Catalytic pyrolysis of various agricultural residues over ZSM-5 derived from rice husk silica

Boongcharoenlab Karakate[1], Tongdang Johnny[1], Jaturapiree Adisak[2], Sukrat Kanjarat[2], Saowapark Thanunya[2] and Chaichana Ekrachan[2*]
1. Department of Chemical Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University, Muang, Nakhon Pathom, 73000 THAILAND
2. Research Center of Natural Materials and Products, Chemistry Program, Faculty of Science and Technology, Nakhon Pathom Rajabhat University, Muang, Nakhon Pathom, 73000, THAILAND
*ekrachan@npru.ac.th

Abstract

Four types of agricultural residues including coconut shell, durian peels, pomelo shells and para rubber seeds were pyrolyzed with and without catalysts to obtain the value-added products especially bio-oil. The catalysts used in the pyrolysis were ZSM-5 derived from rice-husk silica (ZSM-5/RH) and commercial ZSM-5 (ZSM-5/Com). It was found that coconut shells and para rubber seeds provided the higher amount of liquid yield (bio-oil) than durian peels and pomelo peels. This was due to the higher volatile matter content as observed in the proximate analysis result. When introducing the catalysts both ZSM-5/RH and ZSM-5/Com into the pyrolysis systems, it decreased the bio-oil yield for most agricultural residues.

This was because the specific reaction generated by the catalysts including decarboxylation and decarbonylation turned the bio-oil into the pyrolytic gas. The quality of the bio-oils improved with the catalysts as observed that the bio-oil obtained from the catalytic pyrolysis had the lower content of oxygenated compounds especially phenols compared with the non-catalytic pyrolysis. In addition, it was found that ZSM-5/RH was comparable with ZSM-5/Com as they had nearly similar ability in reducing oxygenated compounds in the bio-oils. This provides the alternative way in using the agricultural residue (rice husk) as a catalyst for the pyrolysis besides using it as a biomass feedstock.

Keyword: Agricultural residues, Bio-oil, Catalytic pyrolysis, Zeolite.

Introduction

As one of the most fertile areas in Thailand, the western region of Thailand including Nakhon Pathom and Kanchanaburi produces large amounts of rice, coconut, fruits such as durian and pomelo and also natural rubber.

Therefore, the large amounts of residues from these products i.e. rice husk, coconut shells, durian and pomelo peels and natural rubber seeds are left in the fields causing an environmental impact. Converting these residues into valuable materials through pyrolysis is an interesting way for reducing their environmental impact and adding value to them.

Bio-oil from pyrolysis is considered renewable alternative fuel in replacement of fossil fuels whose production will go into terminal decline[1]. Nevertheless, bio-oil typically possesses high oxygen content when compared with fossil fuels (petroleum oil)[2-4]. The oxygen content in bio-oil originates from oxygenated organic compounds including carboxylic acid and carbonyl compounds which result in high acidity in bio-oil[5].

In order to reduce the oxygenated organic compounds, deoxygenation by cracking or dehydrating the compounds into the small molecules is perhaps efficient reaction to be used[6]. These reactions could occur on the solid surface with acid active sites. Therefore, solid catalysts with available acid sites were introduced into pyrolysis (catalytic pyrolysis) to generate the mentioned reactions. There have been many reports about the catalysts which can improve the bio-oil properties such as ZSM-5[7], FCC[8], HZSM-5[9], Y-zeolite[10] and $Ca(OH)_2$[11]. For zeolite, its remarkable catalytic performance is due to its highly porous structure and specific surface chemistry.[12,13]

Veses et al[14] suggested that the acidic sites on the zeolite surface play a central role in aromatization reactions and cracking of the oxygenated compounds in pyrolytic vapors. Kumar et al[15] also found that modified-zeolite with a high number of weak and strong acid sites provide deoxygenation for all the oxygenated compounds and favoured the production of aliphatic hydrocarbons.

In general, zeolite can be synthesized via a solvothermal method in the presence of silica and alumina precursors. Silica, a main precursor in zeolite synthesis, is so abundant and it can be locally obtained from agricultural residues like rice husk. Utilization of silica from rice husk for zeolite synthesis also conforms to an environmental issue consistent with producing bio-oil from agricultural residues. In our previous studies[16,17], the rice husk-derived silica has shown capability for used as a catalyst for pyrolysis when modified with vanadium.

The obtained bio-oil from the pyrolysis in the presence of the rice husk-derived silica/vanadium has lower acidity compared with the one in the absence of the catalyst.

Therefore in this study, to extend the use of rice husk-derived silica, it was employed as precursor for synthesis of zeolite ZSM-5 and then introduced to the catalytic pyrolysis of agricultural residue i.e. coconut shell, durian and pomelo peels and Para rubber seeds. The different properties of the agricultural residues could differently affect the pyrolysis system.

The synthesized ZSM-5 was also compared with its catalytic activity with the commercial one. The characteristics of these two catalysts were determined with various techniques. The different characteristics between two catalysts which influenced the catalytic performance during the pyrolysis were then further discussed. In addition, the effects of the catalysts on the pyrolysis were also emphasized.

