



## Exceptional Aromatic Distribution in the Conversion of Palm-Oil to Biohydrocarbon Using Zeolite-Based Catalyst

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### Highlights:

- Cylindrical shaped ZSM-5-based catalyst was used to convert palm oil into biohydrocarbons.
- The liquid product contained aromatics at up to 98%.
- Benzene, toluene, and xylene were the major aromatics.

**Abstract.** A series of four catalysts, i.e. ZSM-5 (Si/Al = 25) (Z1), a combination of ZSM-5 (Si/Al = 25) and zeolite Y (Si/Al = 25) (Z2), zeolite Y (Si/Al = 25) (Z3), and ZSM-5 (Si/Al = 80) (Z4), was successfully prepared for catalytic cracking of palm oil. All three catalysts utilized silica as a binder without other additional components. Catalytic cracking tests showed that the aromatic distribution was very high, according to the following order: Z4 (98%) > Z1 (90%) > Z2 (84%) > Z3 (60%). It was shown that ZSM-5 promotes the formation of aromatics better than zeolite Y does. From 98% of aromatics products in Z1, 71% were benzene, toluene, and xylene (BTX). It appears that the formation of aromatics needs milder acidity since a higher number of acids extends the cracking reaction, resulting in the formation of more gaseous and heavy aromatics products. The results of this study show potential for the sustainable production of bio-hydrocarbons with exceptional aromatic distributions, which may fulfill the demands of the petroleum, petrochemical, and fine chemical sectors.

**Keywords:** aromatic; bio-hydrocarbon; catalytic cracking; palm-oil; zeolite.

## 1 Introduction

The increasingly limited fossil fuel reserves and their negative impact on the environment due to excessive CO<sub>2</sub> emissions, which induce global warming, have driven worldwide research on alternative, renewable sources for fuel production. One of the most promising alternative sources is vegetable oil, since it is renewable and significantly decreases CO<sub>2</sub> emissions. Palm oil is regarded as one of the most important vegetable oils in the world. The palm oil industry is one of Indonesia's major agricultural enterprises. From 1962 to 2012, palm oil plantation across the globe has expanded exponentially to around 13 million hectares, establishing it as the fastest-growing monoculture globally [1,2]. In 2014, the global production of palm oil reached 62.34 million tons, with almost half of it (30.9 million tons) coming from Indonesia, establishing Indonesia as the world's largest producer and exporter of palm oil [3].

Palm oil can be transformed into bio-hydrocarbons using several routes, including transesterification [4,5], hydroprocessing [6], thermal cracking [7], and catalytic cracking [8-10]. The former is a process to chemically break down the molecules of triglycerides into glycerol and esters in the presence of alcohols as solvents under basic conditions. The product is called biodiesel, a renewable fuel that has various shortcomings, such as low resistance to oxidation, hygroscopic, high density, as well as high viscosity.

Hydroprocessing is a resultant process of hydrogenation, hydrotreatment, and hydrocracking in which the oxygen atoms are eliminated in the presence of a very active catalyst under high hydrogen pressure. Although several noble metal-based catalysts have shown excellent activity [11,12], their finite availability and burdensome cost limit the utilization of hydroprocessing. Thermal cracking makes use of high temperature and pressure to convert palm oil into bio-hydrocarbons. However, the yield of gasoline fraction is very low despite the relatively high cost of production.

Ultimately, catalytic cracking is, basically, thermal cracking in the presence of a catalyst, mainly based on carbonium ion mechanisms. It includes not only cracking but also a series of reactions such as alkylation, isomerization, cyclization, and aromatization [13,14]. This route is promising since it can produce bio-hydrocarbons similar to those of hydrocarbons from fossil resources without the presence of poisons, i.e. heavy metals, sulphur, and nitrogen. Furthermore, the catalytic cracking of palm oil can utilize the available infrastructure in the refining process of fossil fuel, making it feasible for mass production.

