Catalytic pyrolysis of single-use waste polyethylene for the production of liquid hydrocarbon using modified bentonite catalyst

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Research Article

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Abstract

Bentonite has been modified using $\text{H}_2\text{SO}_4$ at various concentrations to alter Si/Al ratio that is responsible for catalytic pyrolysis of single-use waste polyethylene (SUWP). The XRF analysis confirmed a gradual decrease of $\text{Al}_2\text{O}_3$ content with an increasing concentration of $\text{H}_2\text{SO}_4$. The highest liquid hydrocarbon yield (87.48%) was obtained at Si/Al ratio of 34.24. To further activate acid-modified bentonite, bimetals (Cu/Ni, Fe/Ni, and Co/Ni) impregnation was conducted. The catalytic performance was compared with monometals (Ru, Co, Ni, Cu, and Fe) impregnated bentonite counterparts. The Co, Ni, or Cu impregnated bentonite catalysts (with 86, 83, and 86% yield) outperformed Fe and Ru impregnated bentonite catalysts (with 68% and 79% yield). However, bimetallic (Cu/Ni, Fe/Ni and Co/Ni) catalysts enhanced severe cracking leading to the formation of more gaseous hydrocarbons and thus less amount of liquid (70–80%) is obtained. Incorporation of iron into bentonite or Ni/bentonite increased the amount of 2-Octene, 3,7-dimethyl-, (Z)- compared to acid-treated bentonite and Ni/ bentonite catalysts. Moreover, Fe/Ni/bentonite has also increased the amount of 2-Octene, 2,6-dimethyl- compounds. The BET analysis shows that both surface area and pore diameter increased due to acid treatment resulting in an increase in the percent yield of liquid compared to raw bentonite. The FTIR and GC-MS analysis confirmed that the liquid hydrocarbon consists of linear and branched alkanes and alkenes with some cyclic hydrocarbons. The NMR analysis showed the liquid hydrocarbon is free from the aromatic compounds and polycyclic aromatic hydrocarbons (PAH).

Statement Of Novelty

Although twenty-first century modern society is highly dependent on plastic products, we cannot overlook the environmental pollution caused by waste plastics. However, single-use plastic wastes have become a major environmental concern since plastic is not biodegradable. Plastic wastes escape from landfill sites generally end up in drains, rivers, and oceans if not disposed of safely. Plastic waste is a dangerous threat to aquatic life. So we could neither ban using plastics nor cause harm to the environment. A more feasible solution would be converting these plastic wastes into liquid fuels. Modified bentonite has been found to be a suitable catalyst to convert these plastic wastes into energy. Wastes generated from single-use plastic commodities could be converted into liquid hydrocarbon in presence of modified bentonite catalysts. The liquid hydrocarbon produced in this manner could be used as fuel while reducing plastic waste and eventually protecting the environment.

Introduction

The single-use waste plastics and plastic materials have become integral part of modern life. Unfortunately, plastics do not decompose similar to organic matter and can stay unreacted for decades in the soil. These plastics are also creating some environmental threat to animals and plants [1–3]. For example, in 2017 the United States generated around 35.4 million tons of plastics. Of which only 8.4% was recycled, 16% incinerated, and 40% landfilled. The remaining 35.6% was left to mother nature without any further treatment [1, 2].
The amount of plastic consumption per person in the European Union (EU) and the United States approximately is 50 and 68 kg respectively each year [1]. In 2018, the European Commission proposed a plan to recycle 55% of plastic packaging by 2035. The EU recycled 42% of plastic packaging and between 14 and 18% was recycled globally in 2017 [3]. Bangladesh produces about 3000 tons of plastic wastes every day. About 545,300 tons of plastics were consumed in 2014 in Bangladesh [4]. Around 14 million polyethylene bags are disposed of as garbage each day in the capital city of Dhaka [5]. These plastics are responsible for clogging the drainage system, causing litter in the streets and direct and indirect health issues to animals and humans.

Polyethylene (PE) is a thermoplastic polymer extensively used in manufacturing packaging, plastic bags, films, tubing, and automobile parts. The polypropylene (PP) thermoplastic polymer is used to make food containers, furniture, and automobile parts. Among various types of plastics, about 18% of polyethylene terephthalate (PET), 16% of polyethylene (PE), and less than 1% of polypropylene (PP) were recycled in 2015 [1].

In addition, the COVID-19 has increased the application of polymeric materials used for manufacturing personal protective equipment (PPE), safety glasses, face masks, plastic face shields, plastic shoes, single-use plastics, and disposable gloves [6, 7, 8]. Also, plastic waste increased during this pandemic, due to the excessive use of plastics for packaging application by the supermarkets and food industry for avoiding contamination. Poorly disposed of plastic wastes from these sources have created an increased risk of polluting rivers, waterways, and the ocean.

