

Effect of natural zeolite and kaolin as a catalyst in the isothermal-catalytic cracking of real municipal solid waste (MSW) for bio-oil production

I M Gandidi^{1*}, M D Susila¹ and H Rustamaji²

¹ Department of Mechanical Engineering, Faculty of Engineering, University of Lampung, Jl. S. Brojonegoro, Bandarlampung 35145, Indonesia

² Department of Chemical Engineering, Faculty of Engineering, University of Lampung, Jl. S. Brojonegoro, Bandarlampung 35145, Indonesia

*Email: indra.mamad@eng.unila.ac.id

Abstract. A real MSW conversion into bio-oil by pyrolysis method had been investigated. The pyrolysis experiment was carried out in an isothermal fixed bed reactor at 400 °C for 60 min. Natural activated zeolite and kaolin catalysts were employed in this process with catalyst-MSW at ratio of 0.5 w/w. Influence of activated catalyst to pyrolysis productivity and bio-oil properties were studied. Comparison between zeolite and kaolin catalytic pyrolysis was examined and bio-oil products were analyzed by GC-MS. The yields of liquid fuel or bio-oil were found around 23.6 and 21.4% for kaolin and zeolite catalytic pyrolysis, respectively. The carbon range distribution in bio-oil were 65.38% of gasoline range (C₅-C₁₂) and 33.49% of diesel range (C₁₃-C₂₀) for activated kaolin catalytic cracking. Activated zeolite had 51.62% of gasoline range (C₅-C₁₂) and 48.37% of diesel range (C₁₃-C₂₀). The results showed that both of bio-oil products mostly contained paraffin and olefin. The use of kaolin as catalyst was better than zeolite in converting the real MSW into bio-oil.

1. Introduction

The open dumping system of municipal solid waste (MSW) in Indonesia has created a lot of impacts for people and environment in which the system is no longer relevant due to the limitations in the urban area [1]. The landfill becomes a habitat for insects, pests and bacteria that can spread various diseases in the open environment. The piles of garbage in the landfill will produce some leachate that contaminates the ground and surface water [2]. Furthermore, MSW will be degraded biochemically and produce methane gas into the atmosphere. It is known that the potential of methane gas pollution is about twenty times more dangerous than the pollution by CO₂ [3]. In addition, MSW is one of major contributors for flood and increased risk of global warming and greenhouse gas effect [4].

On the other hand, MSW is a material contains energy in the form of chemical bonds between molecules of carbon, hydrogen and oxygen. When the chemical bonds are destroyed, the organic material will release the chemical energy in the form of gas, liquid and solid which is commonly called biofuel [5,6]. The calorific value content is around 20.57 MJ/kg [7]. Thus, MSW is one of the potential energy materials that can be converted into bio-energy. Pyrolysis is one method proposed for bio-energy production from MSW. Pyrolysis is a thermal degradation in which MSW is converted into solid fraction, liquid fraction consisting of paraffin, olefins, naphthene and aromatics, and gas at elevated

38 temperature in the absence of oxygen [8]. Usually the temperature used is in the range of 400-600 °C.
39 This process is intended to break down the long hydrocarbon chains into short-chain hydrocarbons.
40 Hence, MSW appears to be eligible to be developed as a raw material for bio-oil production by pyrolysis
41 technique [9-12]. MSW converted into bio-oil has attracted much attention due to its ease in storage,
42 transport, and upgrading.

