

Fractional Distillation Process Utilized to Produce Light Fractional Fuel from Low Density Polyethylene (LDPE) Waste Plastic

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Abstract: Plastics are not easily biodegradable; and because of these characteristics they can remain under landfill and water for a very long period of time. All over the world only 6% of waste plastics are recycled and the rest of all waste plastics are dumped into landfills. An experiment was conducted in a laboratory scale batch process under Labconco's fume hood utilizing low density polyethylene (LDPE). The experiment was carried out to obtain a hydrocarbon fuel product utilizing thermal degradation. Many research studies have successfully demonstrated that waste plastics such as low density polyethylene (LDPE), high density polyethylene (HDPE), polypropylene (PP) and polystyrene (PS) can be converted to valuable liquid hydrocarbon fuels. For experimental purposes we used 500 gm of LDPE as raw materials. This particular experiment is a two step process; the first step process involves extracting hydrocarbon fuels as mixture of both short and long chain hydrocarbon compounds. During the second step the fuel obtained in the first process is refracted by thermal degradation process utilizing a distillation column. This process yields a short hydrocarbon chain liquid fuel that has similar properties to gasoline grade fuels. Analysis of these fuels was conducted by Gas Chromatography and Mass Spectrometer (GC/MS), FT-IR Spectrum 100 and Differential Scanning Calorimeter (DSC). The results show that the produced fuels are good quality fuels with high energy content. ASTM test result indicates that fuel has low sulfur level (3.2 ppm) and the fuel hydrocarbon range shown by GC/MS analysis is C₄-C₁₀.

Keywords: LDPE, waste plastic, fractional distillation, fuel, hydrocarbon, FT-IR, GC/MS, DSC, thermal degradation.

1. INTRODUCTION

When compared to other materials like glass and metal, plastic polymers possess greater ability to be recycled. Plastics have low entropy of mixing, which is due to high molecular weight of their large polymer chains. A macromolecule interacts with its environment along its entire length, so its enthalpy of mixing is large compared to that of an organic molecule with a similar structure. When different types of plastics are melted together they tend to phase-separate, like oil and water, and set in these layers. The phase boundaries cause structural weakness in the resulting materials, meaning that polymer blends are only useful in limited applications.

Another barrier to recycling is the widespread use of dyes, fillers, and other additives in plastics. The polymer is generally too viscous to economically remove fillers, and would be damaged by many of the processes that could cheaply remove the added dyes. Additives are less widely used in beverage containers and plastic bags, allowing them to be recycled more often. Yet another barrier to removing large quantities of plastic from the waste stream and landfills is the fact that many common but small plastic items lack the universal triangle recycling symbol and accompanying number. A perfect example is the billions of plastic utensils commonly distributed at fast food restaurants or sold for use

at picnics. The use of biodegradable plastics is increasing; if some of these get mixed in the other plastics for recycling, the reclaimed plastic is not recyclable because of the variance in properties and melt temperatures.

Moreover, the problem of wastes cannot be solved by land filling and incineration, because suitable and safe depots are expensive, and incineration stimulates the growing emission of harmful, greenhouse gases such as Nitrous Oxide, Sulfur dioxide, Carbon dioxide etc. Also at present, it is almost impossible to dispose of waste plastics in land fill due to law, high costs, and higher ecological consciousness of people. Recycling can be divided into further important categories, such as mechanical recycling, and chemical recycling. However, there are also some technological and economic constraints that limit the full and efficient recycling of waste plastics into useful products, e.g. contaminated waste plastics can be only partly recycled into new products and reuse of packaging containers is limited by the collection system. Chemical recycling is virtually a thermal method by which the long alkyl chains of polymers are broken into a mixture of lighter hydrocarbons. This is one of the prospective ways to utilize waste polymers [1-7].

LDPE belongs to the family of polyethylene. It is a thermoplastic made from petroleum. It was the first grade of polyethylene, produced in 1933 by Imperial Chemical Institute using a high pressure process *via* free radical polymerization [8]. Its manufacture employs the same method today in large quality production. LDPE is commonly recycled and has the number "4" as its recycling symbol. LDPE is widely used for manufacturing various containers, dispensing bottles, wash bottles, tubing, plastic

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bags for computers components, and various molded laboratory equipment. Its most common use is in plastic bags. Other products made from plastic include; trays and general purpose containers, corrosion-resistant work surfaces; parts that need to be weldable and machinable, parts that require flexibility, for which it severs very well, very soft and pliable parts, six pack rings, playground slides, plastic wraps etc.