Generally, plastic materials are disposed of as incineration and landfill. Landfilling is undesirable. Incineration could recover energy but this process produces poisonous gases such as furans and dioxins [9]. Plastics can be recycled mechanically but this process provides low-grade materials. Plastic packaging can be recycled mechanically up to a maximum of seven times. After having recycled several times, the quality of the polymer materials becomes too poor to further recycling [2, 3]. The catalytic conversion of waste plastics into liquid fuel such as gasoline and diesel is the most effective recycling method [10, 11]. Researchers have developed different catalysts for the catalytic conversion of waste plastics into liquid fuel. The catalysts that have been reported in the literature include ZSM-5 zeolite [12–17] silica-alumina (SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}) [12, 17, 18], MCM-41 [12, 17, 19] spent FCC catalysts [16, 20, 21] and kaolin clay [22–24].

Interestingly, bentonite exhibits similar compositions to kaolin. It is cheap and widely abundant natural smectite clay having a central alumina octahedral sheet sandwiched between two silica of tetrahedral sheets [25]. Acid treatment of bentonite increases the porosity and surface area. This increase in the surface area improves the efficiency of the catalyst. Only a few studies have been conducted on single-use polyethylene pyrolysis using bentonite catalysts. For instance, Panda et al. [26] investigated different types of polyethylene (LDPE, and HDPE) and PP using calcium bentonite catalyst. The XRF analysis shows that calcium bentonite catalyst contains 53.02% SiO\textsubscript{2}, 20.34% Al\textsubscript{2}O\textsubscript{3}, 9.39% Fe\textsubscript{2}O\textsubscript{3}, 1.14% TiO\textsubscript{2}, 4.85% CaO, 0.33% Na\textsubscript{2}O, 0.03% P\textsubscript{2}O\textsubscript{5}, 0.09% V\textsubscript{2}O\textsubscript{5}, and 0.08% MnO. This catalyst is capable of providing
88.5, 82, 82.5, and 81 wt% liquid from PP, LDPE, and HDPE respectively, at 500°C at 1:3 catalysts to plastic feed ratio [27]. The Liquid obtained contains C_{10} – C_{28} hydrocarbons consisting of linear and branched alkane and alkene. The liquid hydrocarbon does not contain any aromatic compounds. Commercial bentonite and mixed catalysts (bentonite kaolin, silica gel, and activated charcoal) were investigated for the pyrolysis of LDPE at a 10/1 ratio of plastic/catalyst at a range of 550–650°C by Soliman et al. [28]. They found that pyrolysis of 200.0 g LDPE using 20.0 g bentonite provided 63.45% liquid. On the other hand, pyrolysis of 200.0 g LDPE using 20.0 g mixed catalyst (5.0 g activated charcoal 5.0 g bentonite, 5.0 g kaolin, 5.0 g silica gel) provided 76% liquid hydrocarbon [28].

A binder-free bentonite pellet catalyst has been developed for the catalytic degradation of plastics by Budsaereechai et al. 2019 [29]. This research group made pellets of bentonite powder at 50 bars. This catalyst provided around 86–87% oil from LDPE, 88% oil from HDPE, and 90% oil from PP. These researchers also reported that the pyrolysis of plastics without using any catalyst produced highly reactive pyrolysis oil that could undergo polymerization to form a viscous liquid. The catalytic process provided less viscous liquid with hydrocarbons of lower molecular weight. Pyrolysis of PP and HDPE using metal-oxide-impregnated bentonite clays have also been reported by Ahmad et al. 2015 [30]. The bentonite was first washed using 0.1N HCl and then impregnated with transition metals such Zn, Ni, Co, Fe, and Mn by incipient wetness method. Among the catalysts, the cobalt and zinc impregnated bentonite produced the highest amount of liquids compared to non-catalytic tests. The cobalt impregnated bentonite showed high activity by producing the maximum amount of liquid from PP and zinc impregnated bentonite the maximum amount of liquid from HDPE. However, bimetals (Ni/Co, Ni/Fe, Ni/Cu) impregnated on sulphuric acid-treated bentonite have not been explored yet.

This research aims to optimize the conditions for obtaining the best bentonite catalyst through acid (H_{2}SO_{4}) treatment followed by impregnation of mono- (Ru, Co, Ni, Fe, Cu) and bimetals (Ni/Co, Ni/Fe, Ni/Cu) in order to get the highest liquid yield.

**Materials And Methods**

Bentonite powder was purchased from Loba Chemie, India. Sulfuric acid, RuCl_{3}·3H_{2}O, CoCl_{2}·6H_{2}O, Ni(NO_{3})_{2}·6H_{2}O, FeCl_{3}, and CuSO_{4}·5H_{2}O were purchased from Sigma Aldrich. Single-use waste transparent polyethylene was collected from the municipal garbage bins close to the Jagannath University, Dhaka, Bangladesh. The molecular weight of polyethylene ranges between 20,000 and 150,000. The formula of polyethylene to be

\((\text{CH}_2 \text{CH}_2)_n\).