43 Recently, researches are focused on the catalysts to reduce the activation energy and to improve the
44 thermal efficiency due to endothermic reaction at high temperature as well as the decomposition process
45 improvement during catalytic cracking. The presence of catalyst will generate secondary cracking to the
46 solids and liquids. Thus, resulted in higher pyrolytic products. Chika *et al* [13] carried out the catalytic
47 pyrolysis by using Y-zeolite and ZSM-5 as catalyst to convert electric and electronic plastic waste into
48 bio-oil, while Aida *et al* [14] used fluidized catalytic cracking (FCC) catalyst to convert plastic waste.
49 Norbert *et al* [15] performed catalytic pyrolysis by Y-zeolite, FCC, MoO₃ and HZSM-5 to convert MSW
50 and municipal plastic waste (MPW). Almeida and Marque [16] compared between thermal and HZSM-
51 5-catalytic cracking to MPW. Funda *et al* [17] studied the catalyst efficiency of Y-zeolite, β-zeolite,
52 equilibrium FCC, MoO₃, Ni–Mo-catalyst, and HZSM-5 on the catalytic cracking of MSW and MPW.
53 The studies mentioned above, used synthetic or commercial catalysts in the pyrolysis process which is
54 high costs of production, faster deactivation time of catalyst by MSW impurities or contaminant, as well
55 as unfavorable in the viewpoint of economic issues.

56 Nevertheless, available natural catalysts as zeolite, kaolin, and dolomite have been investigated as
57 catalysts on pyrolysis process instead of commercial catalysts. Wenger [18] performed the experiment
58 of catalytic pyrolysis to produce bio-oil from mixed plastic waste by using clay as the catalyst. Kyaw *et al*
59 [19] carried out pyrolysis to compare between clay and dolomite as the catalyst. Panda *et al* [20] used
60 kaolin in the polypropylene pyrolysis and Mochamad *et al* [21] carried out two stage pyrolysis of HDPE
61 and polypropylene as raw material with natural zeolite as the catalyst to produce bio-oil. However, single
62 component pyrolysis or MSW that was specified such as pure and mixed plastic material for bio-oil
63 production was performed. However, the MSW characteristic in developing countries contains a huge
64 variety of mixed waste and it is impossible to collect different kinds separately because of the large
65 quantities. In addition, more information due to bio-oil characteristics from the real unseparated MSW
66 pyrolysis is necessary prior to use as an engine fuel. Moreover, natural catalysts have different
67 characteristics from each other and it is very dependent on the mining location and chemical composition
68 of the natural catalyst. For instance, Si/Al ratios in the catalyst shows strong effects on the pyrolytic
69 products. Significant effect on the decomposition process will be obtained under lower Si/Al ratio and
70 increases the acidity of catalyst [22]. The selection of appropriate natural catalyst for real MSW
71 pyrolysis is required. In addition, kaolin and zeolite are not used as catalyst in the pyrolysis process of
72 real MSW.

73 This research was focused on the productivity and selectivity of natural zeolite and kaolin as a
74 catalyst on pyrolysis process to produce bio-oil from the real MSW. The real MSW consists of biomass
75 waste, various plastics waste, textile waste, papers waste, and rubber waste.

76 The characterization was carried on the composition and yield, chemical, and physical properties of
77 bio-oil. Comparison between pyrolysis and conventional oils such as diesel-48 and gasoline-88 was
78 performed to examine the possibility for conventional fuels substitution.

79 **2. Material and Methods**

80 *2.1. Waste and catalyst for pyrolysis*

81 The MSW was collected from the final disposal site located in Bakung District, Bandarlampung City.
82 This MSW consisted of various wastes such as vegetable waste from the traditional market, garden
83 waste, household waste, plastic waste, paper/cardboard, rubber waste, and textile waste. Samples were
84 sun dried for 3-5 days. The dried MSW was then chopped into pieces smaller than 5-10 cm to provide
85 proportional size with reactor capacity. The dry basis composition of MSW are shown in Figure 1.

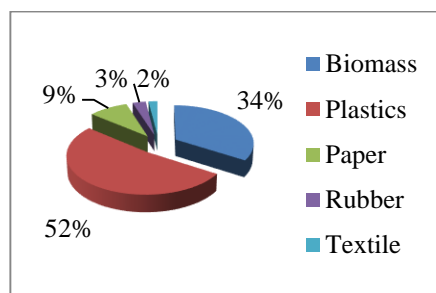


Figure 1. The composition of MSW.

