Research Article Waste Plastic Conversion into Chemical Product Like Naphtha

Moinuddin Sarker, Mohammad Mamunor Rashid, and Mohammed Molla

Department of Research and Development, Natural State Research, Inc., 37 Brown House Road, Stamford, CT 06902, USA Address correspondence to Moinuddin Sarker, msarker@naturalstateresearch.com

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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 (C_6-C_{14}) 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 nitrious 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 C_3-C_{27} . 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 C_6-C_{14} .

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), lowdensity polyethylene (LDPE-4), polypropylene (PP-5) and polystyrene (PS-6) through thermal degradation



Figure 1: Waste plastic to fuel production process.

and fractional distillation. Through this process, other commercial grade fuel substances are also produced. Moreover, the process is very efficient; it exerts traces of light gas, although this gas can be utilized as a heat source.

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), poly propylene (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 C₁ to C₄ 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 $35 \,^{\circ}$ C to $250 \,^{\circ}$ C. The ramping rate of $4 \,^{\circ}$ C/min to $130 \,^{\circ}$ C holds for 1 min and ramp 2 of $10 \,^{\circ}$ C/min to $250 \,^{\circ}$ 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



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.

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–CH3, non-conjugated, conjugated, CH_2 , CH_3 , acetates, secondary cyclic alcohol, –CH=CH₂ and –CH=CH–(cis). It appears that some functional groups reiterate because their

wave number is repeated, such as C–CH₃, 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.

Compound name	Formula	Compound name	Formula
1-Hexene	C_6H_{12}	Cyclopentane-butyl-	C_9H_8
Hexane	C_6H_{14}	Benzene, propyl	$C_{9}H_{12}$
1-Heptene	C_7H_{14}	a-methylstyrene	$C_{9}H_{10}$
Heptane	C_7H_{16}	1-Decene	$C_{10}H_{20}$
Toluene	C_7H_8	Decane	$C_{10}H_{22}$
3,4-Heptadiene	C_7H_{12}	Octane,3,5-dimethyl-	$C_{10}H_{22}$
1-Octene	C_8H_{16}	Lomonene	$C_{10}H_{16}$
Ocatne	C_8H_{18}	2-pentadecynl-1-ol	$C_{15}H_{28}O$
2,4-Dimethyl-1heptene	C_9H_{18}	Cyclopropane,1-heptyl-2-methyl-	$C_{11}H_{22}$
Ethylbenzene	C_8H_{10}	Undecane	$C_{11}H_{24}$
1-Nonene	C_9H_{18}	1-Dodecene	$C_{12}H_{24}$
Styrene	C_8H_8	Dodecane	$C_{12}H_{26}$
1,3,5,7-Cyclooctatetraene	C_8H_8	Tridecane	$C_{13}H_{28}$
Nonane	C_9H_{20}	Tetradecane	$C_{14}H_{30}$
Benzene,(1-methylethyl)-	C_9H_{12}		

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	=-С-Н	16	1641.16	Conjugated
3	2933.39	C-CH ₃	21	1460.04	CH_2
4	2730.96	C-CH ₃	22	1377.48	CH_3
5	2669.39	C-CH ₃	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	$-CH=CH_2$
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/cm ³
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		
Method A		
ASTM D5708_MOD	Calcium	< 1.0 ppm
ASTM D5708_MOD	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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