The most important products of catalytic cracking are benzene, toluene, xylene (BTX), and other light aromatics [15-18]. The aromatics are highly valuable and essential for the petroleum, petrochemical, and fine chemical industries. Besides, they are also utilized as octane-boosters of gasoline. The product distribution of catalytic cracking is greatly controlled by the use of catalysts. A series of previous works emphasized the importance of zeolites, microporous (<2 nm) aluminosilicate materials as catalysts in the catalytic cracking of vegetable oil, especially palm oil. Among many types of zeolites, ZSM-5 has shown high catalytic performance to convert triglycerides into bio-hydrocarbons [8,19,20].

Cracking, isomerization, and aromatization are of great industrial interest because this route would contribute to cost reduction, which would make the use of bio-hydrocarbons feasible and meet the new demands of the petroleum, petrochemical, and fine chemical sectors with great environmental benefits. Herein, we report the exceptionally high distribution towards aromatics using ZSM-5 based catalyst, which may widen the possibility of palm oil utilization not only for fuel production but also in the petrochemical and fine chemical industries.

## 2 Experimental Sections

### 2.1 Materials

The zeolites, i.e. ZSM-5 (Si/Al = 25), ZSM-5 (Si/Al = 80) and zeolite Y (Si/Al = 25) were purchased from Qingdao Wish Chemicals, China. The chemicals used in this study included colloidal silica (Ludox HS-40, Sigma-Aldrich) and deionized water. All reactants were reagent grade and used as received without further purification.

### 2.2 Preparation of the Catalyst

In typical preparation, the zeolite in ammonium form is mixed with Ludox HS-40 using a mortar. Subsequently, water is gradually added while mixing is continued until a homogeneous paste is obtained. The final weight ratio of the mixture would be zeolites: SiO<sub>2</sub>:H<sub>2</sub>O = 4:1:2. The paste is shaped into tubes using an extrusion process and subsequently allowed to dry overnight at ambient temperature. Moreover, the extrudates are calcined at 550 °C for 6 h under air atmosphere. Three types of catalyst were based on the used zeolites, i.e. ZSM-5, 50% ZSM-5 + 50% zeolite Y, and zeolite Y, coded as Z1, Z2, and Z3, respectively.

### 2.3 Characterizations

Powder X-ray diffraction (XRD) analyses were carried out on a Bruker D8 Advance diffractometer using Cu-K $\alpha$  beam ( $\lambda = 1.5418 \text{ \AA}$ ) to identify the phase purity. Before the measurement, samples were grounded and placed in a round and flat specimen holder with a fixed thickness of 5 mm. The XRD patterns were collected in the range of  $2\theta$  from 3 to 50° with a 0.02° interval.

An X-ray fluorescence (XRF) spectrometer (Orbis EDAX) was utilized for analyzing and mapping the chemical composition of the catalysts. The measurement was performed using an accelerating voltage of 40 kV.

A Quantachrome NovaWin instrument was employed to record the N<sub>2</sub>-adsorption isotherms in liquid N<sub>2</sub> medium at 77 K. Before the measurement, all samples were vacuumed at 300 °C for 4 h. The specific surface area ( $S_{\text{BET}}$ ) was determined using the BET (Branauer–Emmet–Teller) method while the point P/Po  $\approx 0.99$  was used to calculate the total pore volume ( $V_p$ ).

A Quantachrome ChemBET Pulsar was utilized to perform NH<sub>3</sub>-temperature-programmed desorption (TPD) measurements. A fixed amount of sample was heated at 350 °C for 1 h under the flow of He. The sample was cooled to ambient temperature and subsequently saturated with NH<sub>3</sub> gas. Desorption of NH<sub>3</sub> was carried out at a heating rate of 10 °C min<sup>-1</sup> under the flow of He. The calibration of the TCD signal was done through the desorption of ammonia gas with a known amount.