Thermal recycling of waste polymers under different catalytic and thermal circumstances has been well investigated by researchers [9-13]. Other important parameters for waste polymer degradation are residence time, and the chemical structure of polymer. Upon investigation by analytical instruments (see method) it seems that the chemical stature of LDPE is well suited for thermal recycling. The product yield by the thermal recycling is a liquid product that contains mixtures hydrocarbons. These hydrocarbons resemble chemical and thermal properties to commercial transportation fuel. The objective of this study is to investigate an actual thermal recycling process utilizing LDPE. The study will include results on the product yield by the thermal recycling process.

2. MATERIALS AND METHOD

2.1. Materials

Raw LDPE waste plastic materials are collected from Norwalk Wall-Mart chain store in Stamford, Connecticut, USA. Collected LDPE waste plastic contained different color shopping bags. Collected waste plastic was mixed with foreign materials such as paper, food particle, dust and sand etc. The foreign particles were manually separated out and washed with liquid soap and then dried in room temperature. The cleaned plastics were cut into small pieces with scissor. During waste plastic washing period some waste water was generated. This waste water is treated with a waste water treatment process using Potash alum $\{K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O\}$ solution and alkali NaOH solution used with different normality.

2.2. Pre-Analysis

LDPE waste plastic shopping bag was pre-analyzed by GC/MS with pyroprobe, FT-IR (Spectrum 100), EA-2400 and TGA pyris-1. GC/MS Clarus 500 series used with CDS pyroprobe 5000 series for solid sample making volatile and

volatile purposed temperature used 1200 °C. By using GC/MS analyzed raw material compound structure bonding and we notice that most of the LDPE compound structure are double bond alkene group. All compounds are straight chain hydrocarbon compound. FTIR spectrum 100 series ATR analysis showed raw LDPE poly bag functional group with different wave number band energy. TGA (pyris-1) analysis showed onset temperature and inflection temperature into raw materials. By using EA-2400 analysis showed carbon, hydrogen and nitrogen percentage. LDPE raw waste plastic metal analysis by ICP and checked metal contain in ppm level shown below Table 1.

During plastic manufacturing period The Companies add different types of additives for better shape of plastics. Plastics are manufactured by polymerization, polycondensation, or polyaddition reactions where monomeric molecules are joined sequentially under controlled conditions to produce high-molecular-weight polymers whose basic properties are defined by their composition, molecular weight distribution, and their degree of branching or cross-linking. To control the polymerization process, a broad range of structurally specific proprietary chemical compounds is used for polymerization initiation, breaking, and cross-linking reactions (peroxides, Ziegler-Natta, and metallocene catalysts). The polymerized materials are admixed with proprietary antioxidants (stoically hindered phenols, organophosphites), UV and light stability improvers (hindered amines and piperidyl esters), antistatic agents (ethoxylated amines), impact modifiers (methacrylatebutadiene- styrene compounds), heat stabilizers (methyl tin mercaptides), lubricants (esters), biostabilizers (arsine, thiazoline, and phenol compounds), and plasticizers used to modify the plasticity, softness, and pliability of plastics (phthalates and esters). World production of plastic additives is on the order of 18 billion pounds per year with plasticizers representing a 60% of the total amount [14]. Raw LDPE waste plastic Carbon percentage is 85.33%, Hydrogen is 14.31 % and Nitrogen <0.30 % showed EA-2400 analysis results.

2.3. Experimental Process

Low density polyethylene (LDPE) waste plastic to fuel production process is conducted in a two step process. LDPE

Table 1. Raw LDPE Waste Plastic Metal ppm Level

ASTM Method	Metals Name	Results in ppm	ASTM Method	Metals Name	Results in ppm
ASTM D1976	Silver	<1.0	ASTM D1976	Sodium	45.2
	Aluminum	197.4		Nickel	<1.0
	Boron	2.8		Phosphorus	26.7
	Barium	<1.0		Lead	<1.0
	Calcium	962.6		Antimony	<1.0
	Chromium	<1.0		Tin	<1.0
	Copper	<1.0		Silicon	90.2
	Iron	6.0		Titanium	2.7
	Potassium	35.4		Vanadium	<1.0
	Lithium	<1.0		Zinc	2.6
	Magnesium	25.1		Molybdenum	<1.0

waste plastics such as shopping bags were used for this experimental purpose. 500 gm of small pieces of waste plastics were placed into the steel reactor. Reactor is made of stainless steel and it is electrically controlled to increase or decrease the temperature (Fig. 1). Reactor has a heat insulator which helps to conserve heat loss. The top of the reactor is hooked up with a 70 ° angle condenser unit, a gas pressure monitoring device and a thermocouple to monitor the interior temperature. The process is setup under a labconco fume hood which filters any unclean gas through ventilation. Reactor temperature range is limited to 500 °C. After the initial reactor setup had finished, heat was slowly applied to liquefy the LDPE waste plastic to convert into fuel. The temperature range of 100-400 °C was used for this conversion process. No catalyst was used during this experiment because pre-analysis result showed that the raw materials initially contained different type metals. These metals act as catalysts when heat is applied (patent pending). Every 15 minutes the temperature is increased by 10°C. When the waste plastics reach their heat tolerance capacity they start to melt into liquid and produce vapor when heat increases even higher and that vapor then travels through a condenser unit in a collection unit as liquid LDPE hydrocarbon fuel. During production period some light gas are generated and this light gas is transferred into gas cleaning device. Gas cleaning device has liquid 0.25N alkali

