

Article

Enhanced Liquid Fuel Production from Pyrolysis of Plastic Waste Mixtures Using a Natural Mineral Catalyst

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Abstract: Since plastic wastes are commonly found and accumulate in numerous types and forms, the pyrolysis of plastic waste mixtures seems more feasible to be selected for large-scale production. However, the process typically produces less liquid than individual plastic pyrolysis. This study proposed a viable approach for catalytic pyrolysis by using natural mineral catalysts without modification. Bentonite was selected as a natural mineral catalyst while HZSM-5 was used for performance comparison. The process was evaluated in situ using a fixed-bed reactor at temperatures between 400 °C and 500 °C. The mixture of plastic waste composition was designed based on the non-recycled plastics data. The results showed that 42.55 wt% of liquid yield was obtained from thermal pyrolysis using Malaysia's non-recycled plastics data. It was then found that using HZSM-5 and bentonite catalysts significantly boosted liquid products to about 56 and 60%, respectively. The presence of catalysts also positively minimized tar formation and eliminated wax formation in the liquid product. Furthermore, the catalytic process showed remarkable improvements in aromatics and alkane compounds in the liquid while only alkenes were found to be high when bentonite was used.

Keywords: catalytic pyrolysis; non-recycled plastic (NRP); liquid fuel; zeolite; bentonite



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1. Introduction

Plastics are valuable products for current consumer usage and offer a vast range of applications like packaging, toys, piping, and various container types. The primary kind of plastic includes low-density polyethylene (LDPE), high-density polyethylene (HDPE), polystyrene (PS), polypropylene (PP), polyvinyl chloride (PVC), and polyethylene terephthalate (PET) [1]. Nevertheless, they pose a severe environmental threat because they do not decompose in landfills. A report by the World Bank indicated that world cities generate 1.3 billion tons of solid waste each year. By 2025, this number may rise to 2.2 billion tons, of which 10% is plastic [2]. Plastic waste is a product made up of fossil fuels, which in principle, can be converted again to their constituting chemicals through the thermal processes [3]. In the current depletion trend of fossil fuels, this waste is a helpful resource for recovering hydrocarbons as fuels or feedstocks for chemical industries.

Currently, the pyrolysis of plastic waste into liquid oil has attracted the attention of researchers and business players to evaluate its feasibility [4]. It is driven by the fact that the method has eliminated the sorting issues typically found in mechanical recycling and is more environmentally friendly than incineration which harms air quality. Since the daily plastic waste rate accumulated in the landfill is high, it may be better to process plastic pyrolysis without separation which speeds up the process, optimizes landfill use, and reduces the waste treatment costs [1]. Therefore, maximizing feed use in the process becomes vital since it expects a high liquid yield, making the method feasible and economically applicable. However, most investigations have found a drawback of pyrolysis of the plastic mixture as liquid yield is low and unstable which leads to wax formation.

Several researchers revealed that over 80 wt% of liquid fuel yield could be obtained from fast pyrolysis of individual plastic. For instance, the authors in [5] carried out pyrolysis

of HDPE in a fixed-bed reactor at 450 °C with a heating rate of 10 °C/min for 45 min with nitrogen at a flow rate of 200 mL/min as sweeping gas. They reported up to 82 wt% of liquid fuel yield with little char and gas yield. However, pyrolysis of a plastic mixture usually produces a low liquid yield. This finding has been described in various reports published by many researchers. William and Slaney pyrolyzed the plastic mixtures at 500 °C under nitrogen pressure and obtained 48.7 wt% of oil [6]. Adrados et al. utilized the mixed plastic waste from a recycling plant in Bizkaia (Spain) and pyrolyzed it at 500 °C with a heating rate of 20 °C/min to obtain a maximum yield of 40.9 wt% [7]. Those studies have proven that pyrolysis of mixed plastic waste produced a lower liquid yield than individual plastic. In addition, pyrolysis of the plastic mixture produces an unstable liquid that turns to wax after being cooled to room temperature.

The kinetic analysis may explain the phenomenon of low liquid yield obtained from the pyrolysis of plastic mixtures. Different types of plastic have different activation energy, where the energy plays a vital role in initiating the decomposition and formation of volatiles, which finally determines the product yield. The sequence of the activation energy of the thermoplastics in ascending order would be PS = 192.6 kJ/mol, PET = 197.6 kJ/mol, PP = 261.2 kJ/mol, LDPE = 267.6 kJ/mol, and HDPE = 202.4 kJ/mol. Li et al. noted that the mixture of plastic in pyrolysis promoted the multiple-step reaction, as shown by the derivative thermogravimetric analysis curve. These indicate the existence of a possible interaction between plastics which could alter their thermal behavior through a synergetic effect [8]. If decomposition involves several steps with different activation energies, the contributions of these steps to the overall decomposition rate will vary with both temperature and extent of conversion [9].

Due to the low yield of liquid product and wax formation during the plastic waste mixture pyrolysis, a proper method to solve these issues is needed for the pyrolysis of mixed plastic waste to be technical and economically feasible [1,10]. To deal with the technical problem outlined above, the application of a catalyst to the pyrolysis process is investigated to obtain a stable and high-quality product [11]. The main advantages of catalytic pyrolysis are reducing the relative amount of heteroatom-containing molecules, increasing the oil's heating value and improving the product's stability, or decreasing the pyrolysis temperature, saving energy in this way [1]. In a study carried out by Auxilio, Choo [12], pyrolysis of a plastic mixture made up of HDPE, LDPE, PS, and PP was carried out in a 5.3 L continuous stirred tank reactor (CSTR) with a plastic feed rate of 600/h. The reactor was operated at 425 °C with an agitator speed of up to 125 rpm for 250 min. Kaolin clay was used as a catalyst in this process. The catalytic pyrolysis of a plastic mixture produced 63 wt% of liquid oil and 37 wt% of gas with negligible solid product [12]. Additionally, a study was carried out on catalytic pyrolysis of mixed plastic waste [13,14]. The plastic mixture was composed of HDPE, PET, PP, and PS. The pyrolysis experiments were carried out under a nitrogen atmosphere in a tubular reactor [14]. The process was operated at 500 °C for 30 min. Using Zr-PILC (Zr-pillared clay), the liquid oil obtained was 62.1 wt% with 36.7 wt% of gas product and 1.1 wt% of residue.

The objectives of the present study are to investigate the influence of reactor temperature, type of catalyst, catalyst amount, and plastic mixture composition on product distribution. Considering the efficiency and feasibility of the process, the catalyst criteria used in this study were designed without modification and categorized as a natural mineral catalyst. HZSM-5 zeolite is one of the most commonly used catalysts in the thermal pyrolysis of plastic into liquid oil [15]. It shows excellent properties as a catalyst for cracking polyolefins into products with high commercial value [16,17]. However, its utilization is limited by forming small product molecules that decrease the liquid product yield and increase the gas product [18]. In the search for another suitable catalyst for catalytic cracking of plastic, bentonite is considered due to its common application of bentonite as drilling mud in the oil and gas industry [19,20]. Moreover, bentonite was also used as a catalyst substrate in the catalytic cracking of petroleum [21]. Due to the similar nature of petroleum and plastic [22], the potential for the application of bentonite in the catalytic pyrolysis of

plastic waste was investigated in this study. In addition, the study is aimed to evaluate the performance of catalytic pyrolysis in reducing wax production, compare the quantity and quality of the liquid product between the catalytic pyrolysis and thermal pyrolysis, and determine the energy potential of liquid fuel from the catalytic pyrolysis of plastic waste.

