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Conversion of Low Density Polyethylene (LDPE) and Polypropylene (PP) Waste Plastics into Liquid Fuel Using Thermal Cracking Process

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Research Article

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ABSTRACT

In every sector of the world today energy is essential. Energy has many forms such as electricity, transportation fuel and so on. A large amount of energy is produced from crude oil, which is used to produce petroleum and petroleum to produce daily usable plastics. The solution to the above mentioned problems can be solved through the utilization of the new develop technology. This new developed technology will remove these hazardous waste plastics from the environment and convert them into eco friendly liquid fuel. The process is used to convert these waste plastics into liquid fuel creates no harmful emissions and can be produced at a very little overall cost. The thermal process utilized to break down the hydrocarbon chains of the polymers and convert them into liquid fuel. A Steel reactor with temperature range from 100 °C to 400 °C is utilized for the plastic thermal degradation process. The process yield about 80-90% liquid product. The experiment is conducted under a fume hood and open air system, no vacuum process is applied in this particular thermal cracking process.

Keywords: Renewable energy; thermal cracking; fuel; environment; waste plastic; hydrocarbon; gas.

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1. INTRODUCTION

In recent years the production and consumption of plastics have increased drastically; as a consequence the responsible disposal of plastic wastes has created serious social and environmental arguments. At present both landfilling and incineration of plastic wastes are widely practiced. In Japan, the percentage of municipal plastic wastes, as a fraction of municipal solid waste (MSW), that was landfilled in the early 1980s was estimated to be 45%, incineration was 50%, and the other 5% was subjected to separation and recycling (Plastic Waste Management Institute, 1985). In the USA, more than 15% of the total MSW was incinerated in 1990; only about 1% of post-consumer plastics were recycled (Yakowitz, 1990; Curlee and Das, 1991; Andrews and Subramanian, 1992). Landfilling of plastic wastes is expected to decrease in the future as landfill space is depleted and plastic wastes are resistant to environmental degradation. Co-incineration of plastic wastes with other municipal solid wastes may be increasingly practiced, because the high caloric value of plastics can enhance the heating value of MSW and facilitate an efficient incineration, while their energy content can also be recovered. But the potential relationship between plastics fed into an incinerator and the formation of some highly toxic pollutants such as dioxins and furans is still unclear.

It has been suggested that the chlorine content in PVC and other plastics is related to the formation of dioxins and furans, which are chlorinated polynuclear aromatic compounds. And although there is considerable evidence that these pollutants would still be generated in the absence of plastics, environmental pressures against incineration have never completely disappeared. Various techniques for the treatment of waste polymers have been investigated to complement existing landfill and mechanical recycling technologies. Ideally, it would be desirable to convert the waste into a value-added product. In the case of polyethylene waste, a particularly interesting potential product would be synthetic lubricants. Furthermore, they are reported to be less damaging to the environment, because they do not contain aromatic compounds. In contrast, conventional lubricants have some aromatic compounds which can be released into the environment when the lubricant is utilized in a two-stroke engine. The most suitable decomposition products from polyethylene for the production of light gases and hydrocarbon liquid products are compounds close to 1-decene in both chain length and molecular structure. Several thermo chemical techniques have been employed to convert waste PP (Polypropylene) and LDPE (Low density polyethylene) into value-added products. Thermal cracking of plastic waste has been studied at temperature from 510 – 520 ℃ to produce light liquid hydrocarbon products (Andras, 2007).

Some researchers investigated polyethylene thermolysis, usually at temperature $250 \,^{\circ}$ C to $450 \,^{\circ}$ C products light gases including liquid hydrocarbon products (WCM et al., 1994). Others investigated continuous processes in which polyethylene (ldpe) was passed through a fixed or fluidized bed of catalyst at elevated temperatures. The reaction products consisted mainly of low-molecular-weight waxes, with some liquid. The use of catalysts increased both liquid production and the formation of aromatic compounds, when compared to the products from non-catalyzed degradation. A study was conducted in utilizing plastic wastes into light hydrocarbon fuel at low temperature with and without the use of catalyst (Sajid et al., 2010) Studies on the degradation of addition polymers and the composition of the products have suggested several possible reaction mechanisms. As a result, several mathematical models have been proposed to describe the degradation of addition polymers. For a purely random process, the theoretical maximum rate of weight loss has been predicted to occur at 26.4% decomposition. The process carried out in this particular experiment uses thermal degradation with temperature ranging from $100 - 400 \,^{\circ}$ C in a vertical stainless steel reactor.