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88 The natural zeolite and kaolin used in this study were obtained from the local source in Lampung
89 Province, Indonesia and then ground by a hummer mill and sieved to 20-30 mesh. Zeolite and kaolin
90 were activated thermally at 500 °C for 2 h to improve the active site and crystallinity. To examine the
91 structure and surface of the natural zeolite and kaolin, the XRD was employed. The composition of the
92 activated natural zeolite and kaolin is shown in Table 1. The high amount of SiO₂ and Al₂O₃ in the
93 natural zeolite and kaolin showed that zeolite and kaolin are proper to use as a catalyst. These
94 compounds could increase the cracking efficiency and increase the pyrolytic products.

95 **Table 1.** X-Ray analysis for chemical composition of activated zeolite and kaolin.

Kind of Catalyst	Compound	Concentration (%)
Zeolite	SiO ₂	68.5
	Al ₂ O ₃	13.17
	Fe ₂ O ₃	2.98
	MgO	1.15
	CaO	2.47
	K ₂ O	1.80
	Na ₂ O	1.06
	TiO ₂	0.14
Kaolin	SiO ₂	43.12
	Al ₂ O ₃	46.07
	Fe ₂ O ₃	0
	MgO	0.27
	CaO	0.3
	K ₂ O	0.01
	ZnO	0.0064
TiO ₂	0.74	

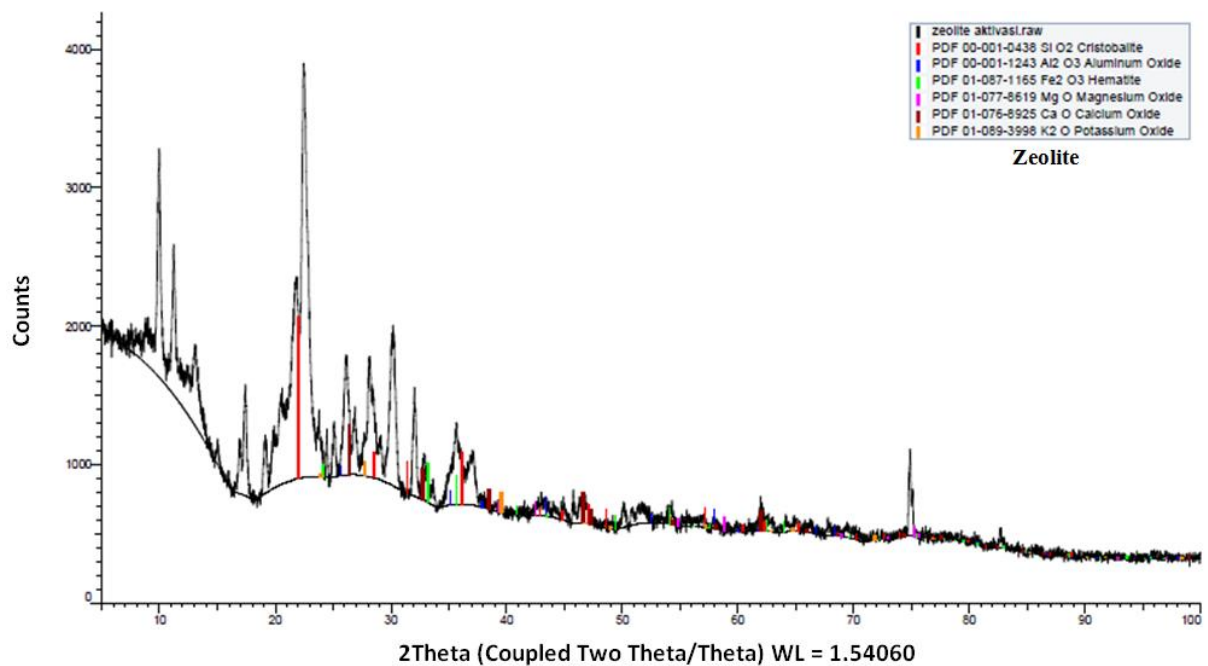
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Source: CV. Mina Tama, Bandarlampung

