Research Article

Waste Plastic Conversion into Chemical Product Like Naphtha

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Abstract Thermal degradation of waste plastics is one method currently being investigated as an alternative to landfill disposal of this increasingly large waste stream. Although the thermal process produces significant quantities of light naphtha range (C6–C14) liquids, there is also a residual fraction that may be considered as a potential feedstock for upgrading. In this study, the fraction of a liquid produced by the thermal degradation process of waste plastics, containing about 29%, +110 °C naphtha chemical, was subjected to thermal reactions. The reactions used a commercial HZSM-5 supported on zeolite catalyst and gave good conversion to naphtha. The process well simulated the experimental data, including experimentally observed trends such as the maximum in naphtha yield.

Keywords naphtha; waste plastic; condensation; thermal; conversion; GC/MS; FTIR; DSC

1 Introduction

The waste plastic pollution has created a major dilemma in the environmental conservation sector. Approximately, 48 million tons (MT) of waste plastics is generated in the USA alone each year [4]. Unlike other waste materials, such as paper and food waste, waste plastics do not bio-degrade, as they occupy landfill for a long period of time. The problem does not end there; the cost of waste plastic management is around $2800/ton of waste plastics. Around 65% of all waste generated each year ends up in the landfill, that is about 32 million tons. About 20–25% ends up in incineration facilities and only about 5–10% is recycled [11]. In incineration facilities, when the waste plastics are burned, harmful gases such as carbon dioxide, sulfur and nitrous oxide are released into the air. This significant expenditure and the environmental hazards caused by waste plastics have led to finding alternates of recycling and creating ways to utilize these waste plastics into valuable resources. However, alternate methods of recycling such as mechanical recycling will at a point require discontinuation because of fragility from oxidation and UV light.

In contrast, the method of converting the polymers present in the waste plastics into liquid chemical products that can be used for various activities has shown dramatic potential results in the previous experiments conducted; as reported in an experiment conducted by James A. Guin and H. S. Joo of obtaining chemical product naphtha from waste polymer liquid through pyrolysis [8]. Not only naphtha, but also reports of converting waste polymers into fuel has been also reported using methods such as thermal cracking [1,3,6,13,15], flow cracking [14], catalytic cracking [2,3,5,7,10,15], and pyrolysis [9,12,16,17]. As it will be discussed further in this paper, in thermal degradation process [1,13], waste polymers are heated at a temperature range of 370–420 °C to de-polymerize the polymers of plastics back to liquid form. The conversion process yields 80–90% liquid, 5% light gas and 5% residue materials. The thermal de-polymerization is carried out in a fractional distillation process, where other liquid grade fuels are also obtained based on temperature profiles used. The naphtha liquid is obtained when the temperature reaches 110°C.

The main focus of this experiment is to extract naphtha liquid from waste plastics utilizing thermal degradation process. The general term for thermal degradation is applying heat in order to breakdown long hydrocarbon chains to form shorter ones thus producing a new substance. In order to produce and obtain different categories of liquid products the thermal degradation process is upgraded to fractional distillation process. Fractional distillation process is basically thermal degradation except the heat applied is divided into different groups based on specific temperature. The long hydrocarbon chain lengths of plastics are broken down to form shorter hydrocarbon chain lengths of C3–C27. Further, during fractional distillation, these chains are divided into different groups based on the type of liquid produced. The naphtha liquid’s carbon chain is in the range of C6–C14.

