the pyrolysis by using Pyroprobe-GC/MS techniques cannot be determined in this experiment setup (Carlson, et al., 2009; Thangalazhy-opakumar et al., 2012). For establishing of baseline measurement, physic nut waste was also tested for comparison.

3. Results and discussion

3.1 Biomass characterizations

TG-DTA analyses were applied to investigate thermal behavior of physic nut waste at heating rates of 10 to 50°C/min (Fig. 1). The degradation curve can be observed in three stages. The first stage (30-100°C) corresponded to the loss of moisture, while the second stages (250-400°C) resulted from the major decomposition of lignocellulosic biomass. Firstly, the decomposition of hemicellulose and some of the lignin occurred at 250°C, while the second degradation at 350°C should correspond to the decomposition of cellulose and the remaining lignin. The last stage, at the temperatures above 400°C, the final decomposition involved the aromatization process of lignin fraction. Furthermore, it was noticed that the degradation curves slightly shifted at high heating rates because the heat could not efficiently

transfer into the inside of biomass residues leading to the thermal gradient between inner and outer surface of the waste particles (Sricharoenchaikul and Atong, 2009).

3.2 Catalyst properties

After synthesis, the crystallization of samples after synthesis was investigated by XRD techniques as exhibited in Fig. 2. The XRD pattern of the powder synthesized at 150°C appeared to be the amorphous phase, which indicated that the proper zeolite crystallization at this composition required a higher reaction temperature (Fig. 2(a)). When increasing temperature up to 160°C (Fig. 2(b)), the crystalline phase of HZSM-5 was found in orthorhombic form according to JCPDS: 44-0003. The main peaks located at the 2θ of 7.9°, 8.8°, 23.1°, 23.7°, and 23.9° are in the range of typical specific peaks of ZSM-5 ($2\theta=7-9^\circ$ and $23-25^\circ$), while the two small peaks determining aluminium content in the zeolite framework were also found at 2θ of 45.0-45.5° (Ahmed et al, 1996; Szostak, 1998). A progressive increase in peak intensities with increasing synthesis temperature was observed (Fig. (c) and (d)). It indicated that the temperature influenced greatly on the ZSM-5 crystallization.

The morphologies of HZSM-5 synthesized with a variation of synthesis temperatures are displayed in Fig.3. At low temperature, 150°C, the large amorphous powder was observed which corresponded well to the XRD results discussed above (Fig.3 (a)). When increasing the synthesis temperature, the formation of zeolite crystal was observed. The powder synthesized at 160°C was closely spherical in shape and appeared in the agglomeration owing to interconnected particles with size less than 5 micron (Fig.3 (b)). It was found that the temperature contributed to enhance the nucleation and crystal growth processes (Cheng et al., 2008). The increase in zeolite crystallization was clearly observed at high temperature of 170 and 180°C. The particles tended to be more cubic in shape, particularly HZSM-5 synthesized at 170°C (Fig.3 (c)).

The particle size, surface area, pore volume and average pore diameter of synthesized powders were summarized in Table 2. H-ZSM5 synthesized at 160, 170, and 180°C for 24 h revealed the agglomerate in size with mean diameter in the range of 11.25 -15.52 μm . HZSM-5 powder synthesized at 160°C had high surface area of 573 m^2/g with average pore diameter of 26.11 $\text{\AA}$ and pore volume of 0.24 cm^3/g , whereas the surface area, average pore diameter, and total pore volume of other conditions were closed to the former one. The micro-mesoporous structure of synthesized ZSM-5 zeolites was performed by N_2 adsorption-desorption isotherms (Fig. 4 (a)). In case of ZSM-5 synthesized at 160°C, a type H4 hysteresis loop was observed on the isotherms at a relative pressure $P/P_0 > 0.4$ which was associated with the slightly larger average pore size. While, the type H4 hysteresis loop of HZSM-5 synthesized at 170 and 180°C was observed with the characteristic step-down in the desorption branch associated with the hysteresis loop closure at relative pressure $P/P_0 \approx 0.4$. Moreover, the pore diameter of all HZSM-5 powders was defined as mesoporous materials in the range of 20 -500 $\text{\AA}$. However, its values were closed to the pore diameter range of microporous materials according to IUPAC (Szostak, 1998). The micro-mesopore structure was clearly confirmed by the NLDFT pore size distribution of samples (Fig. 4 (b)). It showed the similarity of the micro- and mesopore structure of HZSM-5 synthesized at 160-180°C. The uniform micropore was in the range of 7.83-8.23 $\text{\AA}$ closed to the ideal ZSM-5 pore structure (5.2-5.7 $\text{\AA}$) and a variation of mesopore was in the range of 20-65 $\text{\AA}$.