Material and Methods

Materials: Rice husk, coconut shells, durian peels and pomelo peels were obtained from local areas in Nakhon Pathom province while Para rubber seeds from Kanchanaburi Province, Thailand. The coconut shells, durian peels, pomelo peels and Para rubber seeds were prepared as feedstock for the pyrolysis by grounding and sieving to obtain particles with approximately 1.0 mm. Hydrochloric acid (HCl, 37%) was purchased from RCI Limited, New Zealand. Sodium hydroxide (NaOH, 97%) was purchased from Ajax Finechem Pty Ltd., Australia. Sodium aluminate ($NaAlO_2$) and tetrapropylammonium bromide ($C_{12}H_{28}BrN$, 98%) were purchased from Sigma-Aldrich. Sulfuric acid (H_2SO_4, 98%) was purchased from Quality Reagent Chemical, New Zealand. All chemicals were used as received.

Preparation of rice husk-derived silica: Rice husk was soaked into the water for 24 h, filtered and then soaked in the solution of hydrochloric at 80°C for 1 h. The soaked rice husk was washed, neutralized and dried overnight in the oven. The prepared rice husk was then calcined under atmosphere at 700°C for 5 h to obtain the powder-like ash which was silica.

Preparation of ZSM-5: ZSM-5 was used as a catalyst for the pyrolysis and was prepared according to the method described in the work of Panpa and Jinawath[18]. The rice-husk silica (4.49 g) was dissolved in a specific amount of NaOH solution to obtain the desired composition of sodium silicate solution. 50 ml of the sodium silicate solution was mixed with 0.35 g of sodium aluminate, 0.2531 g of TPABr and 50 ml of 0.001 M NaOH solution. The pH of the mixture was adjusted to approximately 11 by the addition of 1 M HCl solution. The final mixture was further stirred for 30 minutes at room temperature to obtain the homogeneous mixture and then transferred to a reactor.

The reactor was heated hydrothermally to 220°C for 24 h. The participated product was separated by centrifugation, washed with DI water until neutral, dried at 110°C for 1 d and subsequently calcined in air at 550°C for 5 h. The obtained product was then subjected to ion-exchange with ammonium nitrate solution by mixing and stirring for 2 h. The mixture was filtered, dried and calcined at 550°C for 24 h. The catalyst (ZSM-5) from rice husk silica was finally obtained.

Pyrolysis: The feedstock was pyrolyzed in 0.5 L batch reactor with heating rate of 10°C/min until 500°C and held for 1 h. N_2 was used as carrier gas with flow rate of 170 mL/min. For the catalytic pyrolysis, the catalyst was impregnated with the feedstock at concentration of 10 wt.%. Products from pyrolysis included of 3 phases: liquid (bio-oil), solid (char) and gas. The percentage of product yield was calculated as follows;

$$\text{Product yield} = \frac{\text{weight of each phase}}{\text{weight of total product}} \text{x} 100\%$$

Characterization of agricultural residues

Proximate analysis: Proximate analysis of the agricultural residue samples was analyzed according to ASTM D-271-48 standard to determine ash content, volatile matter and fixed carbon.

CHNS elemental analyzer: Elemental analysis was obtained using ThermoScitific with combustion technique. Oxygen content was calculated by the difference from the total compositions.

Thermal gravimetric analysis (TGA): Thermal stability was determined using TGA technique with Perkin Elmer TGA 7. Samples of 10–20 mg were examined at a temperature ramping from 25 to 800°C at 10°C/min. The carrier gas was N_2 UHP. The TGA was also used for characterization of the catalysts.

Characterization of catalyst

X-ray fluorescence (XRF): The composition was measured with PANalytical MiniPal 4 EDXRF spectrometer equipped with a 30 kV rhodium anode tube with a helium purge facility. A high-resolution silicon drift detector was used to count X-rays intensity. Matrix corrections were made by using either a ratio to the Compton peak or theoretical alpha coefficients, using minipal 4 software.

Nitrogen physisorption: The surface area and pore characteristics were determined by nitrogen physisorption technique using Micromeritics ASAP 2020 surface area and porosity analyzer. The catalyst sample was thermally heated at 150°C for 1 h before nitrogen adsorption at temperature of -196°C.

Ammonia temperature-programmed desorption (NH_3-TPD): Acidity was investigated by ammonia TPD technique using MicromeriticsChemisorp 2750 Pulse Chemisorption System. First, the sample was heated at 500°C under helium atmosphere before saturating with 15% of ammonia in helium. Then, the physisorbed ammonia molecules were removed from the sample under helium flow at 40°C for 30 min. After that, the chemisorbed ammonia molecules were thermally desorbed from the sample by heating with temperature ranging from 40 to 800°C with a heating rate of 10°C/min. The amounts of ammonia thermally desorbed were measured via thermal conductivity detector (TCD) signal as a function of temperature.

Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX): The morphology was investigated using Tescan Mira3 Scanning electron microscope. The sample was conductive to prevent charging by coating with gold particle by Cressington Sputter Coater 108 sputtering device

Characterization of bio-oil

Fourier transform infrared spectroscopy (FTIR): The functional groups were determined using a Nicolet 6700 FTIR spectrometer. Infrared spectra were recorded with range of scanning from 400 to 4,000 cm^{-1} with scanning time of 64.