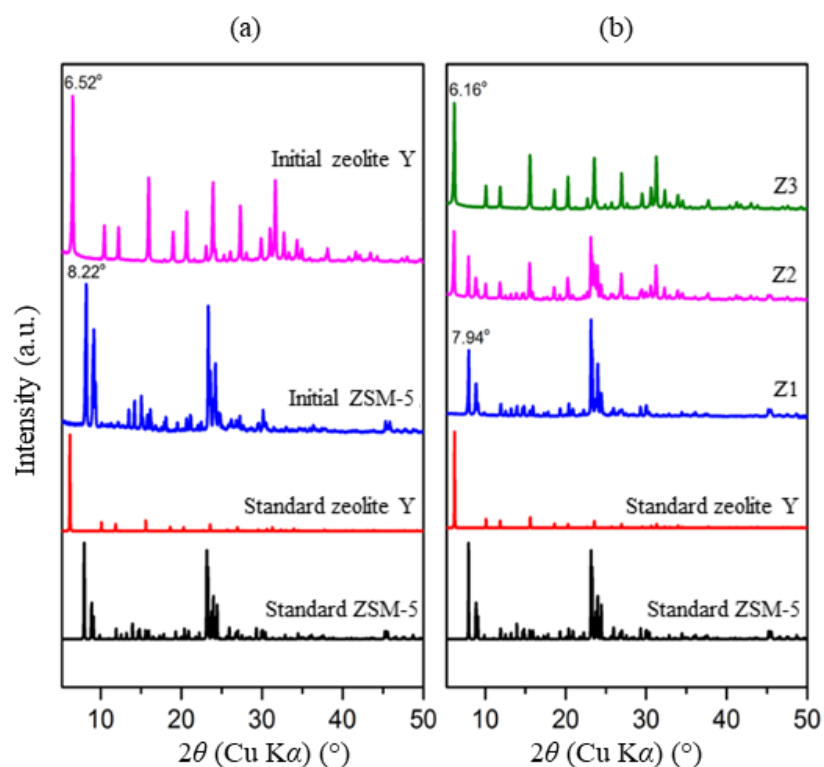
### 2.4 Catalytic Test

The catalytic cracking of palm oil was performed in a micro fixed-bed reactor system. Before the reaction, the reactor was purged with N<sub>2</sub> at a flow rate of 50 mL min<sup>-1</sup> at 500 °C for 60 min to activate the catalyst by removing the adsorbed water. The catalyst weight was fixed at 2.5 g. The palm oil was pumped with a weight-hourly space velocity (WHSV) of 2.6 h<sup>-1</sup> with a flow of 1.2 mL min<sup>-1</sup> without the use of carrier gas. The reaction was carried out for 60 min. A glass condenser with an ice bath was used to separate the gaseous and liquid products. The liquid products were analyzed using gas-chromatography detailed hydrocarbon analysis (GC-DHA) with an Agilent Technologies 7890B GC System using an RTX-5 capillary column.

## 3 Results and Discussion

Figure 1(a) shows the XRD patterns of the two initial zeolites used in this study. It can be seen that the patterns of ZSM-5 and zeolite Y used in this study perfectly matched with the standard patterns of ZSM-5 and zeolite Y, respectively, from

the International Zeolite Association (IZA) database. After the zeolites had been incorporated with the binder (silica) to form the final catalyst, the patterns of ZSM-5 and zeolite Y still appeared, showing the preservation of the zeolites (Figure 1b). In the XRD patterns of Z2, it can be seen that the patterns are a combination of ZSM-5 and zeolite Y. Moreover, the intensity of XRD reflections of the final catalysts shows lower crystallinity compared to that of the initial zeolites owing to the amorphous character of the silica binder. Furthermore, the XRD reflections also shifted toward lower  $2\theta$ , suggesting the presence of more Si–O bonds [21,22,23], which are likely due to the crystallization of some parts of the silica binder into the zeolite phase.