From these results, it can be concluded that synthesis temperature had an effect on the zeolite crystallization. HZSM-5 produced at high temperature, 170 and 180°C, showed high crystallinity, surface area, and achieved the particles with the complete cubic in shape.

3.3 Catalytic activity

Non-catalytic pyrolytic products from the analytical pyrolysis consisted of 10 organic

compounds as demonstrated in Table 3. The yield (%) of each compound calculated based on the peak area (%). Each percentage of peak area was based on the peak areas of selected characteristic molecular or fragment ion chromatograms. The major compounds consisted of acid (51%) and nitrogen containing compounds (20%). Other oxygen compounds were ketones, alcohols, esters, ethers, and phenols. These oxygenated compounds resulted in poor properties such as instability and acidity in bio-oils (Lu et al., 2010; Pattiya et al., 2008). The heavy compounds such as sugar products were detected in small content, 3.7%. Unfortunately, the pyrolytic products contained small amounts of aromatic hydrocarbon (3%) and aliphatic HC (1%). The formation of these organic compounds resulted from three pyrolytic pathways. Firstly, the decomposition of lignin led to phenolic compounds. Secondly, the depolymerization of holocellulose including cellulose and hemicellulose generated anhydrosugars (e.g. levoglucosan), related derivatives and furans. While, the pyrolytic ring scission of holocellulose produced light organic products such as aldehydes, ketones, alcohols, and esters (Lu et al., 2009; Velden et al., 2010).

To upgrade the quality of pyrolytic products from pyrolysis of physic nut wastes, synthesized HZSM-5 zeolite with three-dimensional pore system consisting of sinusoidal and straight channels was used in this experiment.

In the catalytic fast pyrolysis experiment, HZSM-5 catalysts were initially carried out using biomass to catalyst ratio of 1:1. As can be seen in Table 3, the aromatic yields increased noticeably, while the reduction in the amount of oxygenated compounds including acid, ketone phenol, ether, and alcohol was clearly observed. This indicated that synthesized HZSM-5 promoted the deoxygenation reactions such as decarboxylation and decarbonylation of these oxygenated compounds and produced aromatic compounds effectively by undergoing a cyclization reaction (Carlson et al., 2011; Mullen and Boateng, 2010; Thangalazhy-Gopakumar et al., 2012). Among HZSM-5 catalysts, HZSM-5 synthesized at

170°C improved the highest aliphatic and aromatic hydrocarbon yields of 8.4 and 39.1%. However, the pyrolytic products with low catalyst content (1:1) so far consisted of high content of undesirable oxygenated compounds such as acid, ketone, and N-containing compounds. It is known that acid and ketone are responsible for acidity, ageing reactions, and instability of bio-oils. While Hydrocarbon compounds were desirable products from pyrolytic vapors because of their high heating value properties (Lu et al., 2009, 2010; Pattiya et al., 2008).