**Preparation of Catalysts**

**Acidic treatment of bentonite**
In a 1000 mL round-bottom flask, 40 g bentonite and 400 mL sulfuric acid solution (1M) were mixed and refluxed for 4-5 hours at 120-130 °C. After cooling, the reaction mixture was filtered, washed, dried (100 °C for 12 h), and calcined (at 550 °C for 14 h). The mass of the obtained acid-treated bentonite catalyst was 27 g. In a similar manner 25, 23, and 20 g bentonite catalyst were obtained using 3, 5, and 7 M sulfuric acid, respectively.

**Preparation of monometallic catalysts**

Monometal impregnation on 3 M sulfuric acid-treated bentonite was performed following the incipient wetness method [30,31]. In a typical reaction, RuCl₃·3H₂O and bentonite (3 M H₂SO₄ treated) were mixed in the mass ratio of \( m(\text{Ru})/m(\text{bentonite}) \approx 0.05 \) i.e. 100.0 g bentonite containing 5.0 g Ru metal. 3.0 g of acid-treated bentonite was mixed with 100 mL of deionized water. The mixture was heated at 120 °C for 30 minutes and then a solution of ruthenium chloride was added with a continuous stirrer. The ruthenium chloride solution was prepared by dissolving 0.39 g RuCl₃·3H₂O in water (40 mL). The slurry was dried and then calcined at 100 °C (12 h) and 400 °C (4 h) respectively, to obtain Ru/bentonite. A similar method was applied in combination with metal precursors such as CoCl₂·6H₂O, Ni(NO₃)₂·6H₂O, FeCl₃, and CuSO₄·5H₂O, respectively, Co/bentonite, Ni/bentonite, Fe/bentonite, and Cu/bentonite were prepared.

**Preparation of bimetallic catalysts**

The M/Ni/bentonite (M = Co, Fe, Cu) catalysts were prepared according to the procedure of Al-Asadi et al. [32, 33]. For the preparation of Cu/Ni/bentonite catalyst, the Ni/bentonite suspension (5.0 g Ni/bentonite in 150 mL distilled water) was heated with stirring for 30 minutes at 130 °C and then the hydrated copper sulfate solution (dissolving 0.688 g CuSO₄·H₂O in 60 mL distilled water) was added. It was then heated and stirred for another 4 hours at the same temperature. The water from the solution was evaporated from the mixture at 100 °C (14 hrs.) and calcined at 400 °C (4 hrs.). The mass ratio of \( m(\text{Cu})/m(\text{Ni/bentonite}) \approx 0.037 \) or, i.e. 3.7 g Cu metal to 100 g Ni/bentonite. Accordingly, CoCl₂·6H₂O and FeCl₃ metal precursors were used for the preparation of Co/Ni/bentonite and Fe/Ni/bentonite catalysts respectively.

**Characterization**

**Characterization of Catalysts**

The techniques such as X-ray powder diffraction (XRPD), scanning electron microscopy (SEM) and X-ray fluorescence (XRF). The elemental analysis was performed using Shimadzu, Japan, XRF-1800 (Lab Center). For XRF analysis, the sample (1.0 g) was mixed and ground with boric acid (0.25 g). The resultant mixture was converted into pellets. The irradiation source was an Rh x-ray at 140 mA and 30
kV. The GNR Explorer powder X-Ray diffractometer was used for XRD analysis of bentonite catalysts. The source was Cu-Kα1 at 35 kV and 25 mA and step size of 0.1° with data integration time 3s per step over an angular range of 5-80° (2θ). The JEOL-SEM 7600F (with energy dispersive X-ray spectrometry detector at 5 kV) was used for obtaining SEM images of the catalysts. The BET specific surface area and pore volume were determined by measuring nitrogen adsorption-desorption isotherms at liquid N2 temperature (-196 °C) with a PMI's BET-Sorptometer (BET-201A, USA) apparatus. Software BETwin was used for data analysis and evaluation of BET surface area and pore size distribution. Before conducting BET analysis, the samples were degassed at 120 °C under vacuum for 1.5 hours. The last adsorption data point was used to calculate the total pore volume and the same data point was used as the first desorption data point. The characterization of the catalysts was performed based on the best performance of the catalysts. SEM was taken for raw bentonite and 3, 5 and 7 M H2SO4 treated bentonite. Nitrogen adsorption-desorption was carried out for raw bentonite and 3M H2SO4 treated bentonite. The XRD was taken for raw bentonite and 1 and 3 M H2SO4 treated bentonite and Co-, Ni- and Ru- impregnated 3M H2SO4 treated bentonite.