In this experiment, the retrieval of the naphtha liquid will be conducted by converting various types of waste plastics such as high-density polyethylene (HDPE-2), low-density polyethylene (LDPE-4), polypropylene (PP-5) and polystyrene (PS-6) through thermal degradation
2 Experimental process description

A small-scale conversion process has been performed with the simplified process shown in Figure 1 using various types of mixed waste plastics: high-density polyethylene (HDPE-2), low-density polyethylene (LDPE-4), polypropylene (PP-5) and polystyrene (PS-6). The plastics are collected, optionally shorted and cleaned of contaminants. These plastics types were investigated singly and in combination with other plastic types. The plastics were grinded into small pieces in sizes of 14–15 mm. These small plastic pieces were analyzed by EA-2400 (elemental analyzer) in CHNS mode to find the compositions. The analysis is presented as 86% being C, 12% being H, 0.9% being N and about 1.1% being S. The process of conversion involves heating of the waste plastic to form a liquid slurry, thermal liquefaction of 370–420 °C of the slurry, distilling the slurry in the presence of cracking with catalyst and also without catalyst, condensing the liquid slurry with distillate to recover the liquid hydrocarbon liquid fuel materials, no additional chemicals are used in the thermal degradation process. In the mini-scale conversion process, the weight of a single batch of input plastics for the fuel production process ranges from 300 gm to 3 kg. Produced fuel is called 1st (gasoline), 2nd (naphtha), 3rd (aviation), 4th (diesel) and 5th (fuel oil) fraction fuel. Also, during the production process, light gases ranging from C_1 to C_4 are produced and about 3% residue is leftover from the production process. The residue is black colored and contains high BTU value. The 2nd fraction distillation fuel (Figure 1) is called naphtha chemical. The 2nd fraction distillation tower temperature is used at 110–150 °C. Further, fractional distillation NSR fuel production technology obtains almost 38% naphtha chemical product.

3 Fuel analysis result and discussion

GC/MS tests have been performed to investigate the composition of the produced 2nd fraction fuel. The GC/MS Clarus 500 instrument is a product of Perkin Elmer and it uses the Turbomass software to operate all its functions. An Elite-5ms 30 m, 0.25 mm ID column was used. The temperature conditions are from 35 °C to 250 °C. The ramping rate of 4 °C/min to 130 °C holds for 1 min and ramp 2 of 10 °C/min to 250 °C holds for 5 min. Helium is used as a carrier gas. Figure 2 shows chromatograms of producing 2nd fraction fuel illustrating the carbon chain
length. The 2nd fraction carbon chain is $C_6$–$C_{14}$. Gas chromatography and mass spectrometer (GC/MS) (Table 1) show higher peak intensity with retention-time major compound distribution throughout the range of hydrocarbon groups $C_6$–$C_{14}$, with retention time ranging from 2 min to 27 min.

From FTIR (Spectrum 100) analysis of NSR 2nd fractional fuel, we found a perceptible spectrum that has different peak points that we consider as wave numbers. According to the wave numbers in NSR 2nd fractional fuel, functional groups are (Figure 3 and Table 2) = -C–H, C–CH$_3$, non-conjugated, conjugated, CH$_2$, CH$_3$, acetates, secondary cyclic alcohol, –CH=CH$_2$ and –CH=CH–(cis). It appears that some functional groups reiterate because their wave number is repeated, such as C–CH$_3$, non-conjugated, conjugated, acetates and –CH=CH–(cis) groups. Besides, against some wave numbers, we did not find any functional groups but that numbers are not as much as in quantity. It is evident that FTIR analysis of NSR 2nd fractional fuel contains maximum numbers of functional groups (hydrocarbon compounds).

Results obtained from Elemental Analyzer (EA) – 2400 indicates that NSR fuel contains 85.44% carbon and 12.96% hydrogen. The average of the fractionated fuels contains 85.00% carbon and 13.00% hydrogen. The empirical formula indicates that the Naphtha Chemical product’s carbon and hydrogen ratio is 1:2 and the carbon hydrogen ration is 6.53.

Figure 2: Gas chromatography and mass spectrometer chromatogram of waste plastic to produce naphtha category chemical.