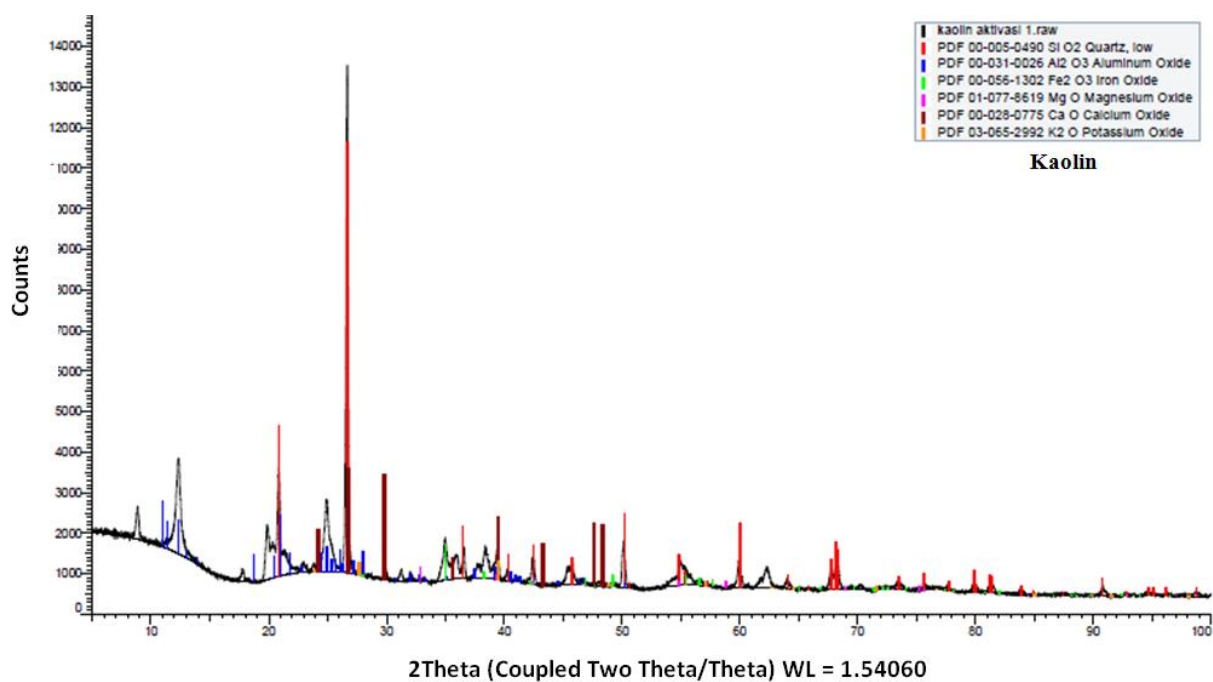
97 Figure 2 shows the X-ray patterns for both catalysts. The sharp peaks implied that natural zeolite and
98 kaolin had good crystallinity and possibly gave strong effects in the decomposition of MSW and stable
99 at high temperature.

100 2.2. Pyrolysis experiment and bio-oil analysis

101 The MSW sample was pyrolysed using a fixed bed vacuum reactor equipped with air lock valve between
102 reactor and hopper to avoid the air took place of reactor entry. The reactor was made from stainless
103 cylinder with 310 mm in height and 160 mm in internal diameter. The electrical heating jacket was
104 connected to thermo-controller and thermocouple was taped around the reactor. The reactor was set
105 vertically and connected to a nitrogen tank using rubber tube and then N₂ gas was introduced into the
106 reactor for 3 min from the top, passed through and flowed out through the top of the reactor. The flow
107 of nitrogen replaced the air from the reactor and permitted the pyrolysis reaction took place under inert
108 vacuum condition.



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Figure 2. X-Ray patterns of the activated zeolite and kaolin.