The Results obtained from the experiment indicated that the liquid product obtained is all light and heavy hydrocarbon compounds.

2. EXPERIMENTAL SECTION

Thermal cracking process without catalyst was used in converting waste plastic into liquid fuel. Two types of waste plastic are selected for this particular experiment. By weight 50% of each Low density polyethylene and polypropylene was selected for the experiment. Both waste plastic are solid hard form. Collected waste plastic was cleaned using liquid soap and water. During waste plastics are cleaned is cerates waste water. This waste water is purified for reuse using waste water treatment process. Washed waste plastics are cut into 3-5 mm size to fit into the reactor conservatively. For experimental purpose we used 600 gm sample 300 gm of PP and 300 gm of LDPE. A vertical steel reactor used for thermal cracking and temperature used ranges from 100°C to 400°C (see figure 1). The experiment is carried out under a Labconco fume hood in open air system with no vacuum process applied during this thermal cracking process. We used low density and polypropylene plastics in a batch process system because conversion temperatures for these plastics are relatively low. Heat is applied from 100° C at start to begin melting the waste plastics, the melted waste plastic turn into liquid slurry form when temperature is increased gradually. When temperature is increased to 270° C liquid slurry turns into vapor and the vapor then passes through a condenser unit. At the end we collect liquid fuel. Between 100° C and 250° C around 20 -30% of the fuel is collected and then when raised to 325° C the next 40% is collected and finally when held at 400° C the yield is fully completed. During the thermal cracking process plastic portions are not broken down immediately because plastics have short chain hydrocarbon to long chain hydrocarbon. 1st stage of heat applied breaks down only the short chain hydrocarbon. When temperature profile is increased the plastic carbon-carbon bond breakdown slowly. As the temperature is increased the long chains are breakdown step by step. During in this thermal cracking process some light gas such as methane, ethane, propane and butane are produced. These compounds are not able to condense because they have negative boiling point. These light gases could be alkane or alkene group and it can also contain CO or CO₂ emissions. Light gas production percentage is about 6%. This gas portion analysis is under consideration. The method which is considered for treating the light gas is an alkali wash system (see figure 1). After experiment is concluded some solid black residue is collected from the reactor. This solid black residue percentage is about 4%. Liquid fuel yield percentage is 90%. To purify the liquid fuel a purification system to remove water portion and ash or fuel sediment is used. Liquid fuel density is 0.75 g. /ml

3. FUEL ANALYSIS METHODS

Perkin Elmer Differential Scanning calorimeter equipment is use for boiling point measurements of produced fuel. Nitrogen gas we used for carrier. 20 ml gas used for per minutes. Temperature profile setup initial program temperature is 5° C and end temperature 400° C. Initial temperature to final temperatures increase rate 5° C per minutes. 50 µL aluminum pan used for sample holding.

FT-IR spectrum 100 (Perkin Elmer) used for produced fuel analysis purposed. Cell used NaCl 0.05mm. Wave range 4000-400 cm⁻¹, scan number 32 and resolution number 4 cm⁻¹.



Fig. 1. Process diagram of the waste plastic conversion

Gas chromatography and mass spectrometer (Perkin Elmer) used for fuel analysis. For GC/MS analysis capillary column use and column dimension is 30 meter length, 0.25 mmID, 0.5 um df, maximum temperature capacity is 350°C. Helium used for carrier gas at 80 psi. GC program setup for sample run initial temperature is 40°C, 1 minute hold for 40°C and final temperature setup 325°C and temperature ramping rate is 10°C per minutes. Final temperature holds for 15 minutes. MS program set up for mass scan 35.00 to 528.00 El+. Data format centroid, scan time 0.25sec, inters scan time 0.15 sec.