2. Materials and Methods

2.1. Materials

LDPE, HDPE, PS, and PP were collected from municipal solid waste. The plastics were cut and ground to a 1–2 mm particle size. The samples were placed in an oven at 105 °C for 24 h to remove moisture. Then, the plastics were stored in desiccators to avoid moisture contamination. The plastic mixture ratio was determined using non-recycled plastic (NRP) data from Malaysia, the UK, the US, and globally, as shown in Table 1. PVC and PET were excluded from the samples in this experiment because of their undesirable properties. Pyrolysis of PVC will produce acidic HCl gases which are toxic, corrosive, and could damage equipment. Additionally, pyrolysis of PET will produce a yellowish liquid which will convert to a solid easily and cause blockage in the piping system.

Table 1. Global composition of plastic waste in municipal solid waste. Reprinted with permission from ref. [23]. Copyright © 2022 Elsevier.

Plastic Material	Malaysia Plastic Waste (wt%)	US Plastic Waste (wt%)	UK Plastic Waste (wt%)	Global Plastic Waste (wt%)
PET	16.2	12.4	15.3	15.43
HDPE	26.2	17.8	13.5	16.97
PVC	3.9	5.5	3.5	3.08
LDPE	31.1	19.6	25	33.95
PP	8.2	13.9	22.2	15.43
PS	13	8.7	4	12.35

HZSM-5 zeolite (Si/Al = 50, surface area = 315 m²/g, pore volume = 0.16 m³/g) was purchased from Zeolyst International, and raw bentonite (surface area = 69.39 m²/g, pore volume = 0.12 m³/g) was purchased from a mineral-oriented company in Chennai, India. HZSM-5 and bentonite were placed in a furnace at 500 °C for 3 h to remove contaminants. After cooling down, HZSM-5 and bentonite were stored in desiccators to prevent contamination.

2.2. Methodology

The catalytic pyrolysis experiments were performed using a two-stage pyrolysis process consisting of a thermal pyrolysis zone and a catalytic upgrading zone. The pyrolysis experiment was performed in a fixed-bed reactor due to its simple design, low gas exit flow rate, high burnout, and high thermal efficiency [23]. The reactor was equipped with a K-type thermocouple to monitor the temperature when an external furnace was used. A condenser was connected to the reactor to condense gases into liquid oil. Figure 1 presents the schematic diagram.

Thermal pyrolysis of NRP from Malaysia, the US, the UK, and globally was carried out to compare liquid yield without a catalyst. An external electric furnace was used to heat the reactor at the desired temperature with a heating rate of 20 °C/min. About 200 g of plastic mixture feedstock from different NRP data was fed into the reactor for the thermal pyrolysis process. For the thermal process, the plastic mixture was converted into vapor and directly entered to a condensation unit, while the vapor passed to the catalyst for the catalytic upgrading process. The liquid product was collected from the condensation unit and then weighted to quantify the yield. Three products were obtained, where the liquid oil and tar yields were calculated using Equation (1), while non-condensable gas was determined by a difference of 100%. Tar is produced in the product stream, which is defined

as a black viscous organic liquid that is generally considered to be aromatic [11]. Each experiment was repeated three times, and the average value was taken as the final result.

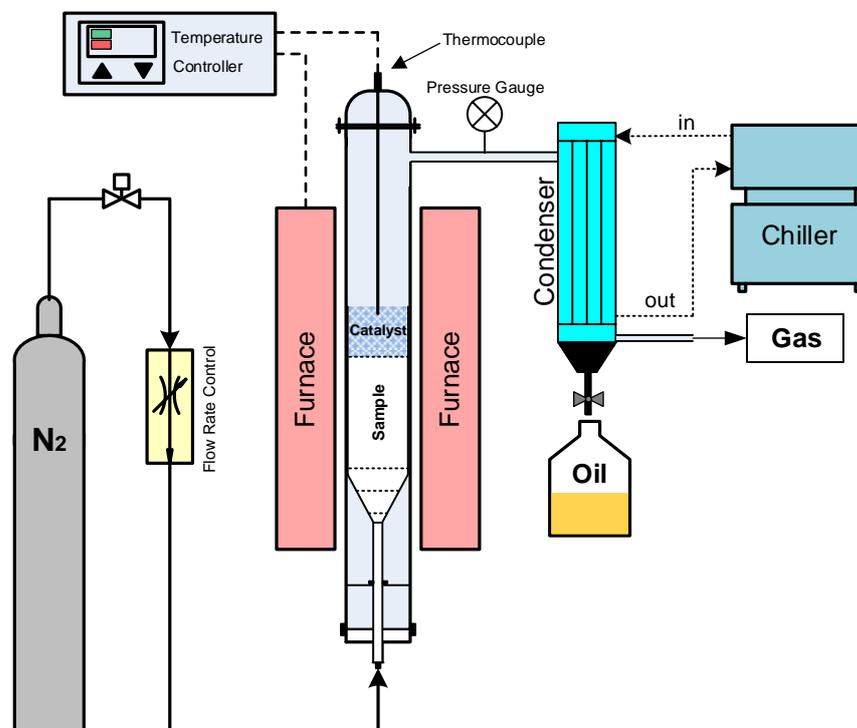


Figure 1. Schematic diagram of the experimental setup for pyrolysis of plastic mixtures.

$$\text{Yield of product (wt\%)} = \frac{\text{Desired product (g)}}{\text{Total feed (g)}} \times 100\% \quad (1)$$

Furthermore, catalytic pyrolysis was carried out using zeolite and bentonite. Malaysia's plastic composition was used as the model data for the impact of a catalyst on thermal pyrolysis. The amount of catalyst used varied from 1 g to 5 g to investigate the effect of the catalyst on liquid yield. Each experiment was performed for 45 min, and the temperature was varied between 400 °C, 450 °C, and 500 °C. The process condition for the highest liquid product was selected to carry out the catalytic pyrolysis of NRP of Malaysia, the US, the UK, and global plastic. The catalytic process results were then compared to the thermal pyrolysis of NRP data. The liquid oil obtained was further analyzed to determine its properties.

2.3. Characterization of Catalysts

The X-ray diffraction patterns of the purchased bentonite and the HZSM-5 zeolite were obtained from a Seifert X-ray Diffractometer JSO 2002, Ahrensburg, Germany, using Cu K- α radiation in the 2θ range of 0–70 °C. The chemical content of the bentonite and the HZSM-5 zeolite was obtained by Benchtop XRF Analyser-X-Supreme 8000, USA. The FTIR spectra of the bentonite and the HZSM-5 were obtained using Bruker Tensor 27 FT-IR 2002, USA, in 400–4000 cm^{-1} range after pelletizing the samples with KBr.