Gas chromatography–mass spectrometry (GC-MS): Types of compounds in the bio-oil were analyzed using GC-MS technique with Thermo Scientific (TG-5MS) equipped with a capillary polar wax column, polyethylene glycol (PEG)-coated (length of 30m, internal diameter of 0.25 mm and film thickness of 0.25 μm). The conditions used were as follows: injection volume of 0.2 μL, oven at 40°C (1 min) and continued with heating rate of 10°C min^{-1} to 300°C, split mode with a ratio of 100:1 and injection temperature of 290°C.

Bomb calorimeter: Heating value was determined with bomb calorimeter (Parr Instrument, IL61265) equipped with water bath and oxygen.

Results and Discussion

Characterization of agricultural residues: Proximate and ultimate compositions of all agricultural residue samples are shown in table 1. From proximate analysis, durian peels and pomelo peels had substantially higher contents of moisture and ash than coconut shells and para rubber seeds. Para rubber seeds exhibited the highest C and H contents among all samples. This may lead to the better properties of the obtained bio-oil from para seeds than the others. High O contents in durian peels and pomelo peels could reduce the calorific value of the obtained bio-oils[19].

Thermal decompositions of the samples were determined with TGA/DTG techniques. Fig. 1 shows TGA/DTG profiles of the samples. The TGA profiles of all samples seem different but still exhibited similar three main decomposition peaks ascribed to the first, second and third decompositions. The first decomposition is due to the moisture removal and evaporation of light volatiles in the samples which occur around 100°C[4]. The second decomposition is derived from cellulose and hemicellulose decompositions which occur between 240°C and 345°C. The third decomposition is the decomposition of lignin present in the samples which occur at high temperature above 350°C as a result of the stable structure of lignin which mostly consists of benzene rings[20,21].

Characterization of catalyst: Two types of catalysts were studied and then characterized here including 1) ZSM-5 synthesized from rice husk-derived silica designated as ZSM-5/RH and 2) commercial grade ZSM-5 designated as ZSM-5/Com. Details of surface and pore characteristics of the catalysts were determined with a nitrogen adsorption-desorption technique as shown in table 2.

Table 1
Proximate and ultimate analyses of the agricultural residues.

Samples	Proximate analysis (wt%)					Ultimate analysis (wt%)				
	Moisture	Volatiles	Fixed carbon[a]	Ash		C	H	N	S	O[a]
Coconut shells	2.90	74.06	21.24	1.80		47.79	5.86	0.11	0.00	46.24
Durian peels	5.59	73.47	16.22	4.72		40.92	5.71	1.07	0.05	52.25
Pomelo peels	4.01	69.68	19.77	6.54		41.02	7.00	1.13	0.02	50.83
Para rubber seeds	2.77	80.16	16.75	0.32		56.81	8.48	2.95	0.06	31.70

[a]by difference

Table 2
Surface areas, pore characteristics and acid properties of the catalysts.

Catalyst	Surface area	Pore diameter	Pore volume	Amount of acid sites (μmol/g)			
	(m^2g^{-1})	(nm)	(cm^3g^{-1})	Weak	Medium	Strong	Total
ZSM-5/RH	94.36	3.13	0.07	1671	526	554	2750
ZSM-5/Com	215.98	4.95	0.27	645	156	266	1067

It was found that the surface area and pore volume of ZSM-5/Com were significantly higher than those of ZSM-5/RH. In addition, the average pore diameter of ZSM-5/Com was also relatively higher than that of ZSM-5/RH. The difference in pore diameters of the catalysts could influence their catalytic performance during pyrolysis by limiting or allowing the accessibility of bulky molecules to be reacted insides the pores[22]. Morphology of the catalysts obtained from the SEM was shown in fig. 2. It was found that ZSM-5/RH had smaller particles than ZSM-5/Com, but they were agglomerated leading to the lower surface area.