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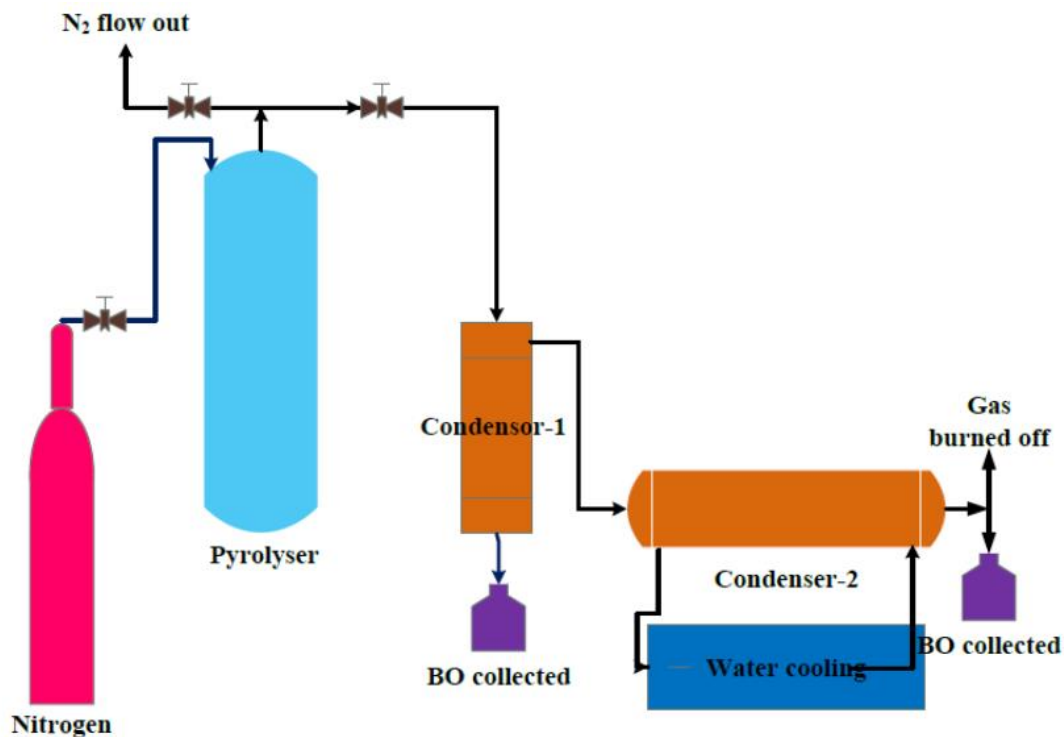
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Nitrogen gas was introduced into the reactor and then the reactor was heated until reactor temperature reached to 400 °C with heating rate of 12°C. An amount of 750 g of mixed catalyst (250 g) –MSW (500 g) was put into reactor by the opened air lock valve. The reaction time was set for 60 min for both of pyrolysis experiments. The gas produced was flowed into vacuum gas cleaner as the first condenser to the shell and tube condensers at 20°C as the secondary condenser to separate the permanent gas and liquid. The gas was burned off to prevent emission from hydrocarbon gases. The char remained in the reactor was collected after the pyrolysis reaction was finished. The experimental apparatus is shown in Figure 3.



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Figure 3. The experiment apparatus.

124 Regarding the pyrolytic products, products obtained from the pyrolysis could be divided into non-
 125 condensable gas fraction, solid fraction and liquid (bio-oil) fraction. From bio-oil yield that could be
 126 recovered, the hydrocarbon chains were in the gasoline range (C₅-C₁₂), diesel (C₁₂-C₂₀) and heavy oil (>
 127 C₂₀) that consisted of paraffin, olefins, naphthenes and aromatics [23]. The pyrolysis liquid was analyzed
 128 using gas chromatography-mass spectrometry (GC-MS, QP2010S Shimadzu) which could be used to
 129 identify carbon number range and chemical composition. The column was DB-1 (Agilent J 100%
 130 dimethyl polysiloxane) capillary column, 30 m length with 0.25 mm diameter and 25 μm film thickness.
 131 Helium was used as the gas carrier. The temperature was set in initial temperature of 60°C for 5 min
 132 followed by a heating rate of 5°C/min to 280 °C and held for 51 min. The estimation of the heating value
 133 of bio-oil was approached by carbon-hydrogen weight ratio [24]. Paraffin had the highest heating value
 134 followed by iso-paraffin, olefin, nepthenes and aromatic (PIONA). Also, the distributions of PIONA in
 135 each range of hydrocarbon were calculated to determine the selectivity behavior of natural zeolite and
 136 kaolin catalysts in the pyrolysis process.