2.4. Characterization of Pyrolysis Oil

The properties of liquid oil, like density, pH, water content, elemental analysis, high heating value (HHV), and FTIR, were evaluated to determine the quality of liquid oil. Oil density was measured using a 25 mL pycnometer at 24 °C. The pH value of the liquid oil was determined using a Mettler Toledo pH meter series 320. pH value is an important measurement to avoid corrosion occurring in the reactor. The water content of the oil was

analyzed using Karl Fischer titration; 15 to 20 mg of the sample was taken for this test. The elemental analysis that described the mass fractions of carbon, hydrogen, nitrogen, and sulfur was performed using a Perkin-Elmer Model 2400 Series II CHNS/O Analyzer, while the oxygen was obtained by the difference. The elemental data were then used to calculate the HHV using Equation (2).

$$\text{HHV}(\text{MJ}/\text{kg}) = \frac{338.2 C + 1442.8 \left(H - \frac{O}{8} \right)}{1000} \quad (2)$$

FTIR analysis was used to identify different functional groups in the liquid oil. The samples were scanned in the range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1} . Gas chromatography/mass spectroscopy (GCMS) was used to identify the component of the liquid product. The Agilent HP-5 50 m column with an inner diameter of 0.32 mm and a film thickness of 0.25 μm was used in the GCMS. High purity of helium was used as carrier gas at a constant flow rate of 1.0 mL/min. The liquid sample was diluted to 100 ppm using hexane as a solvent to avoid damage to the column. The analysis was started by heating the column at 50 $^{\circ}\text{C}$ and kept isothermal for 1 min, then increased to 270 $^{\circ}\text{C}$ at 7 $^{\circ}\text{C}/\text{min}$. This condition was held for 10 min. The sample injected into GCMS was about 1 μL [23]. This analysis used an MS library database to identify the detected compounds. However, since more than 100 peaks were detected, only the peaks with a high degree of probability ($\geq 80\%$) and peak areas of $\geq 0.2\%$ were selected. The compounds were then arranged according to their group classification.

3. Results and Discussion

3.1. Catalyst Characterization

Figure 2a presents the XRD patterns of the samples. The XRD pattern of bentonite typically reflects the characteristics of montmorillonite clay. Moreover, minor quartz (SiO_2) and opal ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) were observed in bentonite as impurities. The basic reflection observed at 6.15 $^{\circ}$ (2θ) indicates 1.435 nm as the value of basal spacing (d_{001}), which is close to the typical calcium bentonite. The peak at 20.67 $^{\circ}$ is ascribed to smectite minerals (ICDD 01-074-1976) [24]. The peak at 21.9 is attributable to feldspar and cristobalite impurities [25]; 26.4 and 39.2 are ascribed to the quartz (ICDD 00-046-1045) [25,26].

The XRD pattern of the HZSM-5 was obtained with standard XRD peak positions. The entire sample spectrum showed the characteristic peaks ($\sim 8^{\circ}$ and 23–25 $^{\circ}$) of ZSM-5 zeolite with the MFI framework.

Figure 2b presents the FTIR pattern of the bentonite and HZSM-5 catalysts. For bentonite, the absorption band at 3630 cm^{-1} represents the OH structural groups stretching vibrations with Al-OH-Mg bonds [27]. The bands around 3400 and 1630 cm^{-1} can be ascribed to the stretching and bending vibrations of the H-O-H group in the hydration water [27,28]. The bentonite also has a band at 1011 cm^{-1} , a strong absorption attributable to tetrahedral sheet-based Si-O bending vibrations [29,30]. The 931 cm^{-1} bands can be attributed to the Al-Al-OH-based OH in bending vibrations [30,31]. The sharp peak at 804 cm^{-1} could be ascribed to Si-O stretching vibrations, representing quartz in bentonite [29,30]. The 628 cm^{-1} bands could be attributed to Al-O-Si bonds [29]. The 530 and 465 cm^{-1} bands are the Al-O-Si and Si-O-Si bending vibrations [29].

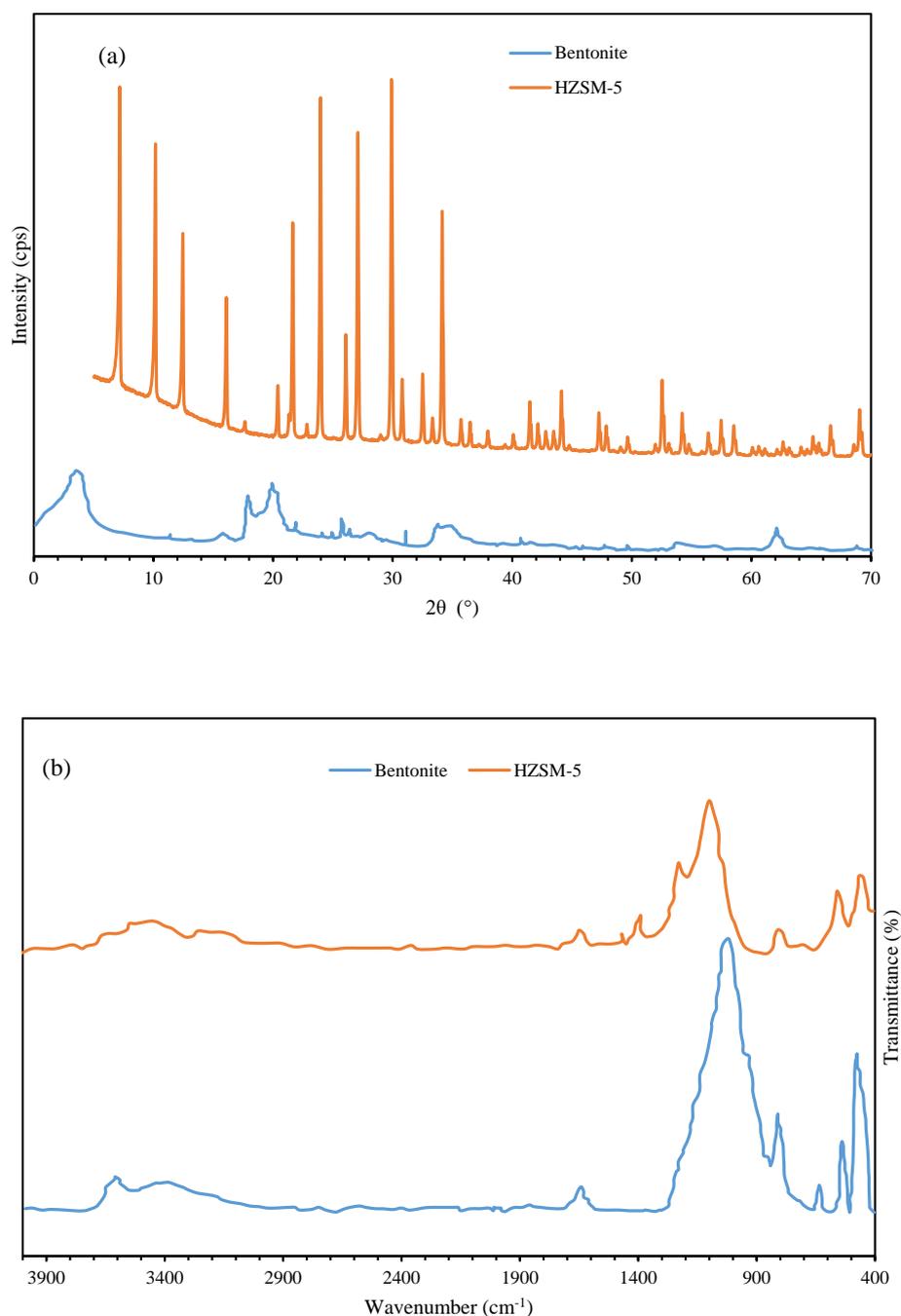


Figure 2. XRD (a) and FTIR (b) pattern of bentonite and HZSM-5.