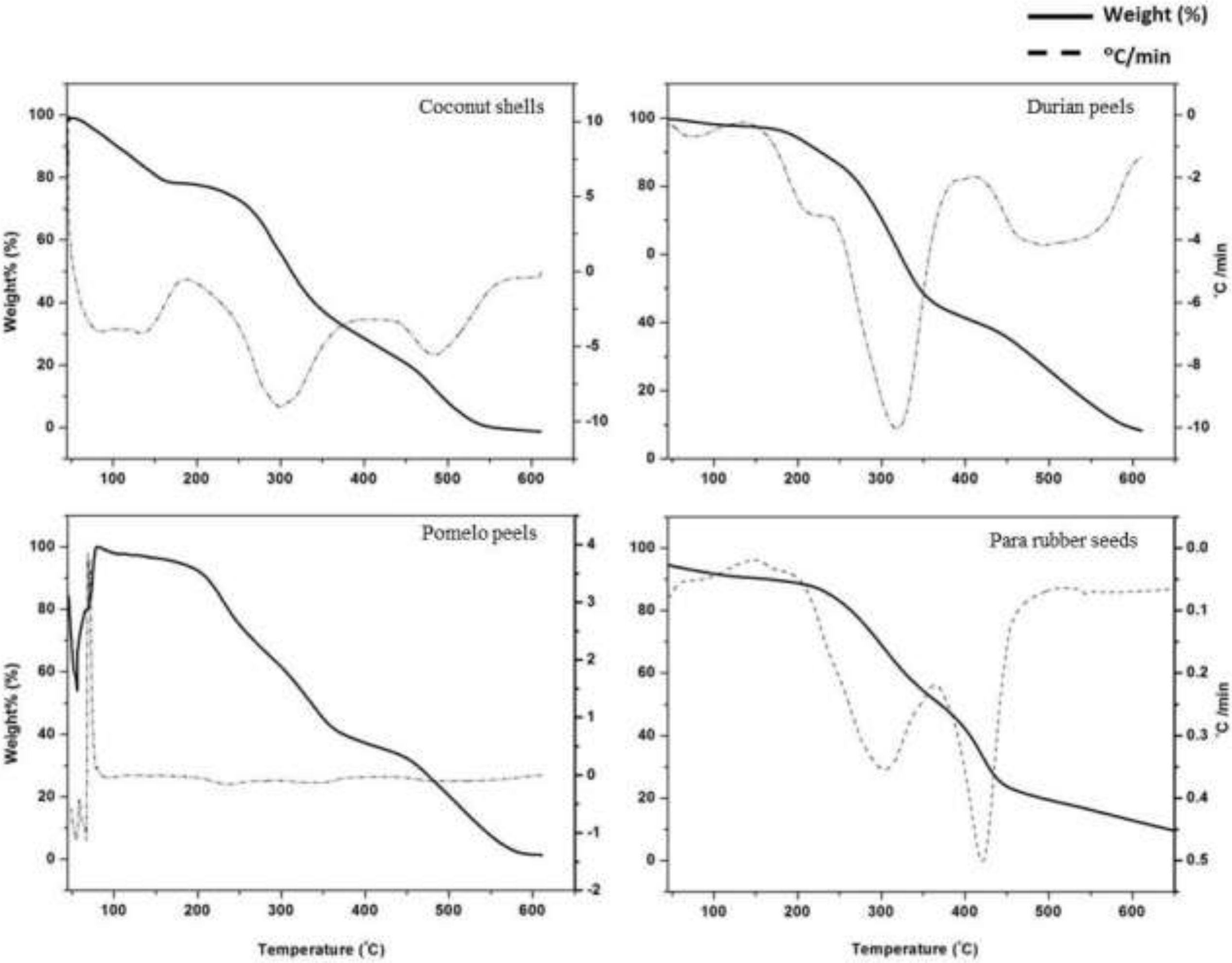

Fig. 1: TGA and DTA profiles of the agricultural residues

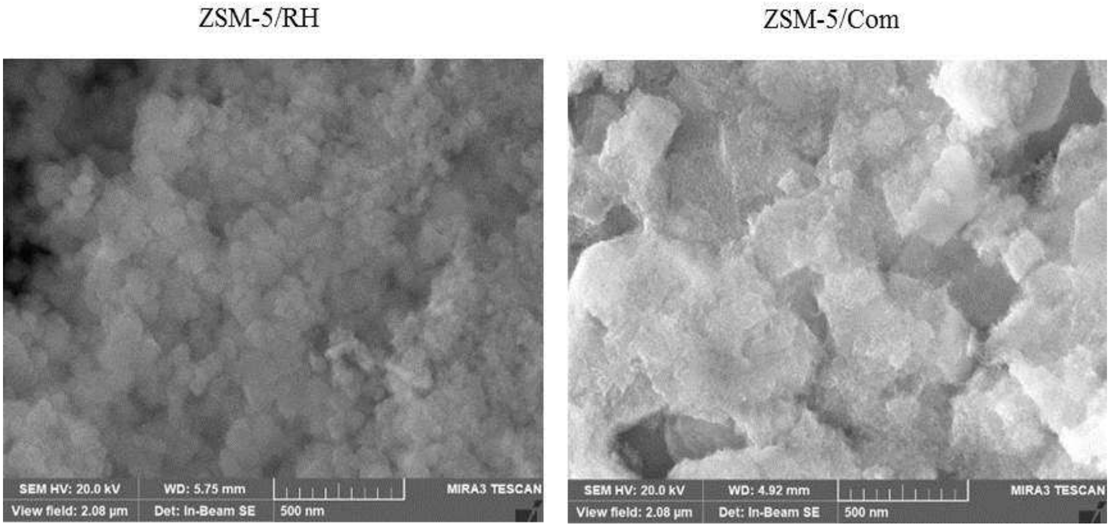
ZSM-5/RH
ZSM-5/Com

Fig. 2: SEM micrographs of the catalysts

Components of the catalysts were analysed by an X-ray fluorescence spectrometers (XRF). It was found that ZSM-5/RH had the higher silica (SiO_2) content than ZSM-5/com (90.86 and 74.30 wt.%), but the lower alumina (Al_2O_3) content (8.68% and 25.78 wt.%). It has been suggested that the higher content of Al could lead to the larger surface area and the higher micropore volume due to development of internal microporous structure caused by the aluminium[23]. This agrees with the pore characteristics of the catalysts as mentioned above.