137 **3. Results and Discussion**

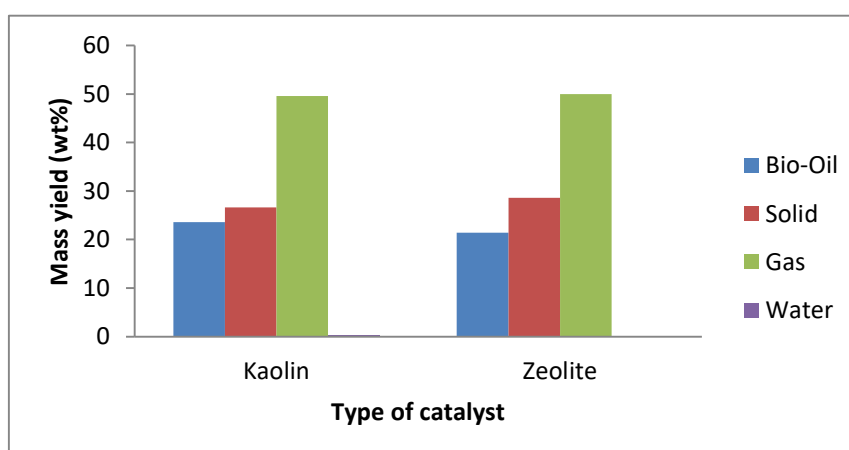
138 *3.1. Physical properties of bio-oil*

139 Table 2 shows the density and viscosity for conventional fuel and bio-oil. It shows that both of bio-oils
 140 from the natural catalytic cracking had similar density values and significantly different viscosity
 141 properties. The kinematic viscosity of natural kaolin was lower than the natural zeolite. It indicated that
 142 the natural kaolin had a good cracking reaction compared with the natural zeolite. However, both of bio-
 143 oils had properties close to diesel-48 and were acceptable to be considered as a future energy. Both of
 144 bio-oils had high solid and water contents due to impurities in the unwashed real MSW and direct
 145 catalytic as well. The solid content in the bio-oil was affected by ash from the biomass material.

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Table 2. The physical properties of bio-oil.

Properties	Unit - Standard	Diesel	Gasoline	Kaolin	Zeolite
Cetane octane number		48 (<i>cetane</i>)	88 (<i>octane</i>)	-	-
Density@15°C	g/cm ³ ASTM D-1298	0.815-0.87	0.7-0.78	0.8038	0.8076
Kinematic viscosity@40°C	cSt ASTM D-445	2.0-5.0	0.4-0.8	2.0345	2.4775
Flash point	°C ASTM D-93	min 60	min 40	min 5	min 5
Pour point	°C	max 18	-	-	-
Water content	% Vol ASTM D-1744	max 0.05	-	3	2.5
Oil content	% Vol ASTM D-1744	-	-	86	90
Solid content	% Vol ASTM D-482	-	-	11	7.5

**Figure 4.** Mass yield of pyrolytic products.

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151 3.2. Yield and chemical properties of bio-oil

152 The products from the MSW pyrolysis are shown in Figure 4. Catalytic cracking produced from natural
 153 kaolin and zeolite by pyrolysis is 23.6 and 21.4%, respectively. Kaolin shows higher yield compared to
 154 zeolite. This indicated that natural kaolin had a better productivity than the natural due its higher active
 155 site and higher acidity. However, the highest yield on the gaseous product and appearance of water
 156 content in the bio-oil implied that further drying for MSW was required and temperature of condensation
 157 environment around 20°C was unfavorable. Moreover, the low bio-oil yield could also be associated
 158 with the short reaction time and the long residence time of the gas in the reactor [25]. A similar result
 159 was presented by Panda and Singh [26] that used kaolin as a catalyst in plastic waste pyrolysis.