For the HZSM-5 zeolite, the 1225 cm^{-1} and 799 cm^{-1} bands represent the external T-O-T asymmetric stretching and symmetric stretching, while 1098 cm^{-1} is the internal T-O-T asymmetric stretching. The 559 cm^{-1} and 450 cm^{-1} are the vibration absorption peak of the five-membered oxygen ring in the framework and the T-O-T bending vibration (T could be Si or Al). Moreover, the broad peaks at 3452 cm^{-1} and 1647 cm^{-1} represent the OH group stretching and bending vibration of physically absorbed water on the HZSM-5 surface.

Table 2 presents the contents of raw bentonite and HZSM-5 zeolite catalysts. Ideally, the theoretical composition of alumina and silica in montmorillonite structure is about 92%, and 2.6 is the silica-to-alumina ratio [32]. The bentonite used in this work exhibited 88.58% composition of alumina and silica, and 4.08% as the silica to alumina ratio. The silica to alumina ratio is about twice the theoretical value, revealing that the silica content

of bentonite is relatively high. The Ca/Na ratio of approximately 3.53 indicates that the bentonite can be categorized as Ca-based. The HZSM-5 used in this work exhibited a 99.73% composition of alumina and silica, and 49.62% as the silica to alumina ratio.

Table 2. Compositions of bentonite and HZSM-5 zeolite.

Component	Bentonite (wt%)	HZSM-5 (wt%)
SiO ₂	71.15	97.76
Al ₂ O ₃	17.43	1.97
MgO	1.95	-
Fe ₂ O ₃	1.91	-
Na ₂ O	0.43	0.17
CaO	1.52	-
K ₂ O	0.44	-
LOI	5.16	-

3.2. Pyrolysis Product Yield without Catalysts

Thermal pyrolysis of mixed plastic waste using NRP data for Malaysia, US, UK, and globally were carried out at 500 °C, and the result was presented in Figure 3. The tar residue in the reactor was 11.1 to 16.7 wt%, which is the highest found in US plastic composition. The highest tar residue in the US composition tended to lower the liquid yield. The tar residue is undesired in thermal pyrolysis while the liquid product is desired to be as high as possible. The liquid/wax yield was 39.9 wt% to 49.9 wt%, with the highest liquid product obtained for the global plastic composition. The global plastic composition had the highest LDPE and PS up to 46.3 wt%, essential to promoting liquid formation [33,34]. However, the liquid yield of mixed plastic obtained in this study is less than the pyrolysis of individual plastic from a previous study, up to 90 wt% [35]. Municipal plastic wastes are mainly mixed with different plastic compositions. It is difficult, time-consuming, and costly to separate different types of plastics for pyrolysis. Therefore, the addition of the catalysts in the pyrolysis process was investigated to determine their influence on the pyrolysis product of mixed plastic waste, especially liquid products.

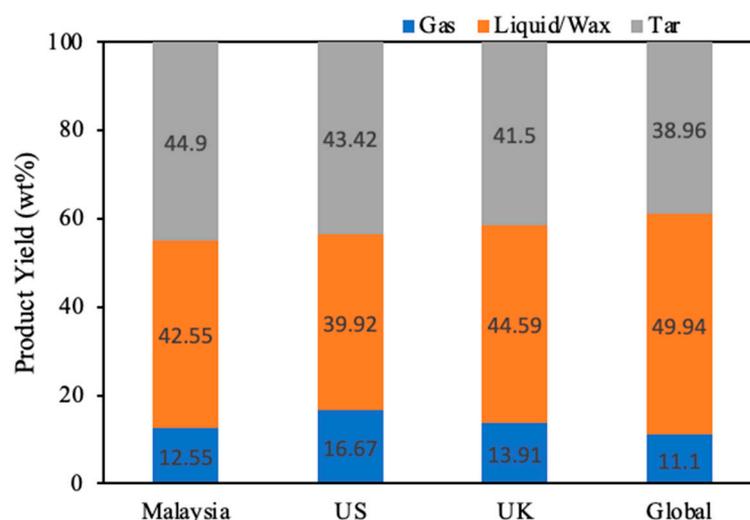


Figure 3. The product distribution of thermal pyrolysis of mixed plastic wastes at 500 °C.

3.3. Pyrolysis Product Yield with Catalysts

3.3.1. Effect of Zeolite on Pyrolysis Product Distribution

The effect of zeolite on the liquid yield was carried out using Malaysia's plastic waste composition. The tar residue decreased to 3 to 9 wt% compared with thermal pyrolysis, which is 12.5 wt%. The liquid obtained for zeolite at 500 °C was between 20 wt% to

40 wt%. It was observed that there was no wax formation during this process. From Figure 4a, it is clearly shown that by increasing the amount of zeolite in pyrolysis, the liquid yield decreases significantly. This could be explained by the high acidity of zeolite which causes a further breakdown of hydrocarbons into non-condensable gas instead of a liquid product [36]. Figure 4a shows increasing gas yield when the amount of zeolite increases. The highest gas yield of 73 wt% was obtained using 5 g of zeolite; therefore, 1 g of zeolite is recommended for further investigation.