Characterization of liquid products

The liquid products of the catalytic pyrolysis experiments were characterized by GC-MS, FTIR, and 1H NMR spectroscopy. The Shimadzu 8400S, Japan was used for FTIR analysis of liquid products with KBr (heated at 100 °C for 1 day before analysis) pellets in the range of 400-4000 cm-1. The Shimadzu GCMS-TQ8040 was used for GC-MS/MS analysis of liquid products. Sample (0.5 µL) was injected in splitless mode in a capillary column Rxi-5ms of 30 m length × 0.25 mm id. The sample was injected at 250 °C. The oven was set to 50 °C for 1 minute and increased to 150 °C at the rate of 5 °C/min and then to 300 °C at 15 °C/min. The flow rate and the total run time of the column were 1 mL/min and 30 min respectively. Electron impact ionization technique was used for MS detection (full scan mode 50-550 m/z). In GC-MS analysis a quadrupole mass analyzer was used. Computer-assisted mass spectral search by NIST-MS library 2009 was used for the identification of individual hydrocarbons. The Bruker (model AVANCE III HD, 400 MHz) was used for the analysis of 1H NMR of liquid product.

Pyrolysis experiments with modified bentonite catalysts

A locally developed stainless steel reactor (Fig. 1) [24] was used for the catalytic pyrolysis of waste polyethylene. Prior to the catalytic pyrolysis experiments, the reactor was cleaned with acetone, and purged with nitrogen gas. The reactor was filled with catalysts and waste polyethylene at different mass ratios. The reactor was purged again with N2 gas after charging the feed. The liquid products were collected at 450 °C temperature. The duration of each experiment was 1 hr. Eq. 1 was used for calculation of yield (wt. %) of liquid. The aim of this study was to obtain liquid hydrocarbon only. For this reason,
gaseous product was vented off. After the completion of each catalytic reaction some coke was deposited on the catalysts. Hence, each catalyst was used in single time only.

\[
\text{Yield(\text{wt\%}) = \frac{\text{mass of product}}{\text{mass of starting material}}} \times 100\% \quad \ldots \quad (\text{eq. } 1)
\]

The pyrolysis of waste polyethylene was investigated in a locally developed stainless reactor with a dimension of length, internal diameter, and outer diameter of 100, 75, and 77 mm respectively (Fig. 1). The maximum capacity of the reactor is 50 g of feed materials. The reactor consists of an electric furnace, thermocouple, temperature controller, condenser, and liquid collection vessel.

**Results And Discussion**

**Characterization of the Catalysts**

The compositions of raw bentonite and sulphuric acid-modified bentonite were determined by XRF (Table 1). The composition of this raw bentonite in this study is comparable to that observed by Budsaereechai et al. [29]. The raw bentonite was treated with 1, 3, 5, and 7 M H\textsubscript{2}SO\textsubscript{4} to change Si/Al ratio. Bentonite and sulfuric acid react according to eq. 2 [18]:

\[
\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O} + 3\text{H}_2\text{SO}_4 \rightarrow \text{Al}_2(\text{SO}_4)_3 + 2\text{SiO}_2 + 5\text{H}_2\text{O} \quad \ldots \quad (2)
\]

A gradual decrease of Al\textsubscript{2}O\textsubscript{3} has been observed with the increase of sulfuric acid concentration (Table 1). The highest amount of Si/Al ratio was observed in the case of 7 M H\textsubscript{2}SO\textsubscript{4} due to the decrease of Al\textsubscript{2}O\textsubscript{3}. For example, the amount of Al\textsubscript{2}O\textsubscript{3} decreased from 13.61 % to 12.50 % after treatment with 1 M H\textsubscript{2}SO\textsubscript{4}. The amount of alumina (Al\textsubscript{2}O\textsubscript{3}) decreases drastically to 1.89 % and 1.09 % after 5 M and 7 M H\textsubscript{2}SO\textsubscript{4} treatment respectively. Accordingly, the ratio of Si/Al in raw bentonite is 6.94 which was increased to 9.73 and 34.24 after treatment with 1 M and 3 M H\textsubscript{2}SO\textsubscript{4} respectively. The Ni, Co, and Ru impregnated bentonite samples exhibit 6.52 % NiO, and 7.37 % Co\textsubscript{2}O\textsubscript{3}, and 6.55 % RuO\textsubscript{2} respectively which is nearly equivalent to 5 % metal precursors added in each case.

**Table 1** Composition (%) of raw and different concentrated H\textsubscript{2}SO\textsubscript{4} treated bentonite obtained by XRF.
The XRD patterns of raw bentonite and H2SO4 treated bentonite have been presented in Fig. 2. The raw bentonite consists of quartz, montmorillonite, feldspar, and a small amount of amorphous materials which were also observed by Zhirong et al. [34]. With the increasing concentration of the acid, the intensity of the diffraction peaks corresponds to montmorillonite and feldspar decreased, which indicates the dissolution of these materials from bentonite due to acid treatment. As a result, the amount of SiO2 increased which was confirmed by observing the increased diffraction peaks of quartz. Vukovic et al. [35] also reported similar observations during HCl acid activation of Bogovina (Serbia) bentonite. The presence of amorphous material was confirmed with the observed hump between 10-20˚ (2θ).