solution. Which cleans light gas and small pump can transfer into Teflon bag for future use. Liquid fuel was transferred into RCI purification device to remove fuel sediment and water contents. Produce fuel density is measured at 0.76 gm/ml. The LDPE plastic yields about 90% liquid fuels, 6% light gas and about 4% solid residues. 500 gm of solid LDPE waste plastic produced 450 gm of liquid fuel (fuel volume 592 ml), 20 gm of solid residue and estimated 30 gm sample as light gas.

The 450 gm (592 ml) of produced fuel is then transferred into another fractional distillation column for the 2nd step of fractional distillation (Fig. 2). Temperature range of 40-65 °C was used to collect the light hydrocarbon fraction fuel. Light fraction fuel density is 0.72 gm/ml. In the present fractional distillation experiment system only 10 % light fraction fuel was collected and rest of fuel collected for different grade with different fractional temperature range wise. Rest of other grade fraction fuel was 88% including naphtha chemical, aviation/jet, diesel and fuel oil and temperature range was for naphtha chemical 110-125 °C, aviation/jet 180-205 °C, diesel 260-285 °C and fuel oil 340-365 °C. During this light fractional process we got some light gas also which is only 2% of the total product output. GC/MS analysis show that the hydrocarbon chain length ranges from C₄-C₁₀. LDPE fuel to fraction fuel production