Acidity of the catalysts was determined using an ammonia temperature-programmed desorption technique (NH_3-TPD). The NH_3-TPD detects acid sites of the catalysts and divides into 3 types; 1) weak acid sites (detected from desorption peaks below 250°C), 2) moderate acid sites (250-400°C) and 3) strong acid sites (>400°C). The amounts of the acid sites are calculated by integration of desorption area of ammonia according to the Gauss curve fitting method. The calculation results are shown in table 2. It was observed that ZSM-5/RH had higher amounts of all types of acid sites and total acid sites than ZSM-5/Com.

Thermal stability of the catalysts was observed by TGA/DTA measurement. It was observed that ZSM-5/Com showed higher thermal stability with the weight loss value at 800°C about 5% compared to ZSM-5/RH with the value of 12%. Both catalysts exhibited two decomposition peaks; around 100°C attributed to the removal of adsorbed water and around 500°C attributed to the removal of tetrabutyl ammonium ion which was used as template in the catalyst synthesis[24].

Pyrolysis: Three pyrolysis systems were conducted in this study including: 1) non-catalytic pyrolysis (no catalyst), 2) catalytic pyrolysis with ZMS-5/RH and 3) catalytic pyrolysis with ZSM-5/com. Four various types of agricultural residues i.e. coconut shells, durian peels, pomelo peels and para rubber seeds were used as feedstock for the pyrolysis. Product yield from all pyrolysis systems were shown in table 3.

Considering on liquid yields (bio-oil), it can be seen that for all pyrolysis systems, coconut shells and para rubber seeds provided the higher amount of bio-oil than durian peels and pomelo peels. This was because coconut shells and para rubber seeds had the higher volatile matter content than durian peels and pomelo peels as observed in the proximate analysis result.

Biomass having higher volatile matter content generally provides higher yield of bio-oil via pyrolysis. This is reasoned from the volatile matters being a source of condensable vapor which turns into the liquid bio-oil when condensed[25]. The higher ash contents in durian peels and pomelo peels decreased the bio-oil yields. In fact, ash is responsible for slagging and fouling problems which reduce the efficiency of the thermal conversion process[26,27] thus inhibiting the production of bio-oil[19].

The bio-oil yields of most samples decreased when the catalysts is present in the pyrolysis. These decreases are attributed to the reactions caused by the catalysts including decarboxylation and decarbonylation which turn bio-oil into pyrolytic gas[15]. The increases in gas yields in the catalytic systems compared with the non-catalytic systems could support this attribution. In addition, the char yields in most samples slightly changed due to the presence of the catalysts suggesting that phase transformation from liquid into gas is mainly involved in the catalytic reactions. Apparent discrepancies existed in the pyrolysis of durian peels with ZSM-5/Com; the bio-oil yields increases with the catalysts. This is probably due to the catalysts inhibiting gas and char production through oil as intermediates[28].

Effects of catalysts on the pyrolysis processes related to thermal decompositions of the materials can be observed by the TGA measurement. The agricultural samples were mixed with the catalyst (ZSM-5/RH) at the same ratio as in the pyrolysis systems and then measured with the TGA. Changes in TGA profile patterns due to the presence of the catalyst were observed in most samples but not clearly. In order to clarify the effect of catalyst, maximum decomposition temperatures (T_{max}) of the samples with and without the catalysts were compared as shown in table 4.

The T_{max} values in the first decomposition should not be of concern because vaporization of moisture inside the material can be influenced by many factors. The T_{max} values in the second decompositions of all samples exhibited the same trend increasing with the presence of the catalyst.

Table 3
Product yields from the pyrolysis of various agricultural residues.

Samples	**No catalyst**				**ZSM-5/RH**				**ZSM-5/Com**		
	Product yields (%)										
	Liquid	**Char**	**Gas**		**Liquid**	**Char**	**Gas**		**Liquid**	**Char**	**Gas**
Coconut shells	44.0	31.0	25.0		35.5	32.6	31.9		34.5	32.6	32.9
Durian peels	16.9	38.3	44.8		13.4	14.5	72.1		22.2	35.3	42.5
Pomelo peels	38.1	38.1	23.8		26.0	33.6	40.4		18.3	38.4	43.3
Para rubber seeds	42.0	29.0	29.0		35.7	32.2	32.1		37.1	30.5	32.4

Table 4
Maximum decomposition temperature of agricultural residues and agricultural residues mixed catalysts.

Samples	Catalyst	Maximum decomposition temperature, T_{max} (°C)		
		First	Second	Third
Coconut shells	No	82.4	298.3	488.5
	ZSM-5/RH	81.5	341.6	-
Pamelo peels	No	74.3	317.5	494.3
	ZSM-5/RH	90.2	341.1	463.1
Durian peels	No	88.3	342.1	507.5
	ZSM-5/RH	95.1	352.6	-
Para rubber seeds	No	87.4	304.2	419.7
	ZSM-5/RH	85.2	355.5	-

This may be reasoned as the catalyst also acted as additive in the pyrolysis systems which increases thermal resistance to the host material or the agricultural residues in this place. The thermal stability of the catalysts was also observed by the TGA measurement as mentioned earlier.