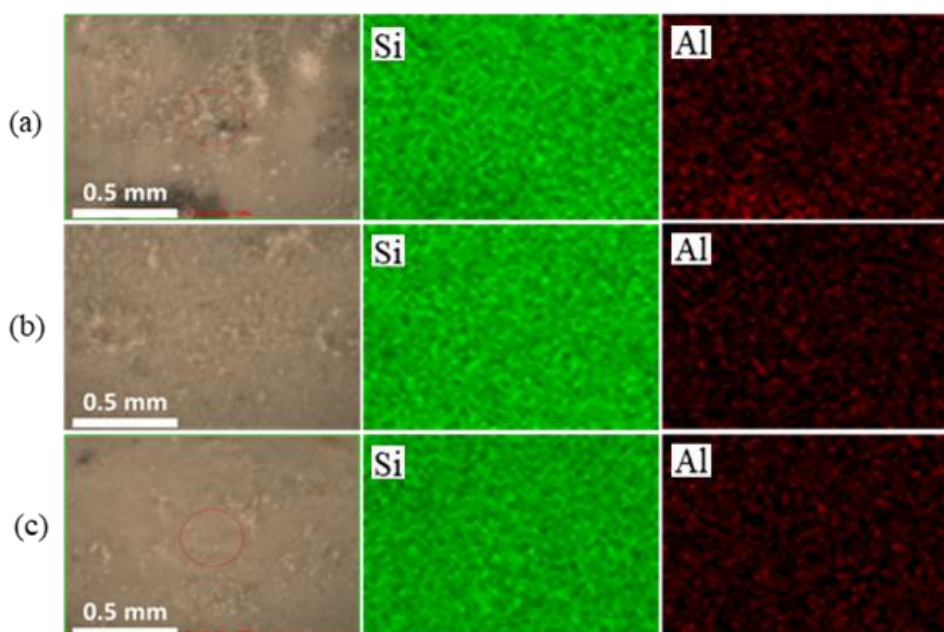


**Figure 1** XRD patterns of (a) the initial zeolites and (b) the final catalysts.

Note that the Si–O has a shorter bond length compared to the Al–O, thus, the d-spacing will be constricted, resulting in lower  $\theta$  or  $2\theta$  based on the Bragg equation,  $n\lambda = 2d \sin \theta$ . The initial zeolite itself may play a role as a seed, presumably acting as nuclei for the crystallization of the silica binder through solid-state transformation, as has previously been reported [24,25].

This leads to three layers of the catalyst, i.e. silica binder, more siliceous zeolite, and initial zeolite. Previously, Twaiq *et al.* [26] also tested various zeolites, including ZSM-5, beta, Y, hybrid ZSM-5-beta, and hybrid ZSM-5-Y, to catalyze the conversion of palm oil into hydrocarbons. However, they used pure, binderless zeolite in powder form to minimize the mass-transfer effect. In this study, a cylindrical shaped catalyst was employed that was combined and extruded with the silica binder. Therefore, our results may better represent the catalytic cracking in the actual industrial processes.

As analyzed by XRF, the Si/Al ratios of the initial zeolites matched well with the Si/Al from the manufacturer, i.e. 24.4 and 25.2 for ZSM-5 and zeolite Y, respectively. As expected, the Si/Al ratios of the final catalysts were lower than those of the initial zeolites due to the addition of the silica binder. These results support the insights obtained from the XRD characterization. Furthermore, we performed elemental mapping on the final catalysts (Figure 2). The green color indicates Si, while the red color represents the presence of Al. The former should merely correspond to the ZSM-5, since it is the only component containing aluminum. As can be seen, the green color is quite homogeneously distributed throughout the map, suggesting that the zeolites were spread evenly in the final catalyst. This is a good property for a catalyst to have in order to get a good distribution of the active sites.