The SEM images of raw bentonite and H2SO4 treated bentonite have been shown in Fig. 3. SEM images of various bentonite samples show that H2SO4 treatment increases the roughness of the surface which is a consequence of surface etching on the surface of bentonite. With the increasing acid concentration, the etching increased. This result is also corroborated with the XRF results which show significant leaching of aluminum and iron out of the samples (Table 1).

Due to sulfuric acid treatment, the specific surface area and pore radius of raw bentonite increased significantly. The N2 adsorption/desorption isotherms of raw and 3 M sulfuric acid-treated bentonite are shown in Fig. 4. The isotherm is type IV and this type of isotherm is found in mesoporous materials [26, 36].

<table>
<thead>
<tr>
<th>Bentonite</th>
<th>SiO2</th>
<th>Al2O3</th>
<th>K2O</th>
<th>Fe2O3</th>
<th>MgO</th>
<th>TiO2</th>
<th>Na2O</th>
<th>CaO</th>
<th>SO3</th>
<th>Co2O3</th>
<th>NiORuO</th>
<th>Si/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw</td>
<td>53.64</td>
<td>13.61</td>
<td>1.60</td>
<td>16.332.54</td>
<td>3.19</td>
<td>4.26</td>
<td>1.18</td>
<td>0.71</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>6.94</td>
</tr>
<tr>
<td>1 M H2SO4 treated</td>
<td>69.03</td>
<td>12.50</td>
<td>1.50</td>
<td>6.62</td>
<td>1.46</td>
<td>3.77</td>
<td>0.30</td>
<td>0.17</td>
<td>4.40</td>
<td>-</td>
<td>-</td>
<td>9.73</td>
</tr>
<tr>
<td>3 M H2SO4 treated</td>
<td>86.89</td>
<td>4.47</td>
<td>1.33</td>
<td>1.37</td>
<td>0.26</td>
<td>4.14</td>
<td>0.16</td>
<td>0.08</td>
<td>1.19</td>
<td>-</td>
<td>-</td>
<td>34.24</td>
</tr>
<tr>
<td>5 M H2SO4 treated</td>
<td>91.64</td>
<td>1.89</td>
<td>1.30</td>
<td>0.67</td>
<td>0.07</td>
<td>3.66</td>
<td>0.15</td>
<td>0.07</td>
<td>0.44</td>
<td>-</td>
<td>-</td>
<td>85.40</td>
</tr>
<tr>
<td>7 M H2SO4 treated</td>
<td>94.66</td>
<td>1.09</td>
<td>1.25</td>
<td>0.32</td>
<td>0.06</td>
<td>1.86</td>
<td>0.15</td>
<td>0.19</td>
<td>0.38</td>
<td>-</td>
<td>-</td>
<td>152.95</td>
</tr>
<tr>
<td>Ni/bentonite*</td>
<td>81.09</td>
<td>4.11</td>
<td>1.25</td>
<td>1.31</td>
<td>0.20</td>
<td>3.88</td>
<td>0.16</td>
<td>0.08</td>
<td>1.26</td>
<td>-</td>
<td>6.52</td>
<td>34.75</td>
</tr>
<tr>
<td>Co/bentonite*</td>
<td>76.95</td>
<td>4.57</td>
<td>1.25</td>
<td>1.43</td>
<td>0.27</td>
<td>3.73</td>
<td>0.16</td>
<td>0.11</td>
<td>1.75</td>
<td>7.37</td>
<td>-</td>
<td>29.66</td>
</tr>
<tr>
<td>Ru/bentonite*</td>
<td>85.834.741.23</td>
<td>1.43</td>
<td>0.293.70</td>
<td>0.200.072.10</td>
<td>-</td>
<td>-</td>
<td>6.5531.89</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Bentonite treated with 3 M H2SO4
The BET analysis shows that the specific surface area of raw bentonite is 63.79 m²/g which increased to 232.35 m²/g after 3 M sulfuric acid treatment (Table 2). The BJH pore size distribution shows that the average pore diameter of raw bentonite is 50.8240 Å which increased to 91.9936 Å due to the treatment by 3 M sulfuric acid. The increased specific surface area and mesoporosity were due to the breakdown of the crystal structure of bentonite and leaching out of Al₂O₃ by the acid.

**Table 2** Summary of BET results of raw bentonite and acid-treated bentonite

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Raw bentonite</th>
<th>Acid treated bentonite (3 M sulfuric acid)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET specific surface area (m²/g)</td>
<td>63.79</td>
<td>232.35</td>
</tr>
<tr>
<td>Total pore volume (cc/g)</td>
<td>0.0811</td>
<td>0.5344</td>
</tr>
<tr>
<td>Skeletal density (g/cc)</td>
<td>1.0000</td>
<td>1.0000</td>
</tr>
<tr>
<td>Porosity based on skeletal density (per gram of sample)</td>
<td>0.0750</td>
<td>0.3483</td>
</tr>
<tr>
<td>Average pore diameter (Å)</td>
<td>50.8240</td>
<td>91.9936</td>
</tr>
</tbody>
</table>

The pore size distribution of raw bentonite and 3 M sulfuric acid-treated bentonite has been compared in Fig 5. As can be seen in Fig 5, due to the increment of specific surface area and pore diameter of bentonite after acid treatment, the percent yield of liquid increased compared to raw bentonite.