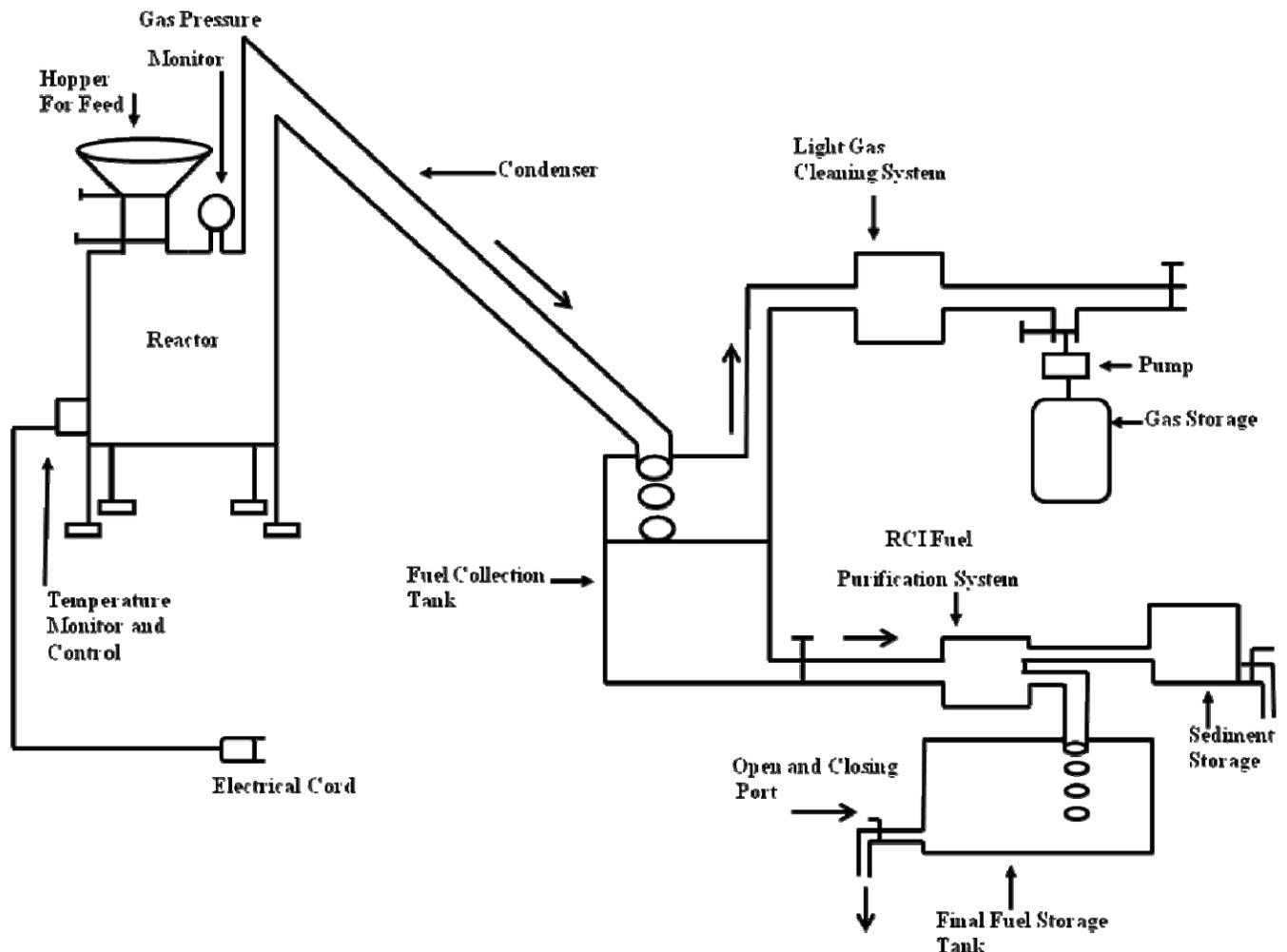


Fig. (1). (Step-1) Fuel production process of LDPE waste plastic.

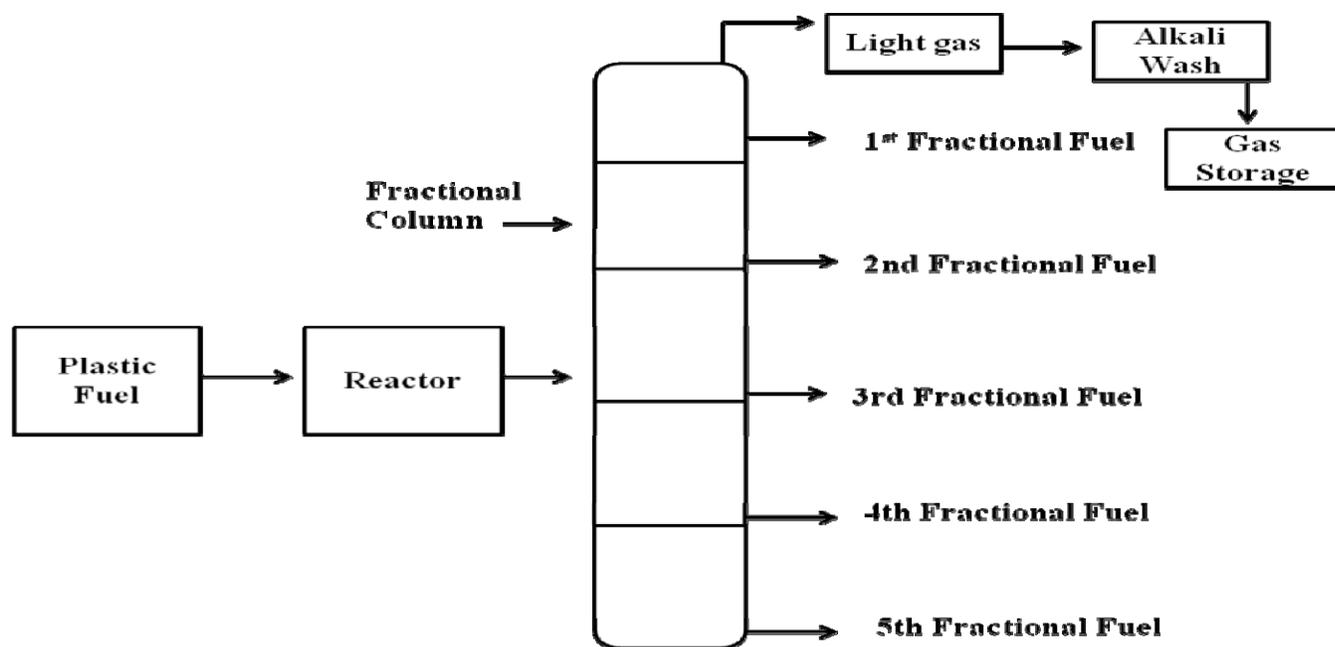


Fig. (2). LDPE fuel to 1st fractional fuel production process (step-2).

mass balance was gasoline grade 45 gm (10%), naphtha chemical 90 gm (20%), aviation 135 gm (30%), diesel 126 gm (28%), fuel oil 45 gm (10%) and light gas 9 gm (2%).