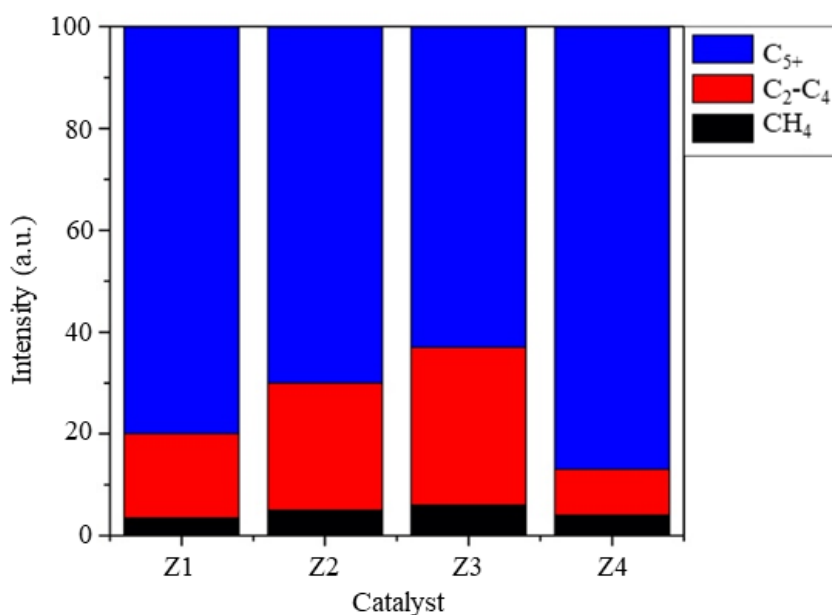


**Figure 2** The elemental mapping of (a) Z1, (b) Z2, and (c) Z3. Green and red colors correspond to Si and Al, respectively.

The textural properties of the final catalyst were determined through the N<sub>2</sub> adsorption isotherms. Z1, Z2, and Z3 exhibited a high surface area of 440 m<sup>2</sup> g<sup>-1</sup>, 498 m<sup>2</sup> g<sup>-1</sup>, and 587 m<sup>2</sup> g<sup>-1</sup>, respectively, while the pore volume was in the following order, Z3 (0.08 cm<sup>3</sup> g<sup>-1</sup>) > Z2 (0.12 cm<sup>3</sup> g<sup>-1</sup>) > Z3 (0.25 cm<sup>3</sup> g<sup>-1</sup>), as displayed in Table 1. The acidity of the final catalyst was measured using NH<sub>3</sub>-TPD and tabulated in Table 1. It was found that the total acid sites increased from Z1 to Z3. The total acid sites can be divided into strong acid and weak acid sites based on the desorbed temperature. The former appeared at high temperatures (>500 °C), while the latter appeared at a lower temperature (200-300 °C). The higher the temperature, the stronger the acid sites. Both the number of strong and weak acid sites increased from Z1 to Z3.

**Table 1** Physicochemical properties of the catalysts.

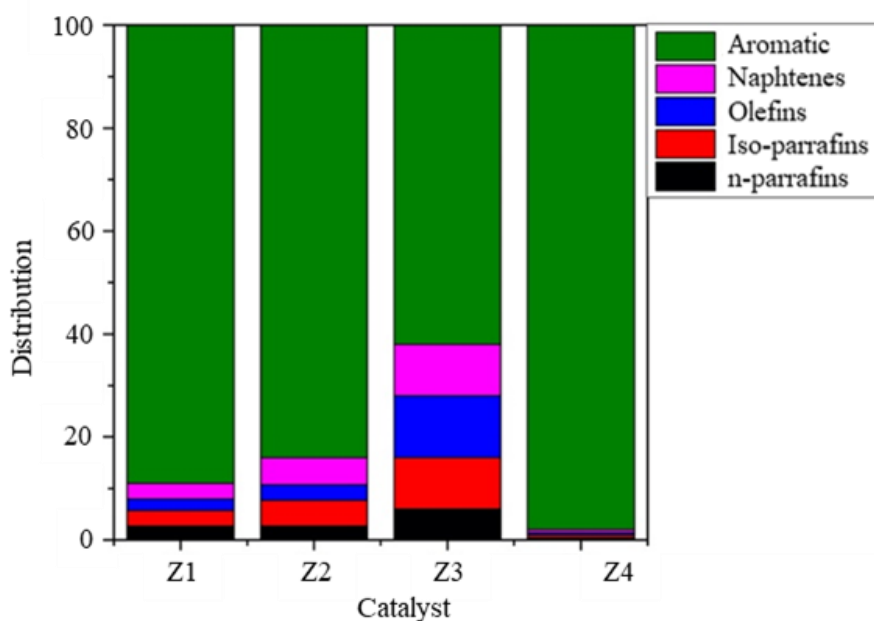
Catalysts	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	V <sub>p</sub> (cm <sup>3</sup> g <sup>-1</sup> )	Total acid sites (μmol g <sup>-1</sup> )	Weak acid sites (μmol g <sup>-1</sup> )	Strong acid sites (μmol g <sup>-1</sup> )	T <sub>weak</sub> (°C)	T <sub>strong</sub> (°C)
Z1	440	0.08	334	232	102	268	610
Z2	498	0.12	363	243	120	272	530
Z3	587	0.25	397	269	128	237	535
Z4	420	0.10	147	93	54	225	580