Figure 3: FTIR spectrum of waste plastic to produce naphtha chemical.
| Compound name            | Formula     | Compound name            | Formula     |
|--------------------------|-------------|--------------------------|-------------|
| 1-Hexene                 | C₆H₁₂       | Cyclopentane-butyl       | C₁₀H₂₀      |
| Hexane                   | C₆H₁₄       | Benzene, propyl          | C₉H₁₂       |
| 1-Heptene                | C₇H₁₄       | a-methylstyrene          | C₁₀H₁₀      |
| Heptane                  | C₇H₁₆       | 1-Decene                 | C₁₀H₂₂      |
| Toluene                  | C₇H₈        | Decane                   | C₁₀H₂₂      |
| 3,4-Heptadiene           | C₈H₁₂       | Octane,3,5-dimethyl      | C₁₀H₂₂      |
| 1-Octene                 | C₈H₁₆       | Lomonene                 | C₁₀H₁₆      |
| Ocatine                  | C₈H₁₈       | 2-pentadecynl-1-ol       | C₁₅H₂₈O     |
| 2,4-Dimethyl-1-heptene   | C₉H₁₈       | Cyclopropane,1-heptyl-2-methyl- | C₁₁H₂₂ |
| Ethylbenzene             | C₉H₁₀       | Undecane                 | C₁₁H₂₄      |
| 1-Nonene                 | C₉H₁₈       | 1-Dodecane               | C₁₂H₂₄      |
| Styrene                  | C₉H₈        | Dodecane                 | C₁₂H₂₆      |
| 1,3,5,7-Cyclooctatetraene| C₉H₈        | Tridecane                | C₁₃H₂₈      |
| Nonane                   | C₉H₂₀       | Tetradecane              | C₁₄H₃₀      |
| Benzene,(1-methylethyl)- | C₉H₁₂       |                          |             |

**Table 1:** GC/MS high peak intensity major compound list of waste plastic to produce naphtha category chemical.

| Band serial number | Wave number (cm⁻¹) | Functional group name | Band serial number | Wave number (cm⁻¹) | Functional group name |
|--------------------|--------------------|-----------------------|--------------------|--------------------|-----------------------|
| 2                  | 3063.12            | =–C–H                 | 16                 | 1641.16            | Conjugated            |
| 3                  | 2933.39            | C–CH₃                 | 21                 | 1460.04            | CH₃                   |
| 4                  | 2730.96            | C–CH₃                 | 22                 | 1377.48            | CH₃                   |
| 5                  | 2669.39            | C–CH₃                 | 30                 | 1029.53            | Acetates              |
| 10                 | 1871.71            | Non-conjugated        | 31                 | 1020.91            | Acetates              |
| 11                 | 1816.96            | Non-conjugated        | 32                 | 990.38             | Secondary cyclic alcohol |
| 12                 | 1799.27            | Non-conjugated        | 33                 | 965.73             | –CH=CH=-(trans)       |
| 13                 | 1743.30            | Non-conjugated        | 34                 | 907.57             | –CH=CH₂               |
| 14                 | 1717.20            | Non-conjugated        | 37                 | 728.99             | –CH=CH=-(cis)         |
| 15                 | 1685.59            | Conjugated            | 38                 | 700.77             | –CH=CH=-(cis)         |

**Table 2:** FTIR spectrum wave number and functional group compound name of waste plastic to produce naphtha category chemical.

Analysis of differential scanning calorimeter (DSC) shows that (Figure 4) NSR 2nd fractional fuel (naphtha) has a boiling point height peak of 150.89 °C and Delta H is 17261.2701 J/g. DSC data indicate that NSR 2nd fraction fuel contains a higher percentage of volatile hydrocarbon compounds.

**4 ASTM test result**

All ASTM test results have been performed by 3rd party interteck, NJ, USA (Table 3).

**5 Conclusion**

As mentioned above, the fraction fuels are obtained at a certain temperature, and NSR still has the option to produce the fuels under different temperatures and see if better results are obtainable from the previous temperature profile. Through the use of GC/MS, FTIR and DSC we can assure the identification and accuracy of the fuel to meet the standard requirements for commercialization of the NSR 2nd fraction fuel for chemical industry. The NSR 2nd fraction fuel has a very high potential to overcome the current demands, but many further tests are required for the fuel to be available to the public.