It can be seen that the catalyst was relatively stable to heat with its weight loss slightly changing upon heating up to 800°C. Therefore, the presence of the catalyst could slow diffusion of heat throughout the system leading to slower decomposition and higher decomposition temperature[29]. There has also been use of zeolite as additive for an increase of thermal stability to many materials such as polymer composites[30,31], film[32] and brake pad[33]. Thus, this evidently indicates the ability of zeolite in improving thermal stability to the host materials.

However, Kim et al[34] have conversely found that the catalytic pyrolysis with zeolite such as beta and ZSM-5 decreased the maximum thermal decompositions of the material (wood polymer) compared with the non-catalytic pyrolysis. The opposite was true for the study of Lazdovica et al[35] which the maximum thermal decomposition was slightly higher in the presence of the catalysts i.e. MCM-41 and ZSM-5.

Therefore, different materials may be affected differently by the same type of catalyst during pyrolysis leading to differences in thermal stability of the materials. In the third decompositions of all samples, it exhibited uncertainty values probably due to alteration during the second decomposition, consequently affecting thermal behavior in the third decomposition. In fact, in the third decomposition, lignin is mainly decomposed and it has been reported that ZSM-5 enhances the deoxygenation reaction during lignin pyrolysis[36].

Therefore, the change in thermal decomposition behavior in the third decomposition was due to the intensive deoxygenation of lignin via the catalyst. In addition, the other reactions during the pyrolysis process may also be affected by the change in thermal decomposition behavior, thus the product yields varied according to the presence of the catalyst.

Characterization of bio-oil: The bio-oils obtained from various materials were designated here as BO-CS, BO-DP, BO-PP and BO-PS for the ones obtained from coconut shells, durian peels, pomelo peels and para rubber seeds respectively. The chemical functional groups of the bio-oils from the pyrolysis without the catalysts were determined with the FTIR measurement. From the FTIR spectra in fig. 3, it can be seen that BO-DP and BO-PP exhibited similar patterns but considerably differed from those of BO-CS and BO-PS, both of which were similar. Broad absorbance peaks **(a)** between 3200 and 3600 cm^{-1} were significantly high in BO-DP and BO-PP.

These peaks corresponding to OH-stretching vibration indicate to water, alcohols and/or phenols in bio-oils. The higher contents of water in BO-DP and BO-PP is plausible resulting from the raw materials (durian peels and pomelo peels) used for the pyrolysis having high moisture content according to the proximate analysis. This suggests that both materials may not be suitable for the bio-oil production.

In addition, peaks b (2800-3000 cm^{-1}) was not observed in BO-DP and BO-PP. These peaks attributed to the C-H stretching vibration indicating the presence of alkanes[37]. Therefore, low amounts of alkanes compound were present in BO-DP and BO-PP. The other peaks found in the bio-oil samples included: peaks c and d (1650-1750 cm^{-1}) corresponding to C=O stretching attributed to ketone, aldehyde or carboxylic acids; peaks e, f and g (1000-1500 cm^{-1}) corresponding to C-O stretching attributed to esters, primary, secondary and tertiary alcohols[4]; peak h (689-900 cm^{-1}) indicating to mono-and polycyclic and substituted aromatic groups.

Types of compounds in the bio-oils were identified using GC-MS measurement. The compounds were classified into 7 groups as shown in fig. 4. It should be noted that due to the high content of water in the bio-oils obtained from durian peels (BO-DP) and pomelo peels (BO-PP), they may not be suitable for applying as fuel and thus their compositions being neglected.

From fig. 4, it can be observed that all bio-oils had phenols as a major fraction. Nevertheless, the presence of the catalysts both ZSM-5/RH and ZSM-5/Com reduced the fractions of phenol in the bio-oils. For BO-CS, it decreased from 85.21% to 76.85% with ZSM-5/RH and to 77.38% with ZSM-5/Com. For BO-RS, it decreased from 81.60% to 78.64% with ZSM-5/RH and to 75.04% with ZSM-5/Com. Phenols are considered oxygenated compounds in bio-oils. Decreasing the amounts of phenols could improve the quality of bio-oils. The amounts of other oxygenated compounds including acids, ketones and aldehydes insignificantly changed upon the presence of the catalysts. The catalysts employed in the pyrolysis here may be highly selective for reactions with phenols.

