Emulsification of Water and Pyrolysis Oil

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Abstract

Emulsification of pyrolysis oil produced from recycled high-density polyethylene (HDPE) was experimentally investigated. Pyrolysis oil was made from recycled HDPE pellets using a pyrolyzer operated under cascade heating steps and heating rates. Water-in-oil emulsion was produced with ultrasonic mixer and homogenizer using Span80 surfactant as emulsifier. The emulsion stability was assessed by water droplet size and visual observation. Rheological properties were measured to confirm the microstructure change. The emulsion viscosity follows the Einstein equation for a dilute emulsion with water content less than 10\%. The ultrasonic mixer was confirmed to be more effective than mechanical homogenizer both in term of smaller water droplet size and lower viscosity. Water-in-oil emulsion was more viscous than its constituting components. A proper droplet size minimization can mitigate the viscous emulsion issue.

Keywords: pyrolysis oil; emulsification; ultrasonic; rheology; emission control

1. Introduction

Plastic is an indispensable part of daily activities and their production and use are therefore growing problem of huge amount of waste. The conversion of waste plastics into fuel by pyrolysis process is a practical approach to resolve the problematic waste management and improve energy sustainability. The pyrolysis oil obtained by fast pyrolysis process has compatible properties to other refinery fuels [1]. This strategy minimizes consumption of raw materials and natural resources with benefit of recovered fuel. The pyrolysis process can accept wide ranges of plastics feedstock which substantially reduce labor...
intensive sorting process. One of the drawbacks impeding the wide spread usage of the pyrolysis oil is the considerable amount of alkenes and nitrogen compounds leading to soot and nitrogen oxide [2].

Emulsification of pyrolysis oil and water can significantly improve NOx, CO, and soot emission. In addition, the microexplosion phenomena which water droplet vaporized within the emulsion contributes to greater mixing and improves combustion characteristic. A proper emulsification process is indispensable given the immiscible nature between oil and water. The ability to produce fine disperse phase droplet can greatly enhance the fluid properties. In addition, small disperse phase droplet size is less likely to coalescence and exhibits lower viscosity. Subsuksamran et al. [3] employed cascade heating steps and heating rates pyrolysis process provides 80% product yield using waste plastic or recycled high-density polyethylene (HDPE) pellets as a raw material. The gross calorific values of both raw material sources are of similar value. As a result, grocery bags can be reasonably substituted by recycled HPDE pellets. The emulsion prepared by Span80 is more stable than that made from Span 83 or Span 85 which has lower HLB numbers [4].

In the present study, emulsification of water and pyrolysis oil has experimentally investigated with particular attention to microstructure and the corresponding rheological properties. The water-in-oil emulsion made from pyrolysis oil and water of various mixing ratio has been emulsified by Span80 using homogenizer and ultrasonic mixer. Effect of water content on various fuel properties has been explored. The emulsion microstructure is evaluated in terms of average and size distribution of dispersed water droplet. The water droplet dispersed in pyrolysis oil under various preparing conditions are measured and compared to the corresponding change in viscosity.

<table>
<thead>
<tr>
<th>Nomenclature</th>
<th>Description</th>
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<tbody>
<tr>
<td>( \eta )</td>
<td>emulsion viscosity</td>
</tr>
<tr>
<td>( \eta_c )</td>
<td>continuous phase viscosity</td>
</tr>
<tr>
<td>( \eta_r )</td>
<td>relative viscosity</td>
</tr>
<tr>
<td>( \phi )</td>
<td>disperse phase volume fraction</td>
</tr>
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2. Experimental Methods

Pyrolysis oil was produced from recycled HDPE pellets by thermochemical conversions using a batch-type pyrolyzer as illustrated in Fig. 1. A 3-liter capacity of 316 stainless steel pyrolyzer is externally heated by an electric furnace operated under cascade heating steps and heating rates as shown in Table 1 [5]. Industrial grade nitrogen gas was fed into pyrolyzer to purge air out of the reactor prior to each run. Pressure relief line is connected through a water tank for safety. The pyrolysis oil was collected from the main line after passing through a water-cool condenser maintained at about 15°C. The fast pyrolysis process provides 80% product yield using recycled HDPE pellets as a raw material.

![Fig. 1 Schematic diagram of pyrolysis process](image_url)
Table 1 Cascaded temperature control of pyrolysis process [3]

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Time (hr.)</th>
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<tbody>
<tr>
<td>30-400</td>
<td>0.37</td>
</tr>
<tr>
<td>400-500</td>
<td>1</td>
</tr>
<tr>
<td>500</td>
<td>1</td>
</tr>
<tr>
<td>500-600</td>
<td>1.4</td>
</tr>
<tr>
<td>600</td>
<td>1</td>
</tr>
</tbody>
</table>

Water-in-oil (w/o) emulsion was produced with a commercial grade of Sorbitan monooleate (Span 80) as emulsifier. The w/o emulsion were prepared by gradually adding distilled water into the pre-mixed pyrolysis oil and Span80. The surfactant concentration was kept at 2% by volume following the optimal concentration range previously investigated [4]. The oil and water mixture were emulsified at room temperature by either (a) ultrasonic mixer (Bandelin Sonopuls) operated at 20 kHz (176 watt) or (b) homogenizer (IKA-Ultra-Turrex T50) operated at 4,000 rpm (440 watt). The mixing time was kept constant at 15 minutes.