**Figure 3** The catalytic performance of the catalysts in the catalytic cracking of palm oil.

All the final catalysts were tested in the catalytic cracking of palm-oil. The majority of the products were  $C_{5+}$  fraction, which is a liquid phase. From Z1 to Z3, the distribution of liquid products was reduced, probably due to an increase in the number of acid sites, which promote the occurrence of cracking reactions (Figure 3). The liquid products were further analyzed to determine the hydrocarbon distributions and the group of compounds shown in Figure 4.

As can be seen, aromatics dominated the hydrocarbon distribution in the liquid products of all catalysts. Z1, which utilizes only ZSM-5, even possesses an aromatic distribution of 90%. Meanwhile, the aromatic distributions of Z2 and Z3 diminished to 84% and 62%, respectively, showing the preference of aromatic formation within ZSM-5. Furthermore, we plotted the aromatic distribution versus the acidic properties of the catalyst to understand the role of the acid sites (Figure 5).



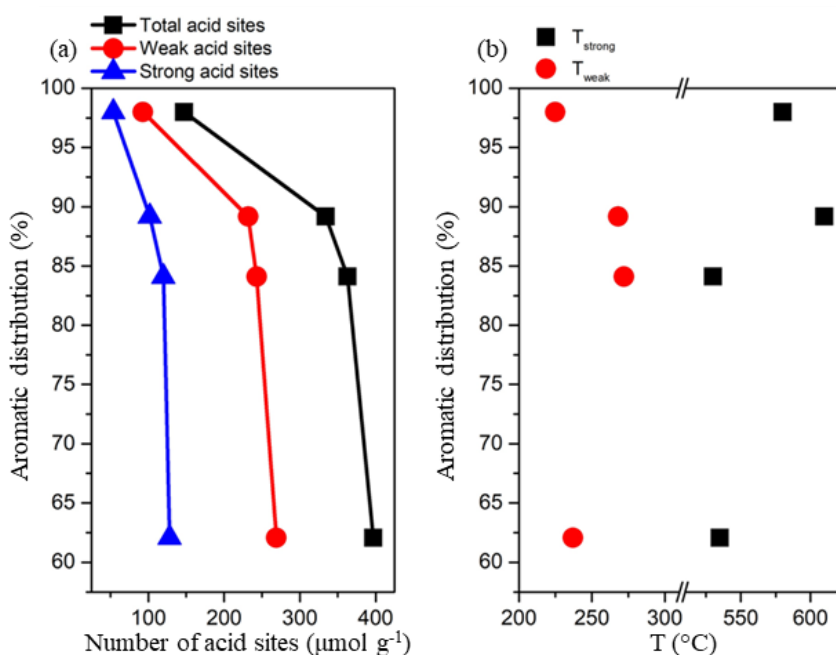
**Figure 4** The distribution of the liquid products.

As can be seen, the aromatic distribution showed an inverse correlation with the number of acid sites with no certain correlation to the acid strength. Hence, our study suggests that the formation of aromatics is preferred at lower acidity. At a higher number of acid sites, it appears that the cracking reaction is promoted to form more gaseous products and heavy aromatics. The aromatic distribution in this study was higher than reported in previous studies on catalytic cracking using ZSM-5, whose range was from 15 to 70% [27-29]. To further confirm our study,



we also tested ZSM-5 with a higher Si/Al ratio, i.e. 80 (coded as Z4), which possesses less acid sites. The  $C_{5+}$  fraction can be further enhanced to 90%, with the aromatic percentage in the liquid product reaching 98%.