3. RESULTS AND DISCUSSION

GC/MS analysis of LDPE waste plastic fuel into 1st fractional hydrocarbon fuel (Fig. 3 and Table 2) shows GC/MS chromatogram and chromatogram compound list. Chromatogram and compound data table shown first compound is Butane (C₄H₁₀) at retention time 1.63 minutes and molecular weight of this compound is 58. This compound intensity is low in percentage. We collect all compound based on low peak intensity to high peak intensity compounds. From this fuel analysis we got some compound that is cyclic and aliphatic compounds such as aromatic compound, alcoholic compound and most of the compounds are aliphatic compound some are single bond and some are double bond compounds. All compounds are short chain hydrocarbon compound because when we fractionate waste plastic fuel to 1st fractional fuel we used low temperature of 40 to 65 °C temperature to collect all light fraction compound similar to gasoline grade. Cyclohexane (C₆H₁₂) hydrocarbon compound appeared at retention time 2.52 minutes. As well as retention time 2.60 and trace mass 42, functional group is Hexane (C₆H₁₄), retention time 2.65 and trace mass 41, functional group is 2-Hexene, (Z)- (C₆H₁₂), retention time 2.74 and trace mass 55, functional group is 3-Hexene, (Z) (C₆H₁₂), retention time 2.91 and retention time 69, functional group is Cyclopentane, methyl- (C₆H₁₂), retention time 3.16 and trace mass 67, functional group is Cyclopentene, 1-methyl- (C₆H₁₀). Furthermore at middle of the analysis phase as retention time and trace mass numerous compounds are noticed among that only few of them are elaborated and mentioned in the analysis. At the end phase

of the analysis aromatic compound Toluene (C₇H₈) shown at retention time is 4.82 minutes. GC/MS analysis indicates this fuel has a long chain hydrocarbon compound Decane (C₁₀H₂₂) at retention time is 8.77 minutes. Hexane (C₆H₁₄) hydrocarbon compound peak intensity is higher than other hydrocarbon compound. Therefore from the detailed analysis of LDPE 1st fractional fuel appeared as hydrocarbon compound limit available in range of C₄-C₁₀.

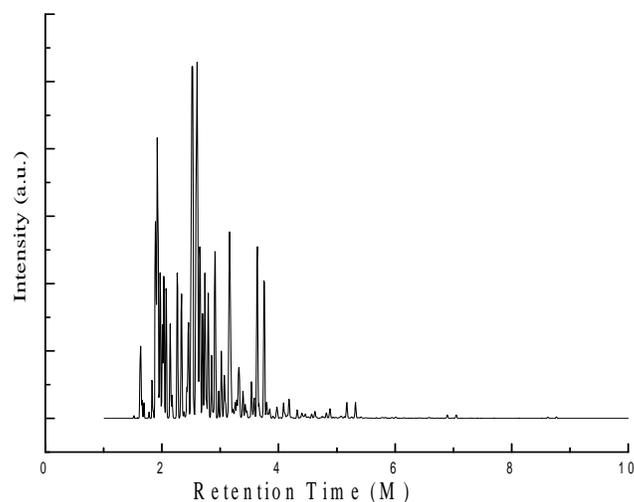


Fig. (3). GC/MS Chromatogram of LDPE fuel to 1st fractional fuel.

FT-IR (spectrum100) analysis of LDPE fuel to 1st fractional fuel (Fig. 4 and Table 3) indicates the following types of functional groups such as at wave number 3635.27 cm⁻¹, derived functional group is Free OH, wave number 2890.88 cm⁻¹, 2732.73 cm⁻¹ and 2671.05 cm⁻¹ functional group is C-CH₃, wave number 1897.93 cm⁻¹, 1822.28 cm⁻¹,