160 Figure 5 shows the carbon distribution range in the conventional and pyrolytic oils. The pyrolytic oil
 161 from mostly contains gasoline (C₅-C₁₂) followed by diesel (C₁₃-C₂₀) and a small amount of heavy oil
 162 (>C₂₀).

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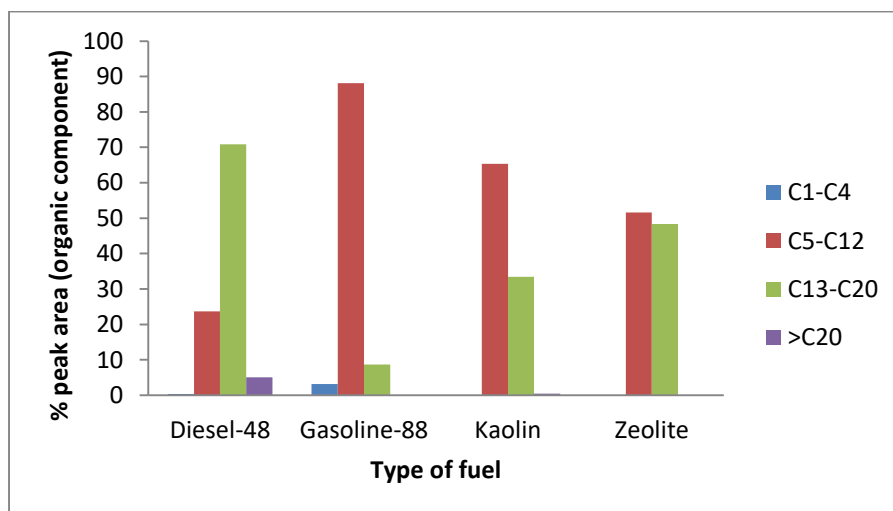


Figure 5. Carbon distribution range on conventional and pyrolysis fuel.

Bio-oil by natural kaolin catalytic consisted of 65.38% gasoline fraction and 33.49% of diesel fraction. Meanwhile bio-oil by natural zeolite showed 51.62% of gasoline fraction and 48.37% of diesel fraction. Clearly, natural kaolin had shown better properties as a catalyst for the production of bio-oil from MSW compared with natural zeolite, although natural zeolite did not have heavy oil fraction in the bio-oil.