**SUWP pyrolysis using modified bentonite catalyst**

As a baseline experiment, 50 g waste polyethylene was pyrolyzed in the absence of a catalyst at 550°C under N₂ atmosphere. This pyrolysis experiment provided 47% black waxy liquid. Later, the waste polyethylene was pyrolyzed at a comparatively lower temperature (450 °C) using untreated raw bentonite (Si/Al ratio of 6.94). This experiment provided a 79.53% yield of viscous liquid. To understand the influence of the Si/Al ratio on the waste polyethylene pyrolysis, raw bentonite (Si/Al ratio 6.94) was
treated with 1, 3, 5, and 7 M H$_2$SO$_4$. The treatment of bentonite with H$_2$SO$_4$ at different concentrations caused to alter the Si/Al ratio. The 3 M H$_2$SO$_4$ treated bentonite was then impregnated with mono- and bimetals for optimizing the conditions in obtaining the highest liquid yield. These catalysts were tested for waste polyethylene pyrolysis at 450 ºC. Each pyrolysis experiment was carried out for 30 minutes duration. Table 3 shows the summary of these experimental results.

Table 3 Results of pyrolysis experiment in presence of different types of modified bentonite catalysts (Temperature: 450 ºC).
<table>
<thead>
<tr>
<th>H$_2$SO$_4$ treated and metal impregnated bentonite</th>
<th>Catalyst to plastic ratio</th>
<th>Produced oil (mL)</th>
<th>Observed Physical appearance</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Catalyst (g)</td>
<td>Plastic (g)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Amount (g)</td>
<td></td>
</tr>
<tr>
<td>1 M</td>
<td>3</td>
<td>9</td>
<td>1:3</td>
<td>8.0</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>15</td>
<td>1:5</td>
<td>14.0</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>21</td>
<td>1:7</td>
<td>23.0</td>
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<tr>
<td></td>
<td>3</td>
<td>30</td>
<td>1:10</td>
<td>32.5</td>
</tr>
<tr>
<td>3 M</td>
<td>5</td>
<td>15</td>
<td>1:3</td>
<td>15.0</td>
</tr>
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*mono- and bimetals impregnated on 3 M sulfuric acid-treated bentonite

**Only thermal pyrolysis was performed at 550 °C [the gaseous hydrocarbon was vented off after pyrolysis and small amount of coke was deposited onto the catalyst after pyrolysis. Hence, each catalyst was used single time only.]

Among the various catalysts, 1 and 3 M H$_2$SO$_4$ treated bentonite catalysts were found to be most effective in providing the highest amount of liquid hydrocarbon. Note that the Si/Al ratios of 1 and 3 M
H₂SO₄ treated bentonite catalysts are 9.73 and 34.24 respectively. The bentonite treated with 1 and 3 M H₂SO₄ provided the highest yield of 87.10% and 87.48% respectively. The density of the liquid product is found to be 0.7953 g/mL. The yield of liquid products obtained by 1 and 3 M H₂SO₄ treated bentonite catalysts is much higher than that obtained with calcium bentonite catalysts reported by Panda [27]. The acid treatment of bentonite was found to be more effective in pyrolysis than untreated bentonite. Soliman et al. [28] obtained only 63.45% liquid using untreated bentonite by reacting 200 g waste plastics with 20 g untreated bentonite. They also obtained 66.85% liquid by reacting 200 g waste plastics with 10 g raw bentonite and 10 g raw kaolin [28].

A general trend of increasing the quantity of liquid with the increase of the ratio of catalyst to plastic was observed. For example, modified bentonite (treated with 1 M sulfuric acid) provided 70.69% liquid which increased to 87.1% with increasing the catalyst to polyethylene feed ratio (from 1:3 to 1:7). Similarly, bentonite modified with 3 M sulfuric acid provided 79.53% liquid which increased to 87.48% at a catalyst to polyethylene feed ratio from 1:3 to 1:10.

The liquid obtained by bentonite modified with 5 and 7 M sulfuric acid was highly viscous. The Si/Al ratio in the bentonite treated by 5 and 7 M H₂SO₄ was 85.40 and 152.95 respectively. The higher value of the Si/Al ratio was due to the presence of a lower amount of Al₂O₃ in these catalysts. The 5 and 7 M H₂SO₄ treated bentonite catalysts contain only 1.89% and 1.09% Al₂O₃ respectively. The presence of a lower quantity of alumina caused the catalyst to be less acidic. This less acidic catalyst was responsible for the formation of longer oligomers that were viscous. This indicates that the catalyst must have a certain quantity of Al₂O₃ and proper acidity for generating smaller hydrocarbon molecules desirable for producing anti-knocking fuel.