Table 2. GC/MS Chromatogram of LDPE Fuel to 1st Fractional Fuel Compound List

Peak Number	Retention Time (M)	Trace Mass (m/z)	Compound Name	Compound Formula	Molecular Weight	NIST Library Number
1	1.63	43	Butane	C ₄ H ₁₀	58	18940
2	1.83	43	Butane, 2-methyl-	C ₅ H ₁₂	72	291251
3	1.89	42	2-Pentene, (E)-	C ₅ H ₁₀	70	291780
4	1.92	41	Pentane	C ₅ H ₁₂	72	291244
5	1.97	55	2-Pentene	C ₅ H ₁₀	70	19079
6	2.07	68	1,3-Pentadiene	C ₅ H ₈	68	291890
7	2.26	67	2-Pentene, 3-methyl-, (Z)-	C ₆ H ₁₂	84	114483
8	2.34	42	1-Pentanol, 2-methyl-	C ₆ H ₁₄ O	102	19924
9	2.46	57	Pentane, 3-methyl-	C ₆ H ₁₄	86	19375
10	2.52	39	Cyclohexane	C ₆ H ₁₂	84	291493
11	2.60	42	Hexane	C ₆ H ₁₄	86	291337
12	2.65	41	2-Hexene, (Z)-	C ₆ H ₁₂	84	114458
13	2.74	55	3-Hexene, (Z)-	C ₆ H ₁₂	84	114381
14	2.80	69	2-Pentene, 3-methyl-, (Z)-	C ₆ H ₁₂	84	114483
15	2.91	69	Cyclopentane, methyl-	C ₆ H ₁₂	84	114428
16	3.02	79	1,3-Cyclopentadiene, 5-methyl-	C ₆ H ₈	80	419
17	3.16	67	Cyclopentene, 1-methyl-	C ₆ H ₁₀	82	107747
18	3.32	56	Cyclohexane	C ₆ H ₁₂	84	228008
19	3.39	79	Cyclopentene,3-methylene-	C ₆ H ₈	80	151094
20	3.54	67	Cyclohexene	C ₆ H ₁₀	82	114431
21	3.64	56	1-Heptene	C ₇ H ₁₄	98	107734
22	3.75	43	Heptane	C ₇ H ₁₆	100	61276
23	3.97	81	Cyclopentene, 4,4-dimethyl-	C ₇ H ₁₂	96	38642
24	4.09	81	Cyclopentane, 1-methyl-2-methylene-	C ₇ H ₁₂	96	62523
25	4.18	83	Cyclohexane, methyl-	C ₇ H ₁₄	98	118503
26	4.32	69	Cyclopentane, ethyl-	C ₇ H ₁₄	98	231044
27	4.63	67	1-Ethylcyclopentene	C ₇ H ₁₂	96	114407
28	4.75	43	1-Octyn-3-ol	C ₈ H ₁₄ O	126	113255
29	4.82	91	Toluene	C ₇ H ₈	92	291301
30	4.89	81	Cyclohexene, 3-methyl-	C ₇ H ₁₂	96	139433
31	5.17	41	1-Octene	C ₈ H ₁₆	112	1604
32	5.25	55	Cyclopentane, 1-ethyl-2-methyl-	C ₈ H ₁₆	112	150594
33	5.32	43	Octane	C ₈ H ₁₈	114	229407
34	5.83	67	1-Methyl-2-methylenecyclohexane	C ₈ H ₁₄	110	113437
35	6.01	83	Cyclohexane, ethyl-	C ₈ H ₁₆	112	20181
36	6.58	81	Cyclohexene, 1,6-dimethyl-	C ₈ H ₁₄	110	113442
37	6.90	41	1-Nonene	C ₉ H ₁₈	126	107756
38	7.05	43	Nonane	C ₉ H ₂₀	128	2665
39	8.62	41	1-Decene	C ₁₀ H ₂₀	140	107686
40	8.77	43	Decane	C ₁₀ H ₂₂	142	291484

1717.83 cm^{-1} and 1642.49 cm^{-1} functional group is Non-Conjugated, wave number 1603.52 cm^{-1} functional group is Conjugated. As well as wave number 1461.87 cm^{-1} and 1376.42 cm^{-1} functional group is CH_3 , wave number 994.97 cm^{-1} and 912.93 cm^{-1} , functional group is $-\text{CH}=\text{CH}_2$ and ultimately wave number 726.86 cm^{-1} and 674.64 cm^{-1} functional group is $-\text{CH}=\text{CH}-$ (cis). Energy values are calculated for LDPE fuel to 1st fractional fuel, using formula is $E=h\nu$, Where h =Planks Constant, $h = 6.626 \times 10^{-34}$ J, ν = Frequency in Hertz (sec^{-1}), Where $\nu=c/\lambda$, c =Speed of light, where, $c=3 \times 10^{10}$ m/s, $W=1/\lambda$, where λ is wave length and W

is wave number in cm^{-1} . Therefore the equation $E=h\nu$, can substitute by the following equation, $E=hcW$. According to their wave number such as for wave number 3635.27 cm^{-1} (Free OH) energy, $E=7.22 \times 10^{-20}$ J, wave number 2890.88 cm^{-1} ($\text{C}-\text{CH}_3$) calculated energy, $E=5.74 \times 10^{-20}$ J. Similarly, wave number 1897.93 cm^{-1} (Non-Conjugated) energy, $E=3.77 \times 10^{-20}$ J, wave number 1461.87 cm^{-1} (CH_3) energy, $E=2.97 \times 10^{-20}$ J, wave number 994.97 cm^{-1} ($-\text{CH}=\text{CH}_2$) energy value, $E=1.98 \times 10^{-20}$ J and ultimately wave number 726.86 cm^{-1} ($-\text{CH}=\text{CH}-$ (cis)) calculated energy, $E=1.44 \times 10^{-20}$ J respectively.