4. RESULTS AND DISCUSSION

Analysis of the liquid produces fuel is conducted using a Differential Scanning Calorimeter (DSC) (graph fig.2) to measure the boiling point. The onset temperature is 101.57°C. 123.99°C is the peak boiling point of the produced fuel, which means that at 123.99°C the fuel has the highest concentration of compounds. The Heat flow Endo up is 29.0887 mW and enthalpy for fuel delta H is 14448.0931 J/g.

From FT-IR Spectrum-100 analysis of low density polyethylene (LDPE) and polypropylene (PP) fuel (shown fig.3 and table 1) in favor of wave number several types of functional groups are appeared. In accordance with wave number 3075.90 cm⁻¹, functional group is H bonded NH, wave number 2936.06 cm⁻¹ and 2729.01 cm⁻¹ compound is C-CH₃ and wave number 1821.43 cm⁻¹,1781.43 cm⁻¹,1710.76 cm⁻¹ and 1649.94 cm⁻¹ functional compound is Non-Conjugated. The raw material of PP and LDPE contains <0.30 trace of Nitrogen (ASTM D 5291.a). Since the raw material contains Nitrogen it appears when the liquid fuel's compounds are analyzed in the FT-IR. When the plastics are made, 2 - 3% extra additives are used to mold the plastics into different shapes, which contains trace metals and such. Then wave number 992.38 cm⁻¹, functional group Secondary Cyclic Alcohol, wave number 964.90 cm⁻¹ functional group is -CH=CH-(trans), ultimately wave number 674.89 functional group is -CH=CH-(trans). Energy is calculated using the formula E=hu, Where h=Planks Constant, h =6.626x10⁻³⁴ J, u= Frequency in Hertz (sec⁻¹), Where u=c/ λ , c=Speed of light, where, $c=3x10^{10}$ m/s, $W=1/\lambda$, where λ is wave length and W is wave number in cm⁻¹. Therefore the equation E=hu, can substitute by the following equation, E=hcW. According to equation high wave number light has more energy than low wave number light such as wave number 3075.90 cm⁻¹ (H bonded NH), energy= 6.11×10^{-20} J, wave number 2936.06 cm⁻¹ (C-CH₃) energy, E=5.83X10⁻²⁰ J, wave number 1821.72 cm⁻¹ (Non-Conjugated) energy, E =3.61X10⁻²⁰ J and ultimately wave number 884.03 cm⁻¹ (C=CH₂) energy, E=1.34x10⁻²⁰ J. These results provide the functional group band energy of the fuel compounds, thus, providing us with the calorific value of the fuel.

The GC/MS analysis (fig.4 and table 2) Indicates that the starting compound is Propene (C₃H₆) at retention time 1.53 minutes and molecular weight of this compound is 42. This compound is a short chain hydrocarbon compound. From the analysis we saw some alcoholic group compound also present in the fuel. Such as Ethanone, 1-(1, 2, 2, 3-tetramethylcyclopentyl)-, (1R-cis)- (C₁₁H₂₀O), (2,4,6-Trimethylcyclohexyl) methanol (C₁₀H₂₀O), 1-Decanol, 2-hexyl- (C₁₆H₃₄O) etc with different retention time. The compounds with the highest peak intensity appear in retention time 2.51 min compound 1-Pentene, 2-methyl-, 7.08 min compound Nonane and 13.47 min.



Fig. 2. DSC graph of produced fuel



Fig. 3. FT-IR spectrum of produced fuel

Number of Wave	Wave Number (cm ⁻¹)	Functional Group	Number of Wave	Wave Number (cm ⁻¹)	Functional Group
1	3075.90	H bonded NH	9	1649.94	Non-Conjugated
2	2936.06	C-CH₃	16	992.38	Secondary
					Cyclic Alcohol
3	2729.01	C-CH₃	17	964.90	-CH=CH-(trans)
6	1821.72	Non-Conjugated	18	884.03	$C=CH_2$
7	1781.43	Non-Conjugated	20	674.89	-CH=CH-(trans)
8	1710.76	Non-Conjugated			· /