To understand the nature of liquid yield, the effect of catalysts containing monometals (Fe, Co, Ni, Cu, Ru) and bimetals (Fe/Ni, Co/Ni, Cu/Ni) impregnated on bentonite modified with 3 M sulfuric acid was studied. The Ni/ZSM-5 catalyst has a higher ability to crack C-C single bonds [37]. Therefore, this catalyst should be more efficient for the pyrolysis of polyethylene. Pyrolysis of waste polyethylene using Ni/bentonite at a ratio of 1:10 (catalyst/plastic) provided 83.15% liquid which is lower than the liquid obtained (87.48%) by only 3 M H₂SO₄ treated bentonite.

Surprisingly, the Co/bentonite and Cu/bentonite catalysts provided a similar quantity (86.16%) of liquid which is higher compared to the liquid obtained (83.51%) by the Ni/bentonite catalyst. The Fe/bentonite provided comparatively less liquid with a percentage of 68.93. Due to over cracking of plastics molecules by this catalyst, more gaseous hydrocarbon was formed and thus less amount liquid was obtained.

To understand the effect of bimetals impregnated bentonite on pyrolysis, bimetallic catalysts consisting of Cu/Ni, Fe/Ni, and Co/Ni impregnated on 3 M H₂SO₄ modified bentonite were investigated. The presence of (Cu, Fe, and Co) in Ni impregnated bentonite decreased the yield of liquid significantly. For
example, liquid yield by Ni/bentonite catalyst was 83.51% which decreased to 72.90% by Cu/Ni/bentonite, 79.53% by Fe/Ni/bentonite, and 70.25% by Co/Ni/bentonite catalyst. The bimetallic catalysts promote severe cracking leading to more gaseous hydrocarbon formation and a comparatively lower amount of liquid generation. Al Asadi et al. [32,33] reported that bimetals loaded on ZSM-5 catalyst also produced a higher amount of gaseous hydrocarbon which is similar to this observation.

It is evident from Fig. 6 that modified bentonite treated with 1 and 3 M H$_2$SO$_4$ as well as monometal (Co, Ni, Cu) impregnated bentonite catalyst can outperform ZSM-5 [13], red mud [13], kaolin clay [23], and nickel/silica-alumina [18]. Moreover, the modified bentonite might be better than calcium bentonite [27], kaolin catalyst [26], and silica-alumina [26].

The Liquid obtained using bentonite catalyst modified with 3 M H$_2$SO$_4$ contains alkanes and alkenes which was confirmed by FTIR spectrum (Fig. 7). The % transmittance peak values at the wavenumber of 2958, 2904, 2873, and 2835 cm$^{-1}$ are the indication of the existence of C-H stretching of methyl and methylene groups of alkane. The wavenumbers at 1649 and 1458 cm$^{-1}$ are related to C=C stretching and C-H bending (scissoring) respectively. The C-H bending was observed at 1377, 1157, 1112, 970, and 887 cm$^{-1}$.

The liquid products did not contain any functional groups of aldehyde, ketone, and ester since no peak was observed at the wavenumber range of 1740-1710 cm$^{-1}$ for C=O stretch. The liquid product also did not appear to contain any band between 2500 – 3600 cm$^{-1}$ which corresponds to OH stretch of alcohol or carboxylic acid. The liquid hydrocarbon produced using 1, 5, 7 M H$_2$SO$_4$ treated bentonite catalysts (Fig. S1) as well as Ru, Co, Ni, Cu, Fe, Cu/Ni, Fe/Ni, and Co/Ni impregnated bentonite catalysts show similar bands.

The $^1$H NMR spectrum of the liquid obtained using all the modified bentonite catalysts shows peaks of methyl and methylene protons in the range of 0.8-2 ppm (Fig. 8). There is no peak at 7-8 ppm in the aromatic regions which indicates the absence of aromatic compounds and polycyclic aromatic hydrocarbons (PAHs) in the liquid products of pyrolysis of plastic waste. Note that the PAHs are known to be carcinogenic and harmful to the environment.

The GC-MS analysis of compositions of the liquid hydrocarbon is also supported by the data obtained from the FTIR and NMR. The NIST-MS library 2009 spectral search was used to identify the individual hydrocarbons in GC-MS (Table 4). The liquid consists of different components of linear and branched saturated (alkanes) and unsaturated (alkenes) hydrocarbons with a carbon chain from C$_{10}$ − C$_{27}$. The liquid contains a higher amount of alkenes compounds than alkanes. The presence of some substituted cycloalkanes was also observed. The liquid products consisted of mostly branched organic compounds. The compositions of the liquid produced by 3 M H$_2$SO$_4$ treated bentonite, Fe/bentonite Ni/bentonite, and Fe/Ni/bentonite have been shown in table 3. The compositions of the liquid produced by Cu/bentonite Co/bentonite, Ru/bentonite, and Cu/Ni/ bentonite have been provided in Table S1. Our result is in contrast to the findings of Kaltume et al. (2019) [38]. They found that metal (Ni, Fe, Mo, Ru, and Co) impregnated
Y-zeolite produced aromatic compounds from high-density polyethylene (HPDE). However, our bentonite catalytic system did not produce any aromatic compounds.