Table 3. LDPE Fuel to 1st Fractional Fuel Functional Group Name

Number of Wave	Wave Number (cm^{-1})	Functional Group	Number of Wave	Wave Number (cm^{-1})	Functional Group Name
1	3635.27	Free OH	12	1603.52	Conjugated
2	2890.88	$\text{C}-\text{CH}_3$	13	1461.87	CH_3
3	2732.73	$\text{C}-\text{CH}_3$	14	1376.42	CH_3
4	2671.05	$\text{C}-\text{CH}_3$	22	994.97	$-\text{CH}=\text{CH}_2$
8	1897.93	Non-Conjugated	23	912.93	$-\text{CH}=\text{CH}_2$
9	1822.28	Non-Conjugated	25	726.86	$-\text{CH}=\text{CH}-$ (cis)
10	1717.83	Non-Conjugated	26	674.64	$-\text{CH}=\text{CH}-$ (cis)
11	1642.49	Non-Conjugated			

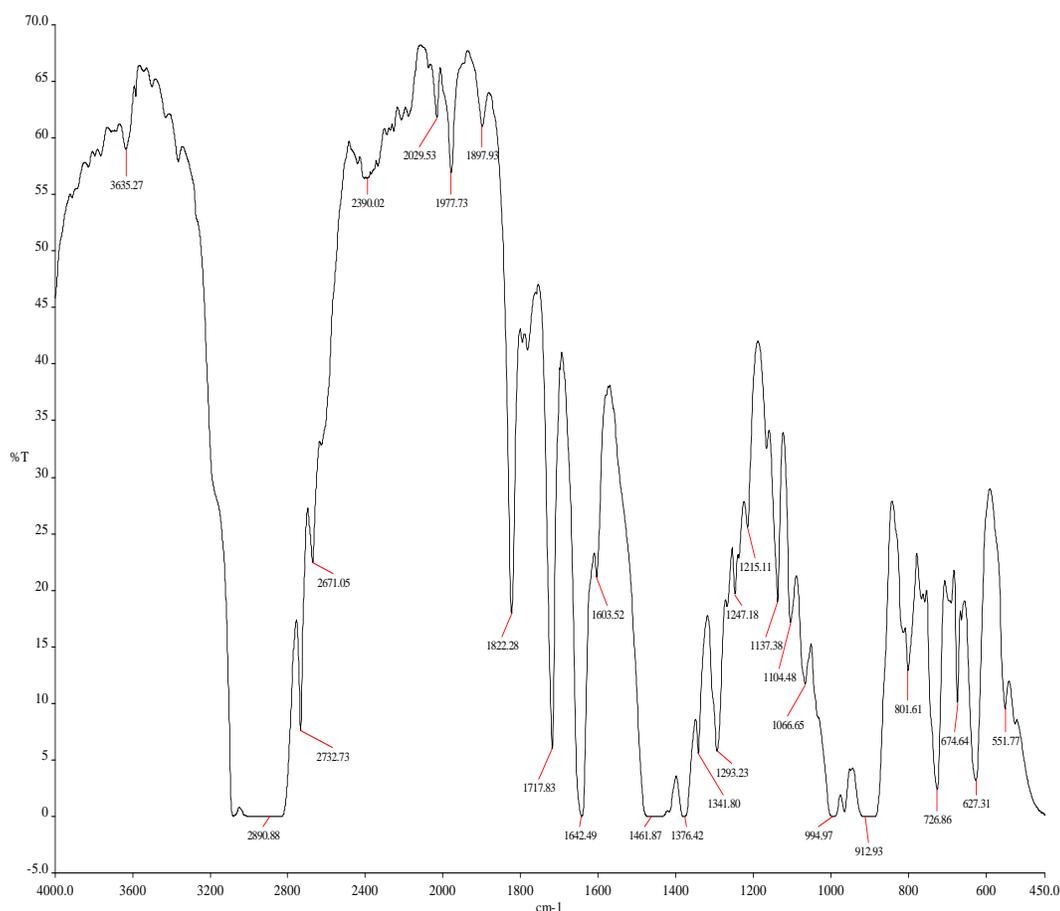


Fig. (4). FT-IR Spectrum of LDPE fuel to 1st fractional fuel.