For the production of aromatics, acidity is of course needed, but only to a certain extent. Zeolite comprises Brønsted acid sites in which aromatics are formed through a series of dehydration, decarbonylation, decarboxylation and aromatization reactions. However, too high acidity will shift the selectivity toward heavy molecules and polyaromatics, which can be further converted to cokes, undesired products that deactivate the catalyst. Engtrakul, *et al.* [30] studied the effect of ZSM-5 acidity on the upgrading of pine pyrolysis vapors.



**Figure 5** The dependence of aromatic distribution on (a) the number of acid sites and (b) the acidity strength.

They found an unstable relationship between total aromatics (sum of 1, 2 and 3 rings) and acidity. There are two regimes. The first regime is when the acidity is proportionally related to the total aromatics, while the second regime occurs when the acidity is increased but the total aromatics decreases. The second regime is because the aromatics are consumed for the formation of cokes. It is possible that our study was located in the second regime so that aromatics were preferred at the lower acidity.

We further analyzed the BTX (benzene, toluene, xylene) distribution within the liquid products resulted from all three catalysts, as shown in Table 2. Z4 possessed the highest BTX distribution (70.88%), followed by Z1 (66.10%), Z2 (53.33%), and Z3 (29.69%), showing the influence of ZSM-5 on directing the formation of BTX compounds. In the liquid products of Z1, the major constituent is toluene. When 50% of ZSM-5 is replaced with zeolite Y (Z2), the BTX distribution amends and the toluene distribution decreases. Moreover, when ZSM-5 is totally replaced with zeolite Y (Z3), the BTX distribution further declines and there is no preference for a certain product.

**Table 2** BTX distribution in the liquid product.

Catalyst	Benzene (%)	Toluene (%)	<i>o</i> -Xylene (%)	<i>m</i> -Xylene (%)	<i>p</i> -Xylene (%)	BTX (%)
Z1	7.99	32.30	5.88	13.02	6.91	66.10
Z2	2.18	17.14	6.02	14.52	13.47	53.33
Z3	2.56	9.03	4.31	7.33	6.46	29.69
Z4	1.43	22.98	10.16	23.59	12.72	70.88%

Lastly, we measured the research octane number (RON) based on the contribution of the octane number of each constituent to the liquid products based on the following equation,

$$RON = \sum_{i=1}^{31} (F_i \times W_i) \quad (1)$$

where  $F_i$  and  $W_i$  are the factor of the octane number of constituent  $i$  and the weight ratio of constituent  $i$ , respectively. This method is comparable to ASTM D6730-1 [27,31,32]. The RONs of the liquid product resulted from the use of Z1, Z2, Z3, and Z4 were 112, 107, 94, and 124, respectively. These high RONs were, undoubtedly, owed to the dominant presence of aromatics. The exceptionally high aromatic distribution obtained in our study may widen the possibility of palm oil utilization not only for fuel production but also for petrochemical and fine chemical industries.

#### 4 Conclusions

In summary, this study has shown that a simple preparation of zeolite-based catalysts can be successfully applied to the catalytic cracking of palm-oil and boosting of the aromatic distribution in liquid bio-hydrocarbons. The aromatic distribution reached 98% with 71% being BTX compounds. This promising result was based on the use of ZSM-5, which effectively promotes the formation of aromatics. Using another zeolite such as zeolite Y, the aromatics as well as the BTX distribution become significantly reduced. Interestingly, we found that the aromatic distribution correlated with the number of acid sites and not with the strength of the acid sites.

The RON of the liquid products reached 124, which must be considered very high due to the presence of rich aromatics. Our results are promising for rendering bio-hydrocarbons feasible and meet the new demands of the petroleum, petrochemical, and fine chemical sectors, with great environmental benefits.

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