When the catalyst was loaded to five times of biomass (Fig. 5), high content of HZSM-5 catalysts contributed to increase the aliphatic and aromatic hydrocarbons significantly and decreased both oxygenated and nitrogen containing compounds remarkably. This was because the increase in active site and their pore structures promoted the deoxygenation, denitrogenation and hydrocarbon formation. HZSM-5 synthesized at 160 and 180 °C showed the similarity in hydrocarbon yields. The yields of aromatic and aliphatic hydrocarbons were in the range of 64-69% and 12-15%, respectively. In contrast, HZSM-5-170°C exhibited more effective to enhance both the conversion of oxygenated compounds to aromatic compounds and the alkylation reaction of aliphatic and aromatic compounds to produce substituted benzene derivatives leading to higher aromatic yield of 93%. Moreover, this catalyst provided lower nitrogen compounds, only 2.9% than others, approximately 12 %. The higher aromatic yields from HZSM-5 prepared at 170°C could be attributed to its superior properties including high crystallinity, high surface area and particularly narrow pore diameter. As can be seen in Fig. 4 (b), HZSM-5 synthesized at 170°C showed highest peak intensity of the micropore range ($\sim 7.83 \text{ \AA}$) which is indicative of a greater number of smaller pore size than others. Thus, this catalyst could offer more selective pores in term of beneficially cracking pyrolytic products to aromatic products. The critical diameters of the major aromatics including benzene, toluene, ethylbenzene, xylene, naphthalene were in the

range of 6.63-7.1 Å (Yu et al., 2012), which closed to the pore size of HZSM-5 micropore synthesized at 170°C. This indicated that the pore size of zeolite played an important role in the formation of aromatics. These results can be comparable to other observations using commercial ZSM-5 catalysts in catalytic fast pyrolysis of lignocellulosic biomass operating with a pyroprobe-GC/MS. Thangalazhy-Gopakumar et al. (2012) reported that the presence of ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3=50$, surface area 425 m^2/g) improved the aromatic yields significantly from 23 to 44.9% as biomass (green algae) to catalyst ratio increased from 1:1 to 1:4. In addition, nitrogen containing compounds dropped drastically from 16.7 to 3.1%. Mochizuki et al. (2013) investigated the pyrolysis of Jatropha husk using commercial zeolites such as H-USY, H-Mordenite, H-Beta and H-ZSM-5 and found that H-USY and HZSM-5 increased hydrocarbon yields from 2% to 69 – 80% with an increase in the biomass to catalyst ratio from 1:1 to 1:5.

When increasing catalysts to ten times, a significant change of pyrolysis vapors was noticed in terms of HZSM-5 catalysts synthesized at 160 and 180°C. It was found that high yields of hydrocarbons were obtained as 85 and 88%, respectively. Although, almost oxygenated and nitrogen containing compounds were diminished to less than 1 and 3%, the acid contents were detected considerably high as 11 and 6%. In case of HZSM-5 synthesized at moderate temperature, 170°C, it improved the hydrocarbon yield of 96%, which was as high as the hydrocarbon yield obtained from 1:5 ratio, approximately 95%. The limitation in catalytic performance at high catalyst content might be due to the catalyst deactivation causing by coke formation on/into micro-meso selective pore of 170°C - HZSM-5 framework (French and Czernik, 2010; Murata et al., 2012; Mochizuki et al., 2013; Vichaphund et al., 2014). The result showed that hydrocarbon yield can be satisfactorily improved with moderate catalyst content. Further increase in catalysts to ten times did not alter hydrocarbon yield distinctly beyond 96%.

Considering the major aromatic compounds as shown in Table 4, the main aromatics produced by synthesized HZSM-5 catalysts were benzene, toluene, xylene (m-, p- and o-xylene), ethylbenzene and naphthalene which were in range of gasoline (C₅-C₁₂) (Carlson et al., 2011; Escola et al., 2012). It was noticed that synthesized HZSM-5 promoted the formation of all isomeric xylenes including *meta*-, *para*- and *ortho*-xylene due to larger pore size of ZSM-5 framework with micropore in the range of 7.83-8.23 Å. At low catalyst content (biomass:catalyst ratio of 1:1), HZSM-5 synthesized at 160°C and 180°C had the same aromatic selectivity with toluene> xylene> benzenes>ethylbenzene>naphthalene, while they generated more naphthalene than ethylbenzene at higher catalyst contents. The aromatic distribution at biomass:catalyst ratio of 1:5 and 1:10 were toluenes> xylene> benzene>naphthalenes> ethylbenzene. In contrast, the aromatic selectivity of HZSM-5 synthesized at 170°C was independent of the catalyst content. This catalyst generated slightly high naphthalene yield with the aromatic distribution of toluenes> xylene>naphthalenes>benzene> ethylbenzene whether pyrolyzed at low or high catalyst content. The result showed that toluene and xylene were the major aromatic products obtained from all HZSM-5 catalysts.