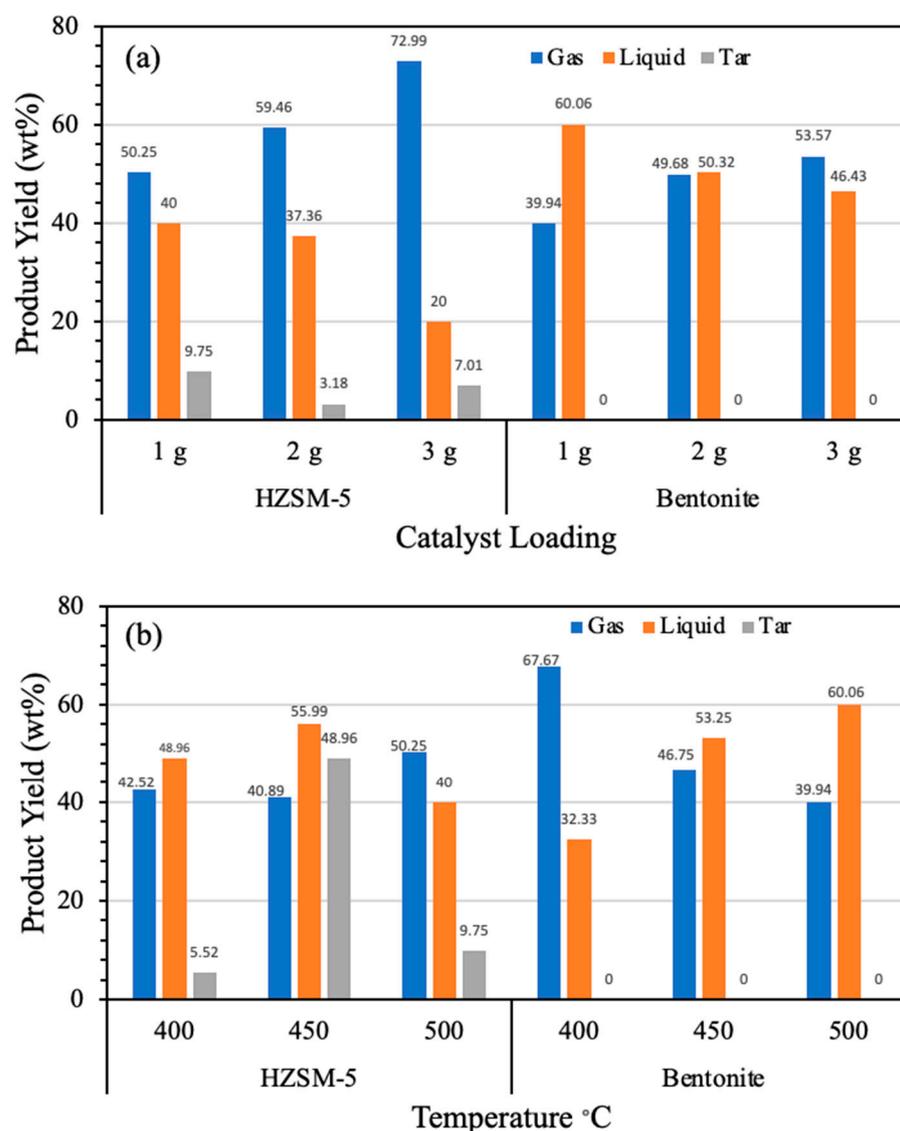


Figure 4. Comparative effect of catalyst usage on product distribution at 500 °C (a) and temperature on product distribution using 1 g of catalyst (b).

Figure 4b shows the effect of process temperature on pyrolysis product distribution for 1 g of zeolite. The liquid product obtained was between 40 wt% to 56 wt%, with the highest liquid yield obtained at 450 °C. This result is comparable with the report of [37] using Al-SBA-15 for pyrolysis of a mixture of HDPE, LDPE, PP, and PS. The gas yield varied between 40 wt% to 50 wt%; the lowest gas yield was obtained at 450 °C. Simultaneously, the lowest tar residue was also gained at 450 °C. The product distribution analysis shows that the optimum temperature to obtain the highest liquid yield and lowest gas and tar formation for 1 g zeolite pyrolysis is 450 °C.

3.3.2. Effect of Bentonite on Pyrolysis Product Distribution

In addition to zeolite, the influence of bentonite on pyrolysis product distribution was further explored. Figure 4a shows that the liquid yield is obtained between 46 wt% and 60 wt%, and the liquid yield increased with decreasing bentonite loading. The highest liquid yield (60 wt%) was obtained using 1 g of bentonite loading. In contrast, the gas yield increased with increasing bentonite loading, where a gas yield of 53 wt% was obtained using 5 g bentonite loading. The liquid yield which decreased, and the gas yield which increased with the increased amount of bentonite may be due to the effect of the acidity strength of bentonite in further breaking down the hydrocarbons to produce non-condensable gases. Another apparent influence of bentonite on the pyrolysis process was that there was no tar residue in the reactor and no wax detected in the liquid. All of the plastics had been converted to liquid and gases.

The influence of process temperature on 1 g bentonite pyrolysis is shown in Figure 4b. The liquid yield was obtained low at low temperatures, and the highest yield obtained at 500 °C was 60 wt%, followed by 53 wt% at 450 °C and 32 wt% at 300 °C. The gas yield increased with a decrease in process temperature, and the gas yield obtained for the experiment was between 40 wt% and 67 wt%, with the highest gas yield obtained at 400 °C. Unlike in zeolite, tar residue was found nil in the bentonite-catalyzed pyrolysis process, even at a lower temperature. It needs to be highlighted that the highest liquid yield obtained using bentonite was 60 wt% at 500 °C with 1 g of bentonite, which was higher than liquid obtained from zeolite pyrolysis, which was 56 wt% at 450 °C with 1 g of zeolite used. This shows that bentonite is a better catalyst for producing a high liquid yield with nil tar residue. The process condition for the highest liquid yield obtained at 500 °C with 1 g of bentonite was then applied to Malaysia, US, UK, and global plastic waste composition for catalytic pyrolysis.

Figure 5 shows the product distribution for catalytic pyrolysis of mixed plastic waste using 1 g of bentonite as the catalyst at 500 °C for different NRP data. It can be observed that the liquid yield obtained was between 54 wt% using UK plastic composition to 63 wt% using global plastic composition. This result is comparable to the report of [14], which investigated the pyrolysis of HDPE, PET, PP, and PS using various supported pillared clay.

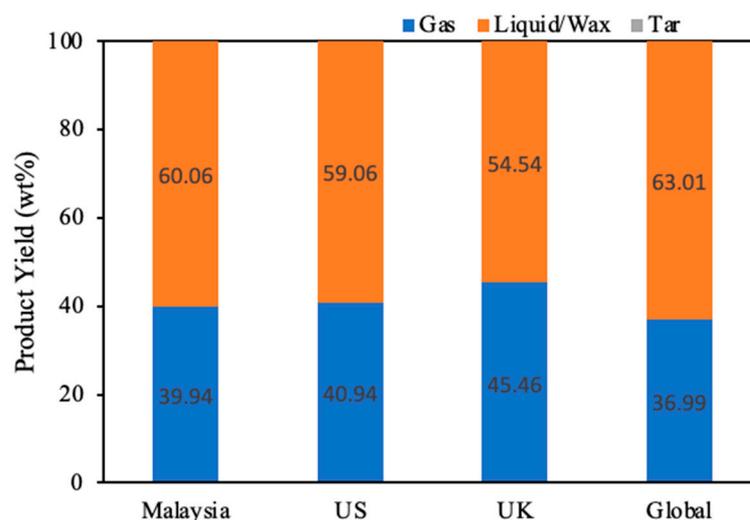


Figure 5. Product distribution for 1 g bentonite pyrolysis of mixed plastic waste at 500 °C.

Compared to thermal pyrolysis, as shown in Figure 3, using 1 g bentonite has improved the liquid yield significantly (see Figure 5). The US plastic composition, which initially produced 39 wt% of liquid by thermal pyrolysis, improved to 59 wt% when bentonite was added to the process. From all observations on the different NRP data, this study recorded that using bentonite has positively impacted the increment of liquid yield in the range of 10–19 wt%. Moreover, there was no tar residue found for the catalytic pyrolysis of mixed

plastic waste, which for thermal pyrolysis consists of 11 to 16 wt%. The application of bentonite catalysts successfully improved the liquid yield and eliminated tar residue in the pyrolysis reactor.