In Table 4, the GC-MS result shows that the compositions of liquid hydrocarbons obtained by using acid-treated bentonite and Ni/bentonite are similar. On the other hand, Fe/bentonite and Fe/Ni/bentonite provided similar compositions. The Fe/bentonite and Fe/Ni/bentonite catalysts significantly increased the amount of 2-Octene, 3,7-dimethyl-, (Z)- compounds compared to acid-treated bentonite and Ni/bentonite catalysts. Moreover, Fe/Ni/bentonite has also increased the amount of 2-Octene, 2, and 6-dimethyl- compounds.

A free radical mechanism is proposed for the thermal cracking of plastic. The bentonite causes the fracture of the C-C bond and produces lighter aliphatic hydrocarbons. We believe in the catalytic process of the pyrolysis experiment in this study, carbenium ions formation dominated over the free radical...
process during the initiation process (Fig 9). The bentonite catalyst abstracts hydride ion from polymer (when the catalyst acts as Lewis acid) leading to the formation of carbenium ions. Proton addition to polymer (when catalyst acts as Bronsted acid) might also occur during the initiation process. Later, $\beta$-Scission may have occurred that produced smaller fragments. Intramolecular and intermolecular hydrogen transfer might have also occurred during propagation. The smaller fragments that were produced might undergo isomerization to produce branched products. Cyclization occurs to produce cyclic compounds. As evident from NMR analysis of the liquid product, no aromatization reaction happens to form aromatic compounds in pyrolysis of bentonite catalytic system.

Conclusions

In this study, single-use waste polyethylene was pyrolyzed using bentonite catalyst modified with sulfuric acid as well as impregnated by monometals (Ru, Co, Ni, Cu, and Fe) and bimetals (Cu/Ni, Fe/Ni, and Co/Ni). The ratio of Si/Al, surface area, and pore of the bentonite catalysts have been shown to play a significant role in the catalytic pyrolysis process. Treatment of bentonite with sulfuric acid increased both surface area and pore diameter. As a result, the percent yield of liquid increased compared to raw bentonite. The XRF results confirmed a gradual decrease of $\text{Al}_2\text{O}_3$ content with an increasing concentration of $\text{H}_2\text{SO}_4$. Bentonite treated with less concentrated acid has been shown to provide a higher yield of liquid with an increasing catalyst to plastic feed ratio. The bimetallic catalysts as well as Fe containing monometallic catalysts promoted severe cracking leading to more gaseous hydrocarbons formation resulted in a lower amount of liquid production. The experimental results from the NMR, FTIR, and GC-MS analysis demonstrated that the liquid contains mostly linear and branched saturated (alkanes) and unsaturated (alkenes) hydrocarbons of $C_{10} - C_{27}$. The presence of iron in bentonite or Ni/bentonite increased the amount of 2-Octene, 3,7-dimethyl-, (Z)- compared to acid-treated bentonite and Ni/bentonite catalysts. The amount of 2-Octene, 2,6-dimethyl- is also increased due to the incorporation of iron into Ni/bentonite. Bentonite clay-based catalysts are relatively inexpensive.

Declarations

The authors declare that this manuscript has not been submitted to any other journal for the publication in the form of monograph or article.

Conflicts of Interest

The authors of this manuscript declare no known conflicts of interest.

Data Availability Statement

All the data regarding this manuscript are available and can be provided if necessary.

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References


Figures
Figure 1

Reactor setup for plastic pyrolysis.
Figure 2

XRD patterns of raw, 1, 3 M H$_2$SO$_4$ treated bentonite and metal (Co, Ni, Ru) impregnated 3 M H$_2$SO$_4$ treated bentonite.
Figure 3

SEM micrograph of raw (a), 3 M (b), 5 M (c) and 7 M (d) H$_2$SO$_4$ treated bentonite (10 μm, x 2000).
Figure 4

$\text{N}_2$ adsorption/desorption isotherms of (a) raw bentonite and (b) 3 M sulfuric acid-treated bentonite.
Figure 5

BJH pore size distribution of (a) raw bentonite and (b) 3 M sulfuric acid-treated bentonite.
Figure 6

Comparison of liquid yield obtained using modified bentonite as a catalyst with reported catalytic systems; this study *, [13] (a), [23] (b), [18] (c), [26] (d), [27].
Figure 7

FTIR spectrum of the liquid obtained by bentonite modified with 3 M H$_2$SO$_4$. 
Figure 8

$^1$H NMR spectra of the liquid obtained by bentonite modified with 3 M H$_2$SO$_4$ (a), Co/bentonite (b), Ni/bentonite (c), Ru/bentonite (d).
Figure 9

Mechanism of pyrolysis of waste polyethylene using bentonite catalyst.

Supplementary Files

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