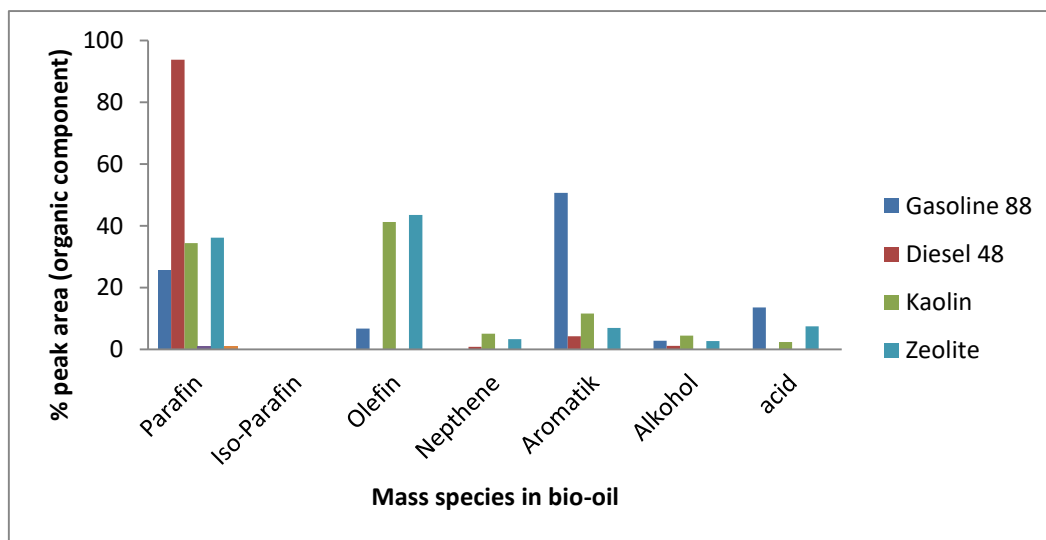
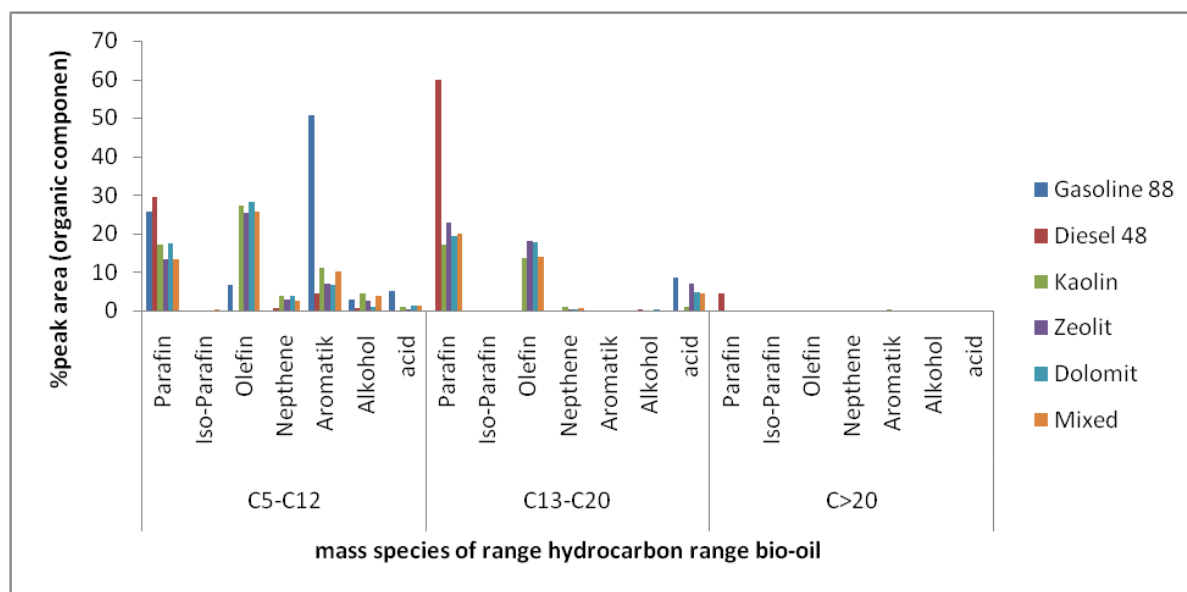


Figure 6. A comparison of mass species between bio-oil and conventional fuel.

Figure 6 reveals the organic components in the bio-oil in which most of organic components in the bio-oil were paraffin and olefin with small amount of aromatic, alcohol and acid. Only slight difference in the amount of paraffin and olefin between natural kaolin and natural zeolite in catalytic cracking process. Consequently, bio-oils from natural kaolin and natural zeolite catalytic pyrolysis showed the same caloric values. It illustrated that both of natural catalysts at 400 °C and 60 min had similarities in the selectivity behavior.

Figure 7 shows the PIONA contents in each hydrocarbon range on the pyrolytic bio-oil, reveals that gasoline fraction contained more olefin than paraffin, otherwise with the diesel fraction for both of pyrolytic bio-oils. This composition was significantly affected by the plastic and biomass in MSW which determined the chemical reaction during the process of pyrolysis. The presence of impurities and natural catalyst in the MSW was also allegedly plays an important role to the bio-oil composition [27].



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Figure 7. Number of mass species in each hydrocarbon range.

186 4. Conclusion

187 Real MSW is a great potential raw material to be converted into paraffin and olefin by thermal-catalytic
188 cracking. Activated kaolin and zeolite can increase the productivity of bio-oil quite low in its selectivity
189 Kaolin demonstrated a better capability for pyrolysis process than zeolite. The upgrading process to
190 enhance the pyrolysis oil yield is necessary to obtain bio-oil with gasoline range.

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