3.4. Composition of Liquid Product

Table 3 presents the oil properties obtained from thermal pyrolysis of Malaysia's plastic composition and catalytic pyrolysis using 1 g zeolite and bentonite at 500 °C. In terms of pH, the application of zeolite reduced the pH value from 3.8 to 3.25, which became a more acidic oil due to the acidity effect of zeolite. In contrast, bentonite had increased the pH value to 4.06, which showed that the oil is less acidic. Low acidity is desired for liquid oil to minimize the corrosion effect of the oil. The catalyst application also influenced the density of liquid oil, which increased the liquid density to 0.839 g/mL using zeolite and decreased the density to 0.772 g/mL by using bentonite as a catalyst. The density of conventional fuel is usually less than 1 g/mL. The lower the density, the higher the calorific value [38]. Moreover, the water content of liquid fuel is desired to be as low as possible to prevent water dispersion in liquid fuel. The water content for zeolite pyrolysis oil had reduced from 0.2299% to 0.1593% and decreased to 0.1437% by using bentonite as the catalyst, which is lower than zeolite pyrolysis oil. Additionally, the use of catalysts improved oil energy density, while zeolite and bentonite both increased the HHV to 42 MJ/kg and 44 MJ/kg, respectively. Based on the comparison of the physical properties of the liquid oil, it indicated that bentonite could produce a liquid product that has closer characteristics to conventional fuel as it is lighter, less acidic, has low water content, and high energy density.

Table 3. The properties of pyrolysis oil using 1 g of catalyst.

Properties	Malaysia *	Zeolite	Bentonite
pH	3.8	3.25	4.06
Density (g/mL)	0.796	0.839	0.772
Water content (wt%)	0.2299	0.1593	0.1437
Elemental composition (wt%)			
C	88.82	90.27	90.43
H	7.18	8.55	9.30
N	0.17	0.19	0.17
S	0.01	0.02	0.01
O (by difference)	3.83	0.97	0.09
High heating value, HHV (MJ/kg)	39.70	42.17	43.99

* no catalyst.

FTIR is a vital analysis procedure that could be employed to determine the functional groups in the oil. The FTIR spectra result for the thermal pyrolysis oil and catalyst pyrolysis oil of Malaysia, US, UK, and global plastic composition were provided in Figure 6. The result of catalytic pyrolysis was taken from the process using 1 g of bentonite at 500 °C. The peaks of the spectra for thermal pyrolysis and catalytic pyrolysis were similar in range but varied in terms of intensity. The results showed that all the oils produced strong peaks corresponding to alkanes at wavelengths around 2854, 2923, and 2955 cm^{-1} due to C–H stretching. For these peaks, thermal pyrolysis oil had a higher intensity, indicating a higher percentage of alkane compounds. The bands around 1456 cm^{-1} represented the presence of alkanes with a methyl group with C-H bending vibration. The signal intensity of the bands was higher for thermal pyrolysis than catalytic pyrolysis of different plastic compositions, indicating that the catalyst reduces the formation of alkanes with a methyl group. Moreover, the intensity of the spectrum signals below 1000 wavelengths increased as the bentonite catalyst was used. The absorption bands at 696 cm^{-1} , 728 cm^{-1} , and 775 cm^{-1} which are attributed to C-H out-of-plane bending vibrations, may refer to the presence of aromatic compounds [39,40]. Then, the sharp spectrum signal, which was

shown by the bands at 907 cm^{-1} (C-H out-of-plane bending), was probably identified as a vinyl group or alkenes [41].

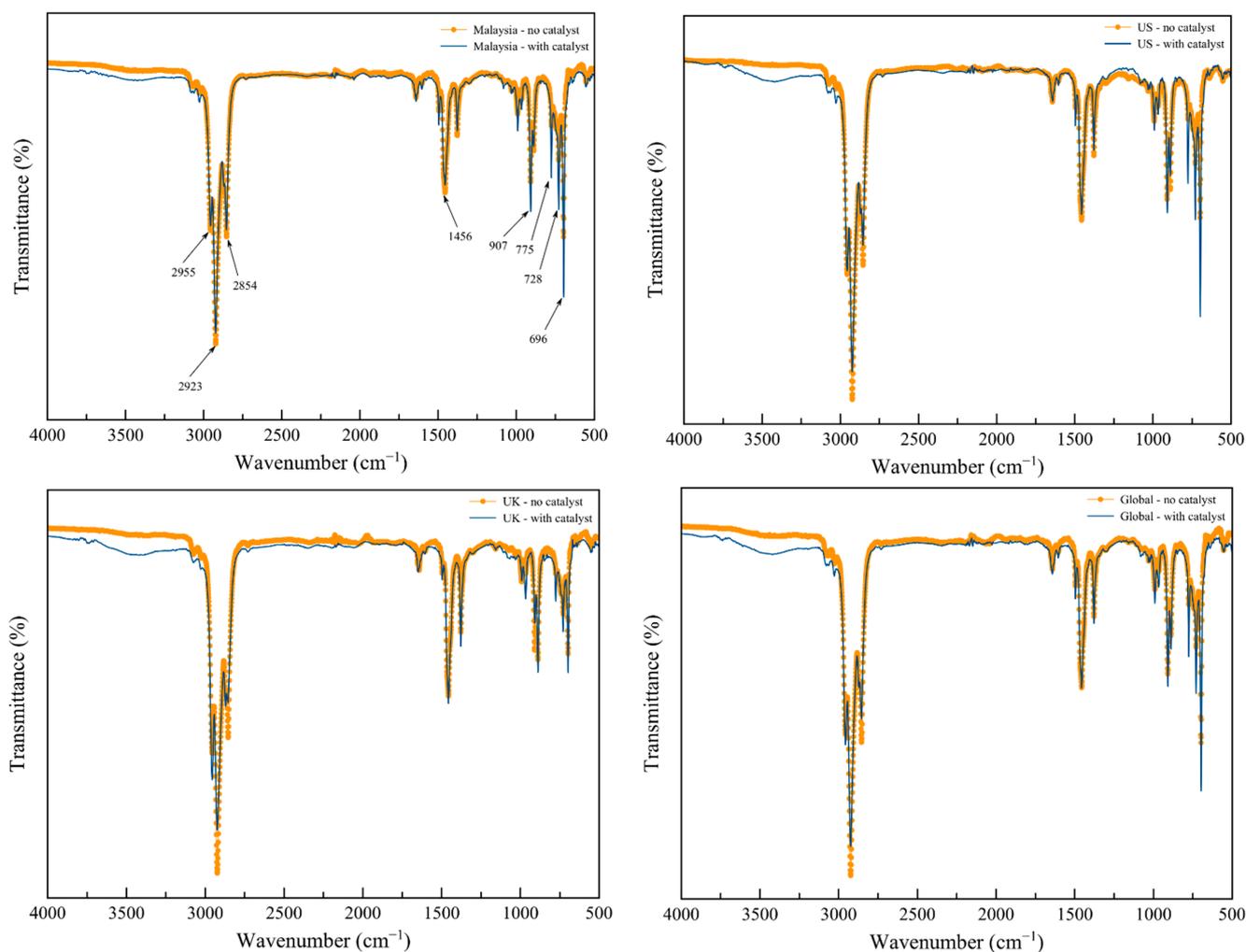


Figure 6. FTIR spectra of pyrolysis oil from thermal pyrolysis and catalytic pyrolysis of mixed plastic.