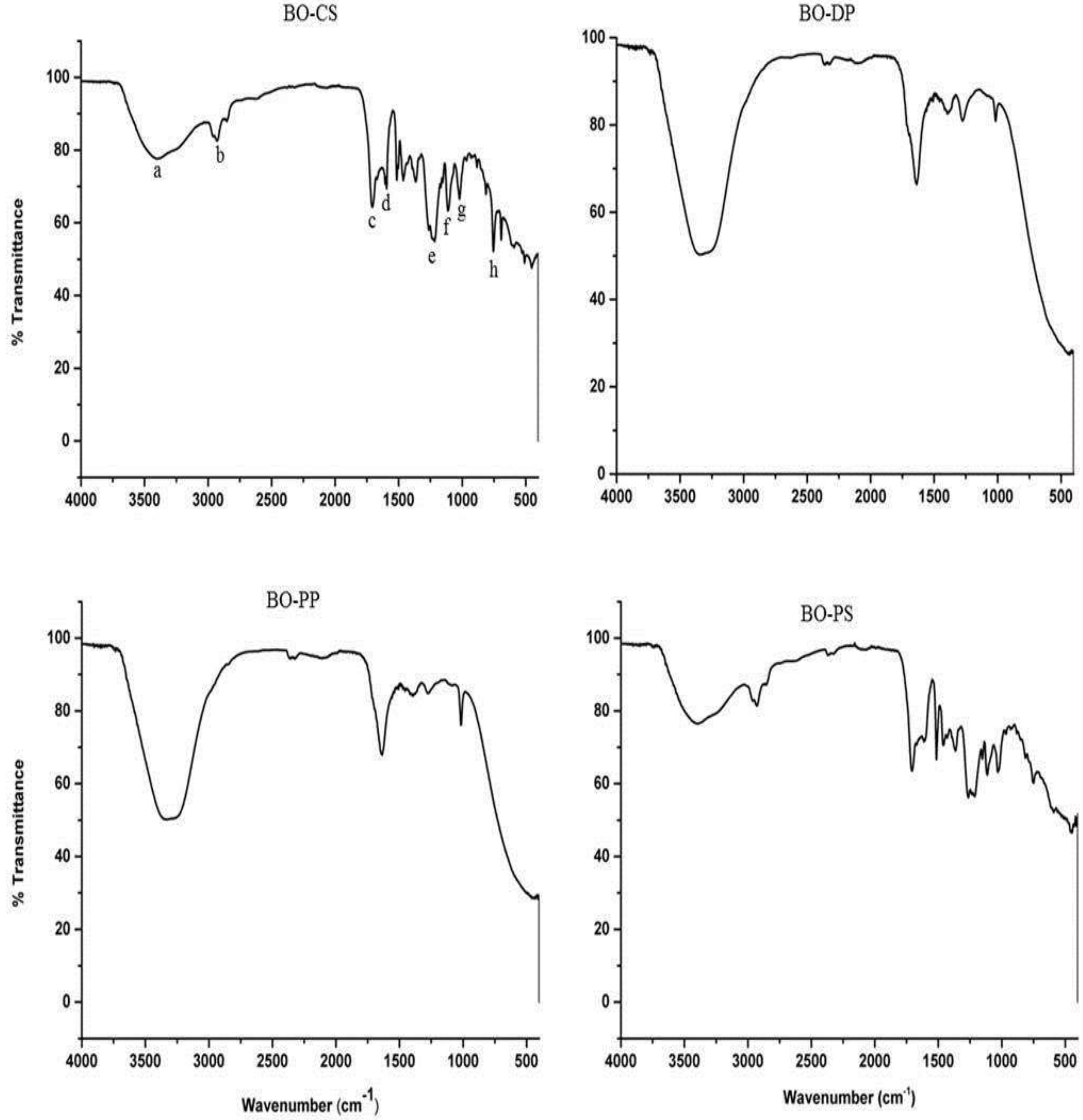

Fig. 3: FTIR spectra of the bio-oils from various agricultural residues.