Table 1. Produced fuel spectrum functional group list



Fig. 4. GC/MS chromatogram of produced fuel

Alcoholic group are formed due to the experiment being conducted in a non vacuumed fume hood. Oxygen is absorbed from moisture during condensation time has manipulated the compound of the produced fuel but results obtain from the fuel is obsolete. This fuel has short hydrocarbon compound to long chain hydrocarbon compound with different retention time and all compound are shown in this chromatogram as compound boiling point wise. From this analysis we found long hydrocarbon compound is Heptacosane (C₂₇H₅₆) at retention time 26.07 minutes. This compound is a straight chain carbon and a hydrogen single bonding compound with molecular weight 380. This fuel has only aliphatic compound such as alkane group and alkene group compound. We used only low density polyethylene and polypropylene waste plastic, these 2 types waste plastic have carbon and hydrogen straight combination chain and polypropylene has also methyl group compounds. GC/MS analysis did not indicate any aromatic compounds. GC/MS analysis shows that short chain hydrocarbon C_3 and long chain hydrocarbon C_{27} is present in this fuel.

Peak Number	Retention Time (M)	Trace Mass	Compound Name	Compound Formula	Molecular Weight
1	1.53	41	Propene	C ₃ H ₆	42
2	1.63	41	1-Propene, 2-methyl-	C4H8	56
3	1.90	42	Cyclopropane, ethyl-	C5H10	70
4	1.94	42	Pentane	C5H12	72
5	2.35	43	Pentane, 2-methyl-	C6H14	86
6	2.51	56	1-Pentene, 2-methyl-	C6H12	84
7	2.98	67	2,4-Hexadiene, (Z,Z)-	C6H10	82
8	3.10	56	1-Pentene, 2,4-dimethyl-	C7H14	98
9	3.18	81	2,4-Dimethyl 1,4-pentadiene	C7H12	96
10	3.60	56	1-Hexene, 2-methyl-	C7H14	98
11	3.65	41	1-Heptene	C7H14	98
12	3.77	43	Heptane	C7H16	100
13	4.20	83	Cyclohexane, methyl-	C7H14	98
14	4.64	41	2-Hexene, 3,5-dimethyl-	C8H16	112
15	4.80	43	Heptane, 4-methyl-	C8H18	114
16	5.11	56	1-Heptene, 2-methyl-	C8H16	112
17	5.19	41	1-Octene	C8H16	112
18	5.35	43	Octane	C8H18	114
19	5.98	69	Cyclohexane, 1,3,5-trimethyl-	C9H18	126
20	6.07	70	2,4-Dimethyl-1-heptene	C9H18	126
21	6.41	69	Cyclohexane, 1,3,5-trimethyl-, (1à,3à,5á)-	C9H18	126
22	6.63	109	Cyclohexene, 3,3,5-trimethyl-	C9H16	124
23	6.92	41	1-Nonene	C9H18	126
24	7.08	43	Nonane	C9H20	128
25	7.30	82	3-Octyne, 2-methyl-	C9H16	124
26	8.13	43	Nonane, 4-methyl-	C ₁₀ H ₂₂	142
27	8.54	56	1-Octene, 2,6-dimethyl-	C ₁₀ H ₂₀	140
28	8.65	41	1-Decene	C ₁₀ H ₂₀	140
29	8.79	43	Decane	C ₁₀ H ₂₂	142
30	8.99	43	Nonane, 2,6-dimethyl-	C ₁₁ H ₂₄	156
31	9.71	83	2-Undecanethiol, 2-methyl-	C ₁₂ H ₂₆ S	202
32	10.07	43	Cyclooctane, 1,4-dimethyl-, trans-	C ₁₀ H ₂₀	140
33	10.14	43	3-Tetradecene, (E)-	C ₁₄ H ₂₈	196
34	10.30	41	Cyclopropane, 1-heptyl-2-methyl-	C ₁₁ H ₂₂	154
35	10.44	43	Undecane	C ₁₁ H ₂₄	156
36	10.82	43	Ethanone, 1-(1,2,2,3-	C ₁₁ H ₂₀ O	168
37	11.20	69	tetramethylcyclopentyl)-, (1R-cis)- (2,4,6-Trimethylcyclohexyl) methanol	C ₁₀ H ₂₀ O	156