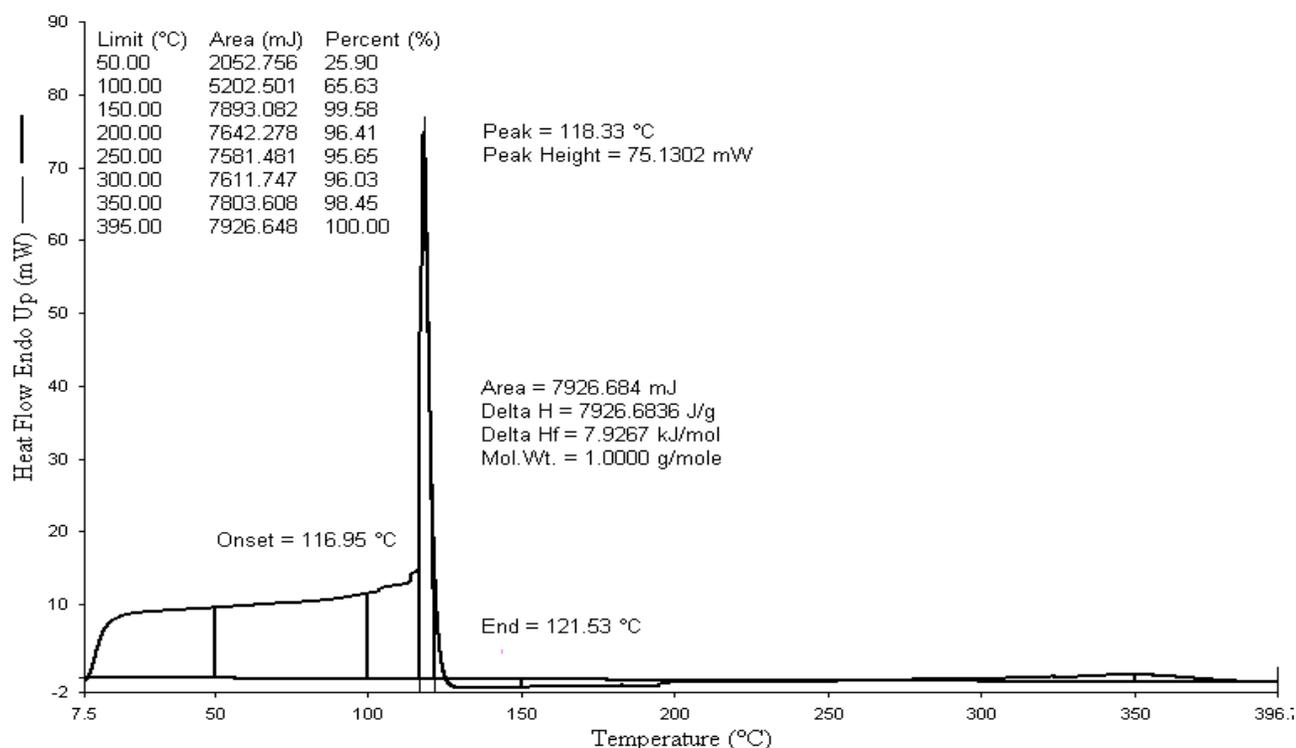


Fig. (5). DSC graph of LDPE 1st fractional fuel.

LDPE fuel to 1st fraction fuel was analyzed by DSC for measuring fuel boiling point temperature. LDPE fuels to 1st fraction fuel (Fig. 5) hydrocarbon compound are low boiling point compounds. 1st fraction fuel has highly volatile hydrocarbon compounds. During fractional distillation time we used temperature from 40–65 °C because we want to collect the light hydrocarbon compounds. The onset temperature is 116.95 °C. 1st fraction fuel has a peak temperature of 118.33 °C, peak height 75.1302 and heat flow Endo up represent 78% from 100. From DSC analysis we found the area 7926.684 mJ, enthalpy delta H value H is 7926.6836 J/g. From this analysis we can calculate this fuel's boiling point is close to gasoline. This fuel peak start at temperature 116.95 °C and peak end temperature 121.53 °C. From analysis graph we notice that at 50 °C temperature fuel boiling 25.90 % and 395 °C fuel boiled 100%.

Produce 1st fractional fuel ASTM test performed by 3rd party Intertek laboratory, New Jersey, USA. Produced light fraction fuel analysis with ASTM test wise such as API gravity @ 60 °F (ASTM D4052), Gross heat combustion (ASTM D240), Freezing point (ASTM D5972), cloud point (ASTM D2500), cold filter plugging point (IP 309), water (ASTM D6304), oxidation stability induction period @ 100 °C (ASTM D525), Average octane (ASTM D4814), calculated cetane index (ASTM D4737), ethanol (ASTM D4815) etc.

4. CONCLUSION

In this experiment low density polyethylene (LDPE) is converted to a mixture of short and long chain hydrocarbon fuels, and then the produced fuel is refractionated to yield a short chain hydrocarbon fuel that resembles similar

properties to gasoline. Analysis of GC/MS data indicates that the produced fuel has a short range carbon chain (C₄–C₁₀). When compared side by side the produced fuel show very similar chemical properties to commercial gasoline fuel. Chemical properties have shown that the fuel we produced has an octane rating of 78 without adding any kinds of oxygen booster. Commercial gasoline available in the market usually contains multiple forms of oxygen boosting additives that increase the octane rating. If these additives are added to the produced hydrocarbon fuel, then the octane rating of the produced hydrocarbon fuel will be similar to that of commercial gasoline.

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CONFLICT OF INTEREST

Declared none.

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