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| Method       | Test                          | Results                  |
|--------------|-------------------------------|--------------------------|
| ASTM D4052   | API gravity @ 60°F            | 58.6 °API                |
| ASTM D4052   | Density @ 15 °C               | 0.7442 g/cm³             |
| ASTM D240    | Gross heat of combustion      | 19213 BTU/lb             |
| ASTM D240    | Gross heat of combustion      | 10674.0 Kcal/kg          |
| ASTM D5453   | Sulfur content                | 0.0003 Wt%               |
| ASTM D5134 MOD | n-paraffins               | 28.8 Vol%                |
| ASTM D5134 MOD | Iso-paraffins             | 10.9 Vol%                |
| ASTM D5134 MOD | Olefins                    | 28.3 Vol%                |
| ASTM D5134 MOD | Naphthenes               | 23.3 Vol%                |
| ASTM D5134 MOD | Aromatics                  | 6.1 Vol%                |
| ASTM D5134 MOD | Naphthenes and aromatics   | 29.4 Vol%                |
| ASTM D5134 MOD | >200 °C                    | 1.6 Vol%                |
| ASTM D156    | Saybolt Color Units          | −2                      |
| ASTM D86     | IBP recovery                 | 55.4 °C                  |
| ASTM D86     | 10% recovery                 | 91.3 °C                  |
| ASTM D86     | 50% recovery                 | 123.6 °C                 |
| ASTM D86     | 90% recovery                 | 165.9 °C                 |
| ASTM D86     | FBP recovery                 | 217.7 °C                 |
| ASTM D86     | Residue                      | 0.5 Vol%                 |
| ASTM D86     | Corrected loss               | 0.8 Vol%                 |
| ASTM D86     | Corrected recovery           | 98.7 Vol%                |
| ASTM D5191   | Dry vapor pressure equivalent, EPA | 3.20 psi               |
| ASTM D5708_MOD method | Calcium                   | < 1.0 ppm               |
| Method A     | Lithium                      | 1.9 ppm                  |
| ASTM D5708_MOD | Nickel                     | < 1.0 ppm               |
| ASTM D5708_MOD | Phosphorus                 | < 1.0 ppm               |
| ASTM D5708_MOD | Potassium                  | < 1.0 ppm               |
| ASTM D5708_MOD | Sodium                     | < 1.0 ppm               |
| ASTM D5708_MOD | Vanadium                   | < 1.0 ppm               |
| ASTM D5708_MOD | Zinc                       | < 1.0 ppm               |
| ASTM D4176   | Temperature                  | 74 °F                    |
| ASTM D4176   | Appearance                   | Clear and bright clear, Bright & free of entrained matter |
| ASTM D4176   | Free water and/or particulates | No water or particles present |
| ASTM D445    | Kinematic viscosity @ specified temp. | 0.7926 cSt |
| ASTM D974    | Acid number                  | 0.2 mg KOH/g             |
| ASTM D974    | Base number                  | 0.0 mg KOH/g             |
| ASTM D482    | Ash                          | 0.001 Wt%                |
| ² ASTM D5291 | Carbon content               | 85.67 Wt%                |
| ² ASTM D5291 | Hydrogen content             | 13.87 Wt%                |
| ² ASTM D5291 | Nitrogen content             | < 0.75 Wt%               |
| ² ASTM D5291 | Carbon/hydrogen ratio        | 6.16                     |
| ASTM D1353   | Nonvolatile matter           | 54.8 mg/100 mL           |
| ITM 1051     | Arsenic                      | 3 ppb Wt                 |
| ITM 1051     | Mercury                      | 3 ppb Wt                 |
| ITM 1051     | Lead                         | < 5 ppb Wt               |

Table 3: ASTM test results of waste plastic to produce naphtha category chemical.
Figure 4: DSC graph of waste plastic to produce naphtha category chemical.

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