Further FTIR analysis was performed for both catalysts with different weight ratios to understand the role of catalysts in producing the various chemical compounds. The Malaysian NRP data were used as a feedstock with a reaction temperature of $500\text{ }^{\circ}\text{C}$, and the result is depicted in Figure 7. The figure shows that the IR spectrum profile of the oil produced from zeolite is similar to the oil obtained from bentonite catalyst. The spectrum profile was also identical, although both catalysts' weights varied. In particular, the band appearing at wavelengths below 1000 cm^{-1} was found to have stronger peak intensities for bentonite. This finding showed that the aromatic and alkenes dominated compounds in the oil produced from bentonite.

Following the FTIR analysis, the oil produced from thermal and catalytic pyrolysis was subjected to GCMS analysis to confirm the results. The results are provided in Figure 8a,b, which shows the comparison of substances in thermal pyrolysis oil and catalytic pyrolysis. Several interesting phenomena can be observed by comparing aromatics compounds, and alkane and alkene compounds. Thermal pyrolysis of mixed plastics produced 7 wt% to 20 wt% of aromatic compounds. However, using bentonite as a catalyst, the aromatic compounds increased from 31 wt% to 48 wt%, marking a significant increase. The highest aromatic compounds of the oil were obtained at catalytic pyrolysis of US NRP data, where PP type was found to dominate in the plastic waste composition.

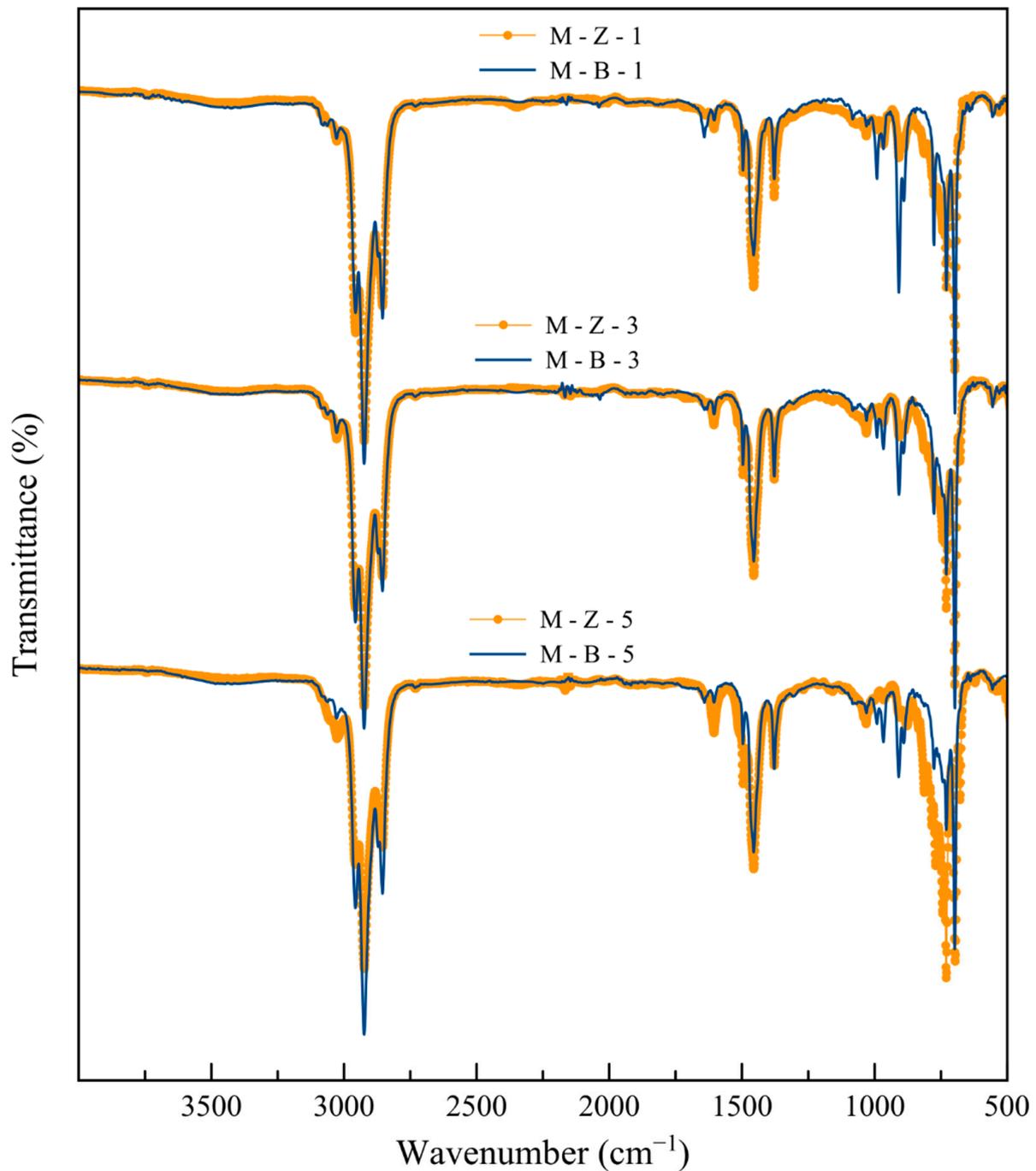


Figure 7. FTIR spectra of catalytic pyrolysis oil using zeolite and bentonite.

In contrast, there is a reduction in the formation of alkane compounds in the catalytic pyrolysis process; 20% to 36% was obtained for thermal pyrolysis, where it was then reduced to 11 wt% to 31% for catalytic pyrolysis. Alkene compounds in pyrolysis oil possessed a similar trend that produced from 34% to 42% for thermal pyrolysis and reduced to 20% to 29% for catalytic pyrolysis of mixed plastics. The result of GCMS analysis highlighted that pyrolysis using bentonite as a catalyst can increase the number of aromatic compounds and reduce alkane and alkene compounds. Other researchers have also reported aromatic compounds produced by catalytic pyrolysis of plastic waste using bentonite, although by applying individual plastics [39].