Table 2. GC/MS chromatogram compound list of produced fuel

Table	2 continue <mark>s</mark>				
38	17.74	56	Cyclopentane, 1-methyl-2-(4- methylpentyl)-, trans-	C ₁₂ H ₂₄	168
39	11.86	55	1-Dodecene	C ₁₂ H ₂₄	168
40	11.98	57	Dodecane	C ₁₂ H ₂₆	170
41	12.45	43	Dodecane, 2,6,10-trimethyl-	C ₁₅ H ₃₂	212
42	13.32	41	1-Tridecene	C ₁₃ H ₂₆	182
43	13.45	57	Tridecane	C13H28	184
44	13.47	43	1-Nonene, 4,6,8-trimethyl-	C ₁₂ H ₂₄	168
45	13.71	43	3-Octadecene, (E)-	C ₁₈ H ₃₆	252
46	14.07	43	1-Decanol, 2-hexyl-	C ₁₆ H ₃₄ O	242
47	14.44	55	7-Octadecyne, 2-methyl-	C ₁₉ H ₃₆	264
48	14.70	55	7-Tetradecene, (E)-	C14H28	196
49	14.81	57	Tetradecane	C14H30	198
50	15.54	43	Decane, 2,3,5,8-tetramethyl-	C14H30	198
51	16.00	55	1-Pentadecene	C ₁₅ H ₃₀	210
52	16.10	57	Pentadecane	C ₁₅ H ₃₂	212
53	16.66	69	1-Decanol, 2-hexyl-	C ₁₆ H ₃₄ O	242
54	17.15	55	1-Docosene	C ₂₂ H44	308
55	17.20	69	18-Nonadecen-1-ol	C ₁₉ H38O	282
56	17.23	41	1-Hexadecene	C ₁₆ H ₃₂	224
57	17.32	57	Hexadecane	C ₁₆ H ₃₄	226
58	17.51	55	E-2-Octadecadecen-1-ol	C ₁₈ H ₃₆ O	268
59	18.32	55	2-Methyl-E-7-hexadecene	C ₁₇ H ₃₄	238
60	18.40	55	E-14-Hexadecenal	C ₁₆ H ₃₀ O	238
61	18.48	57	Heptadecane	C17H36	240
62	19.50	55	1-Nonadecene	C ₁₉ H ₃₈	266
63	19.58	57	Octadecane	C ₁₈ H ₃₈	254
64	19.92	69	1-Eicosanol	C ₂₀ H ₄₂ O	298
65	20.55	43	1-Nonadecene	C ₁₉ H ₃₈	266
66	20.62	57	Nonadecane	C ₁₉ H ₄₀	268
67	21.07	69	1-Hexadecanol, 3,7,11,15- tetramethyl-	C ₂₀ H ₄₂ O	298
68	21.56	43	1-Eicosene	C ₂₀ H ₄₀	280
69	21.62	57	Eicosane	C ₂₀ H ₄₂	282
70	22.52	43	1-Docosene	C22H44	308
71	22.58	57	Heneicosane	C ₂₁ H ₄₄	296
72	23.50	57	Heptacosane	C ₂₇ H ₅₆	380
73	25.23	57	Tetracosane	C ₂₄ H ₅₀	338
74	26.07	57	Heptacosane	C27H56	380

5. CONCLUSION

The products of thermal cracking are mainly paraffin's, olefins as well as hydrocarbon products (carbon number 3-27). Thermolysis is a viable alternative to high temperature degradation for the recovery of products from waste products. The thermolysis of PP & LDPE at moderate temperatures, below 400 °C produces a high yield of liquid products. It is important that the liquid products from thermolysis consist mainly of a mixture of straight chain alkanes and alkenes having an average chain length in the range of C_3 - C_{27} carbons. The liquids were not contaminated with aromatic compounds. Thus, the products obtained from thermolysis are potentially useful as a feedstock for the production of synthetic lubricants, requiring fewer purification steps than liquids obtained from degradation processes. The product is a high grade liquid fuel that is classified as an alternative source of energy. In the future the demand for alternative energy source will increase, so in the renewable sector this fuel may play an important role.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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