These aromatic distributions were corresponded to the results from other researches. Carlson et al. (2009) reported that the aromatic selectivity from catalytic fast pyrolysis of glucose, cellulose, cellobiose, and xylitol at 600°C using ZSM-5 (Si/Al=60) with feed to catalyst of 1:19 was naphthalene> toluene> xylene> benzene> substituted benzene ~ indane. Murata et al. (2012) studied the aromatic distribution from catalytic fast pyrolysis of three parts from jatropha wastes including husk, seed and branch with commercial ZSM-5 (biomass to catalyst ratio of 1:6.25) pyrolyzed at 550°C. All parts of jatropha wastes showed the similarity of the aromatic distribution which was xylene, naphthalenes, toluene, and benzene. In addition, Thangalazhy-Gopakumar et al. (2012) recently studied on catalytic

pyrolysis of green algae using H⁺ZSM-5 catalyst from Zeolyst Company. At biomass to catalyst ratios of 1:4 and 1:9, the major aromatic compounds in catalytic pyrolysis of algae pyrolyzed at 500°C were xylene>toluene>benzene>naphthalenes>ethylbenzene.

From these results, HZSM-5 showed high ability to promote catalytic cracking reaction for reducing oxygenated and N-containing compounds and increasing aromatic hydrocarbon yields because of their superior properties such as acid site, molecular sieve characteristics, high surface area, and high thermal resistance. In addition, the increase in biomass to catalyst ratio had an effect on the enhancement of hydrocarbons yields through deoxygenation and denitrogenation. In catalytic view point, HZSM-5 synthesized at 170°C seemed to be appropriated catalyst to upgrade pyrolytic vapors. It effectively produces the highest yields of hydrocarbons and lowest undesirable oxygenated- and nitrogen containing compounds at moderate biomass to catalyst ratio of 1:5.

Further investigation on the HZSM-5 catalytic cracking performance is in progress in a continuous feed fixed-bed reactor to estimate carbon mass balance and to compare product selectivity with the Py-GC/MS findings. The effect of HZSM-5 catalyst on bio-oil yield and properties will be further analyzed.

4. Conclusion

HZSM-5 zeolite was successfully synthesized by hydrothermal reaction method at temperature of 160, 170 and 180°C for 24h. HZSM-5 produced at high temperature, 170 and 180°C, showed high crystallinity, high surface area of 567-582 m²/g, small pore size of 21.78 - 24.83 Å, and achieved the particles with the complete cubic in shape.

Non-catalytic pyrolytic products of physic nut waste showed high contents of acid (51%), oxygenated compounds (21%), N-containing compounds (20 %) and small amount of

desirable hydrocarbons (4 %). In the presence of HZSM-5 catalysts, the higher aromatic yields and lower oxygenated and N-containing compounds were achieved. The increase in catalyst contents had an effect on the enhancement of hydrocarbon yield, and tended to promote deoxygenation and denitrogenation. HZSM-5 synthesized at 170°C was an appropriated catalyst to upgrade pyrolytic vapors because it produced highest yield of hydrocarbons, 95% which are usually considered to be valuable products because of their high heating values. In addition, it decreased undesirable oxygenated- and nitrogen containing compounds to 1.4% and 3%, at moderate biomass to catalyst ratio of 1:5. The main aromatics generated by HZSM-5 synthesized at 170°C were toluenes>xylene>napthalenes>benzene> ethylbenzene.