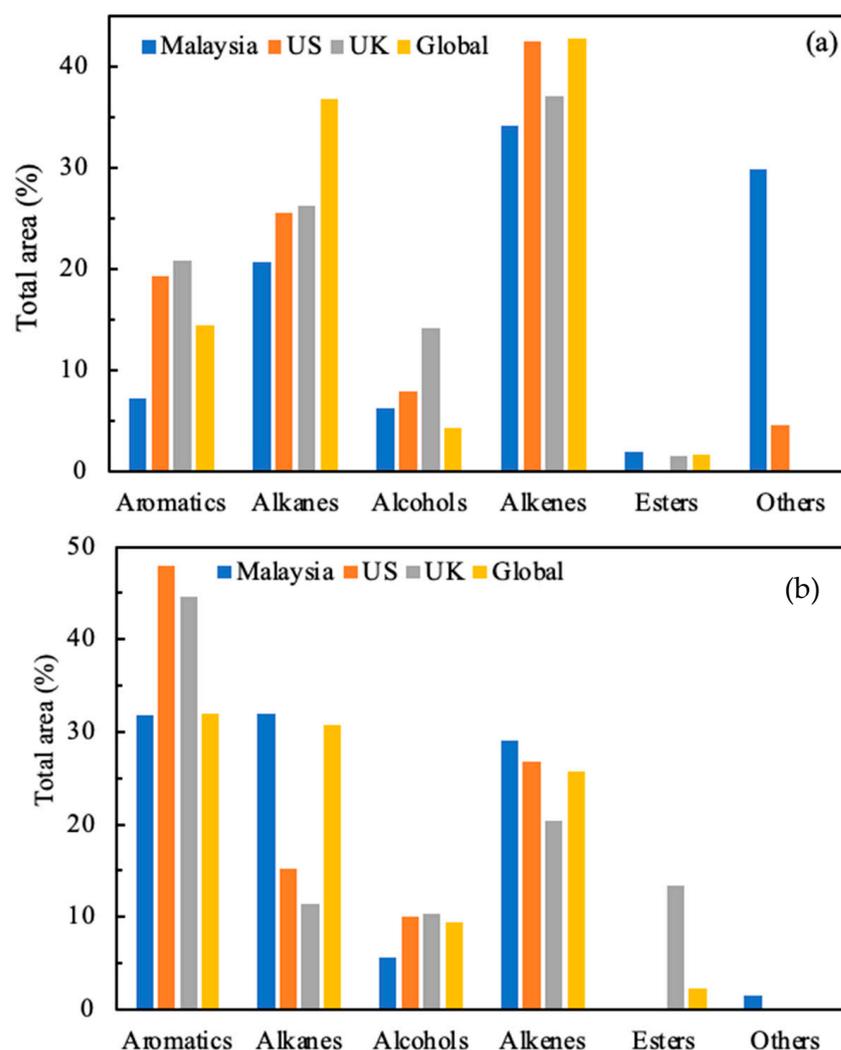


Figure 8. Identified compound for (a) thermal pyrolysis of mixed plastic composition and (b) identified compound for catalytic pyrolysis of mixed plastic composition using 1 g bentonite.

An additional test was performed to observe the compounds produced when the catalyst weight was increased, and the result is shown in Figure 9. It can be observed that pyrolysis using zeolite as a catalyst obtained a significantly higher number of aromatic compounds in pyrolysis oil between 50 wt% to 83 wt%. The higher the zeolite used in the process, the higher the aromatic compounds obtained. In addition, the presence of alkane compounds for bentonite pyrolysis oil was produced higher than zeolite, which obtained in the range of 32 wt% to 41 wt%, compared to zeolite pyrolysis oil which obtained only 7 wt% to 40 wt%. The alkane compounds in the liquid produced by the bentonite catalyst increased with the amount of bentonite, while it was the other way around for the zeolite catalyst. This was due to the use of zeolite promoting the secondary reaction, which leads to the formation of low molecular weight aromatics through cracking, rupture of rings, and aromatization [42]. In addition, the alkene groups were significantly higher in bentonite pyrolysis oil which was between 6 wt% to 29 wt%, as compared to zeolite pyrolysis oil which obtained only 1 wt% to 7 wt%. This GCMS result proved that zeolite and bentonite might produce high aromatic compounds. As an added benefit, bentonite also produced significant alkanes and alkenes.

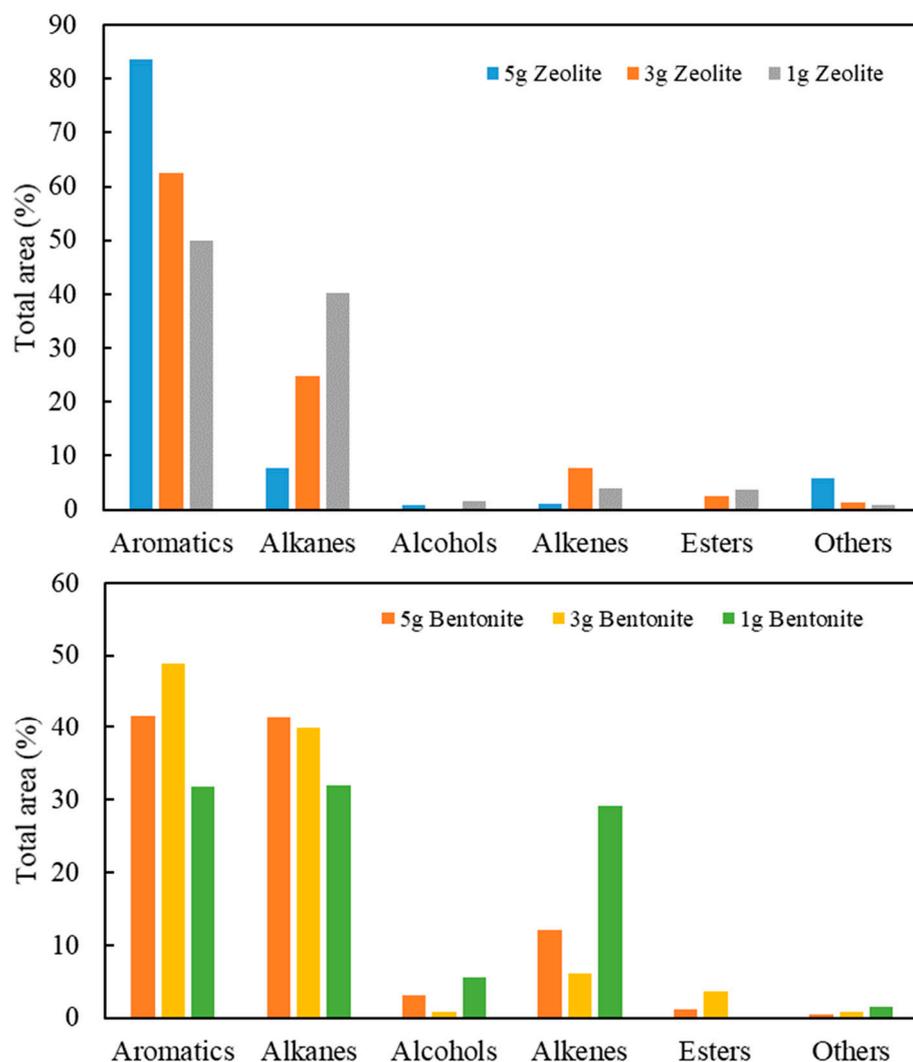


Figure 9. Identified compounds for catalytic pyrolysis using the different weights of zeolite and bentonite.

4. Conclusions

This study has proven that pyrolysis can handle mixed plastic waste and produce alternative fuel. Applying zeolite and bentonite can improve liquid product yield and minimize wax formation. However, bentonite has been proven to be a better catalyst than zeolite. This was due to bentonite promoting liquid product formation, which increased up to 20 wt%, reduced gas yield, and minimized tar residue to zero. Catalytic pyrolysis was optimal at 500 °C with 1 g of bentonite for 200 g of plastic mixture feedstock. The liquid yield was improved from 42.6 wt% (using thermal process) to 60 wt% at this condition. In addition, aromatic compounds were found high in the oil produced by both catalysts. Oil produced from bentonite had higher yields, better physical properties, and produced more alkanes and alkenes than oil produced from zeolite.

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