The visual characterizations of emulsion were assessed in terms of average size and distribution of water droplet. The emulsion microstructure was analyzed by a micrograph taken by microscope (Olympus IX-83ZDC). The micrograph was evaluated by image-analysis software (ImageJ ver. 1.47) to obtain an average and size distribution of water droplet. Also, rheological characterizations of emulsions were assessed in term of kinematic viscosities measured by Ubbelohde No. 2C capillary viscometer and apparent viscosity by rotational viscometer (MV 2000 series II Cannon®). In addition, the Gross calorific value was measured by Parr 6300 Calorimeter according to ASTM D5865.

3. Results and discussion

![Graph showing the relationship between heating value and water volume fraction](image)

Fig. 2 Relationship between heating value and water volume fraction

The presence of water in pyrolysis oil emulsion gives rise to various changes in fuel characteristic and properties. The effect of water volume fraction on the emulsified pyrolysis oil is shown in Fig. 2. The
heating value of pyrolysis HDPE oil is 11,005.2 cal/g which is comparable to that of diesel fuel (11,106.3 cal/g) [1] or bunker oil type A (10,360.8 cal/g) [3]. Adding water into pyrolysis oil reduced the heating value since there is a negligible heating contribution from the water constituent. The reduction of heating value is not considered a negative attribute since this is accompanied with a proportionally decreased fuel requirement. In fact, the actual fuel consumption of emulsified fuel is expected to exhibit some improvement over the theoretical estimation because of microexplosion which results an efficient combustion [6].

The effect of water content on emulsion viscosity can be quite profound. A viscosity flow curve is generated by testing shear stress of pyrolysis oil over a range of shear rate using rotational viscosity. The linear relationship of the flow curve confirms its Newtonian behavior. The shear viscosity is measured to be 150 centipoise at room temperature which is consistent with 154 centipoise obtained by a capillary viscometer. However, the ideal Newtonian behavior is no longer held true for the pyrolysis oil-water emulsion which exhibits a shear thinning behavior. The emulsion viscosity can vary significantly by the water volume fraction. Here, the emulsion viscosity is measured by capillary viscometer and is reported in terms of a relative viscosity ($\eta_r$) defined as the emulsion viscosity normalized by pyrolysis oil viscosity. The experimental results is compared with theoretical Einstein equation for relative viscosity given by

$$\eta_r = \frac{\eta}{\eta_c} = 1 + 2.5\phi$$

where $\eta$ and $\eta_c$ are viscosity of emulsion and continuous phase (pyrolysis oil), respectively and $\phi$ is the volume fraction of disperse phase (water). In Fig. 3, the effect of water content on emulsion viscosity is demonstrated. The emulsion viscosity exhibits behavior similar to that predicted by Einstein equation up to water volume fraction of 0.1. However, the emulsion viscosity dramatically increases when the water content is increased beyond the dilute limit. The rapid viscous trend is one of the drawbacks which hinder the application of high water content emulsion due to increasing complication of subsequent operations, e.g. fuel burner or atomizer

![Fig. 3 Relationship between water content and emulsion relative viscosity.](image-url)
Emulsification mixing process gives rise to variations in the emulsion microstructure and rheological properties. After settling for 24 hours, pictures of pyrolysis oil emulsion with 10% water content prepared by (a) ultrasonic mixer and (b) homogenizer are shown in Fig. 4. The emulsion of water and plastic oil produced by ultrasonic mixing remains homogenous over 24 hours observation period. On the other hand, the emulsion produced by mechanical homogenizer exhibits phase separation with a clear layer at the top as previously reported [3]. In addition, the emulsion made by homogenizer is not entirely homogenous with an apparent milky cloud moving within the emulsified layer as shown in Fig. 4 (b).

In Fig. 5, water droplet average size and its distribution is shown for a 10% water content emulsion prepared by (a) ultrasonic mixer and (b) homogenizer. The droplet produced by ultrasonic (0.6±0.12
micron) is smaller than that by homogenizer (1.02±0.52 micron). The lower average droplet size and sharp distribution of emulsion using ultrasonic gives rise to the reduction of contact surface area between droplets and consequently more stability due to less potential of droplet coalescence. The superior result is attained even though the input power of ultrasonic is higher than that of homogenizer. As for viscosity, the kinematic viscosity of emulsion prepared by ultrasonic and homogenizer is evaluated. There is discernable viscosity variation between one using ultrasonic (3.147 centistokes) and that using homogenizer (3.336 centistokes). The lower viscosity of the emulsion prepared by ultrasonic at the same water content confirms the efficient mixing by ultrasonic mixer. Therefore, the emulsification using ultrasonic mixer has another benefit of mitigating the rapid viscous trend at sufficiently large water content.

4. Conclusions

The emulsification of water and pyrolysis oil was experimentally investigated to explore the effect of water content and mixing method. The heating value was proportionally decreased with the water quantity. At water fraction of 10% or less, the viscosity was also increased proportionally according to the Einstein’s expression. However, at sufficient large volume fraction, the emulsion viscosity exhibited a non-linear increasing trend. Emulsification mixing process is another important consideration. The superior results by ultrasonic mixer were confirmed in terms of visual stability, microstructure and rheology.

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References