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Figure(s)

Fig. 1 (a) DTA and (b) TG of Physic nut residue from Chiang rai with size less than 0.125 mm at different heating rates in the range of 10, 30 and 50 °C/min

Fig. 2 XRD patterns of HZSM-5 products synthesized at: (a) 150°C, (b) 160°C, (c) 170°C, and (d) 180°C

Fig. 3 SEM micrographs of HZSM-5 products synthesized at: (a) 150°C, (b) 160°C, (c) 170°C, and (d) 180°C

Fig. 4 HZSM-5 catalysts with synthesis temperatures of 160, 170 and 180°C: (a) N_2 adsorption-desorption isotherms and (b) Pore size distribution by NLDFT method

Fig. 5 Yields of Pyrolytic products detected from GC/MS technique with physic nut (no catalyst), biomass to catalyst ratio of 1:5 and 1:10 (*Oxygenates: Alcohol, ether, ester, aldehyde, ketone, phenol)

Table 1 Elemental, proximate, and component analysis of the physic nut wastes

	wt%
<i>Element analysis</i>	
Carbon	49.20
Hydrogen	6.35
Nitrogen	4.47
Sulfur	1.10
Oxygen*	39.60
<i>Proximate analysis</i>	
Volatiles	73.80
Fixed carbon	13.60
Ash	5.80
Moisture	6.80
<i>Component analysis</i>	
Cellulose	59.20
Hemicellulose	18.00
Lignin	22.80
Oxygen* by difference	

Table 2 Textural properties of HZSM-5 catalysts

Catalysts	Temperature (°C)	Particle size (μm)	Surface area (m ² /g)	Average Pore size (Å)	Pore volume (cm ³ /g)
HZSM-5	160	11.25	573	26.11	0.24
	170	15.52	567	21.78	0.20
	180	13.54	582	24.83	0.23

Table 3 Pyrolytic products (% area) of non-catalytic and catalytic pyrolysis with the biomass to catalyst ratio of 1:1

Catalysts	Hydrocarbons		Oxygenated compounds						Acid	N-comp.	Sugar
	Aliphatic	Aromatic	Phenol	Ketone	Aldehyde	Ether	Ester	Alcohol			
Physic nut wastes	1.0	3.0	5.1	7.5	-	3.7	2.0	3.0	50.7	20.3	3.7
HZSM-5-160°C	0.5	20.5	2.4	6.1	0.4	0.6	2.5	1.6	39.4	25.6	0.4
HZSM-5-170°C	8.4	39.1	4.6	3.4	-	0.7	2.4	0.4	13.3	22.9	4.4
HZSM-5-180°C	0.9	31.0	2.1	8.4	0.4	-	1.4	0.7	22.0	30.3	2.7

Table 4 Major aromatic yields detected from Py-GC/MS

Major aromatic compounds	Aromatic yields (%)									
	Biomass : catalyst				1:5			1:10		
	Physic	HZSM-5	HZSM-5	HZSM-5	HZSM-5	HZSM-5	HZSM-5	HZSM-5	HZSM-5	HZSM-5
	nut	160°C	170°C	180°C	160°C	170°C	180°C	160°C	170°C	180°C
Benzene	-	3.7	3.4	5.7	9.4	9.5	17.6	11.8	13.5	11.9
Toluene	3.0	6.1	12.9	9.1	16.5	28.8	16.8	21.0	22.8	21.9
Toluene, m-ethyl	-	2.2	2.3	2.8	4.9	2.6	2.2	3.5	1.5	2.4
Ethylbenzene	-	1.4	2.5	1.7	4.5	4.4	2.7	4.3	3.5	3.2
m-/p-xylene	-	-	9.4	-	1.6	-	11.4	2.6	-	16.9
o-xylene	-	3.8	0.5	6.2	13.5	24.4	-	16.2	27.0	2.2
Napthalene	-	0.8	2.4	1.2	2.2	5.0	2.0	2.7	7.0	5.1
Napthalene, 2-methyl	-	-	4.6	-	3.6	7.0	3.4	4.4	8.0	6.2