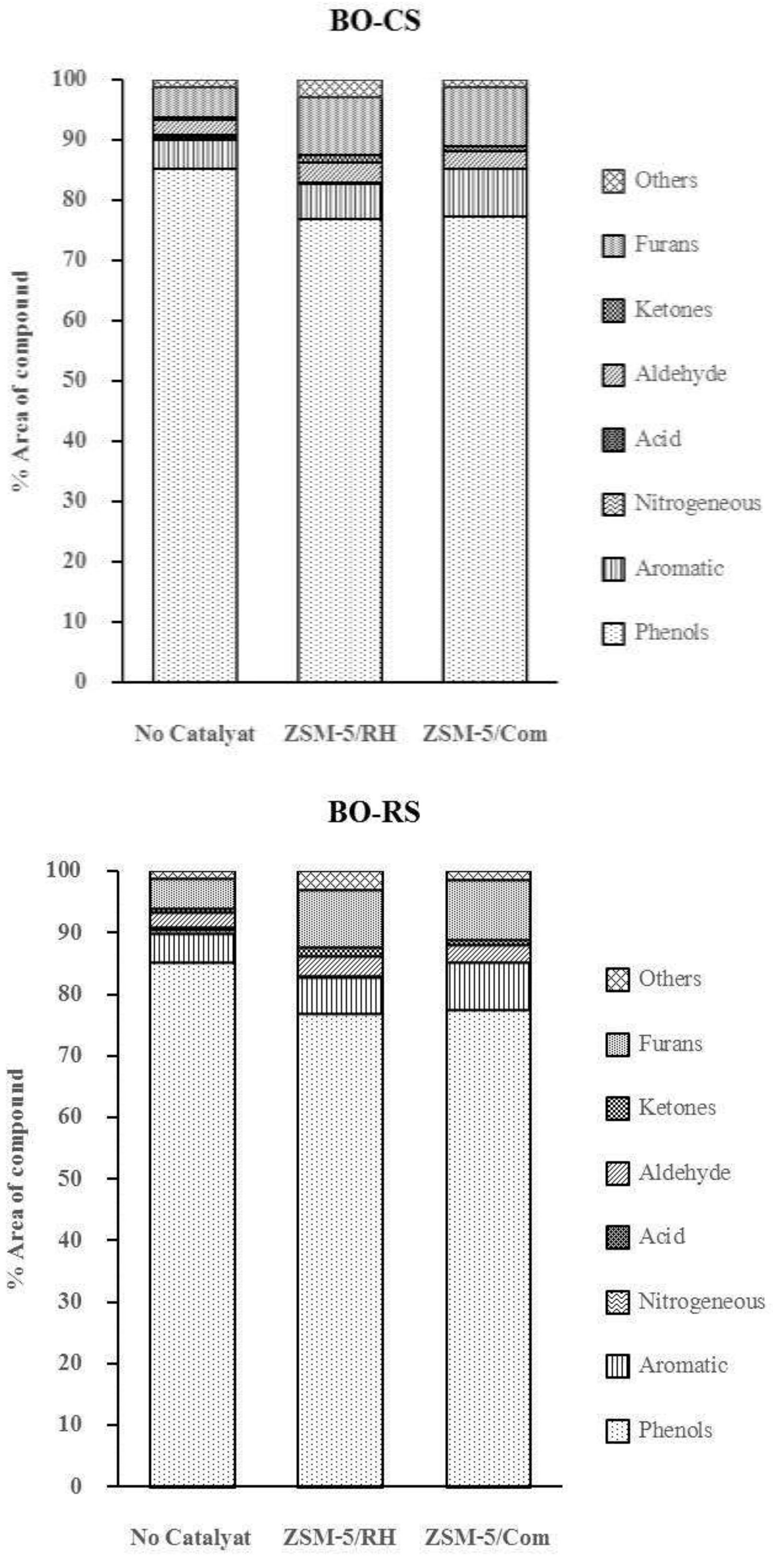

Fig. 4: Bio-oil compositions of BO-CS and BO-RS obtained from various pyrolysis systems

Kumar et al[15] also found that the used catalysts showed higher deoxygenation activity for phenols as compared to other catalysts in the previous study[38]. The deoxygenation of phenols could be through dehydrogenation producing alkenes or naphthene, which are consequently cracked or ring opened to be straight chain alcohols and then olefins[39]. These olefins can further undergo aromatization to generate aromatic hydrocarbons. This is also in consistent with the increases in aromatic compounds in the bio-oils obtained from the pyrolysis with the catalysts for both ZSM-5/RH and ZSM-5/Com as also seen in fig. 4.

For BO-CS, the content of aromatic increased from 4.73% to 5.79% with ZSM-5/RH and to 7.79% with ZSM-5/Com. For BO-RS, it increased from 4.22% to 5.18% with ZSM-5/RH and to 4.98% with ZSM-5/Com. In addition, the *in-situ* catalytic pyrolysis or mixing catalyst and biomass together in pyrolysis as conducted in this study have proved to produce more aromatic carbon than the *ex-situ* catalytic pyrolysis (biomass and catalyst separately pyrolyzed)[40].

This is because for *in-situ* system, the catalyst is exposed to a concentrated stream of pyrolysis vapors, thus small olefins generated during the process are having more opportunity to oligomerize to larger aromatic compounds at acid sites within the zeolite pores.

Comparing between the two catalysts, it was found that ZSM-5/RH which was derived from rice-husk silica can be comparable with the commercial zeolite (ZSM-5/Com) as observed that both catalysts had nearly similar ability (catalytic activity) in reducing oxygenated compounds in the bio-oils. The remarkable ability of ZSM-5/RH was probably developed from the high acidity of the catalyst[41,42]. However, the low surface area and the small pore diameter may deter ZSM-5/RH from having greater advantage than ZSM-5/Com.

Thus, the preparation method of zeolite catalysts from rice-husk silica should be further improved. To introduce the agricultural residue (rice husk) into the pyrolysis system as a catalyst provides an alternative way in using it for the pyrolysis besides using it as a biomass feedstock. The heating value of the bio-oil (Para rubber seeds) from the catalytic pyrolysis with ZSM-5/RH was also higher than that of the bio-oil from the non-catalytic pyrolysis (24.78 and 22.26 MJ/kg). This was due to the lower content of oxygenated compounds in the bio-oil from the catalytic pyrolysis.

Conclusion

Coconut shell, durian peels, pomelo shells and para rubber seeds were used as feed stock for non-catalytic pyrolysis and catalytic pyrolysis with ZSM-5 derived from rice-husk silica (ZSM-5/RH) and commercial ZSM-5 (ZSM-5/Com). Coconut shells and para rubber seeds provided the higher amount of liquid yield (bio-oil) than durian peels and pomelo peels due to the higher volatile matter content. The catalysts both ZSM-5/RH and ZSM-5/Com decreased the bio-oil yield for most agricultural residues and also reduced the contents of oxygenated compounds especially phenols in the obtained bio-oils.

It was found that ZSM-5/RH was comparable with ZSM-5/Com as they had nearly similar ability in reducing oxygenated compounds in the bio-oils. In addition, the bio-oil from the catalytic pyrolysis with ZSM-5/RH also exhibited higher heating value than the one from the non-catalytic pyrolysis.

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