International Journal of Engineering and Technology Research
Vol. 1, No. 1, February 2013, PP: 01-16, ISSN: 2327-0349 (Online)
Available online www.ijeatr.org

Research article

Mixture of LDPE, PP and PS Waste Plastics into Fuel by Thermolysis Process

Moinuddin Sarker *, Mohammad Mamunor Rashid

Natural State Research, Inc. Department of Research and Development, 37 Brown House Road (2nd Floor),
Stamford, CT-06902, USA Phone: (203) 406-0675, Fax: (203) 406-9852

*E-mail: msarker@naturalstateresearch.com, mamun_sarker2002@yahoo.com

Abstract

Energy is needed in every sector, due to the high demand for energy in the World today, crude oil; one of the largest sources is being heavily relied on. To fulfill the energy demand, crude oil production is increasing every year. According to World crude oil demand and supply source nearly 26.28 billion barrels of crude oil is produced each year whereas, the consumption is 28.57 billion barrels per year. The deficient amount is generated from other sources such as Solar, Wind, Hydrogen, Geothermal and other alternate sources. Petroleum derives from crude oil; petroleum is then is used for daily transportation use and production of plastics for daily use. In 2008, 245 million tons of plastics were produced worldwide. After daily use the plastics becomes abundant and occupies landfill and remain in the landfill for a long period of time. The exposure of these waste plastics to air creates many problems to the environment. A simple thermolysis and economically viable process to remove these waste plastics from landfill and converting them into liquid hydrocarbon mixtures fuel has been developed and temperature range 25 to 390 ºC, which is environmental friendly. The produced fuel contains long carbon chain lengths C_3–C_{27} determine by GC/MS, FT-IR analysis result showed produced fuel functional group band energy and DSC analysis result showed fuel heat enthalpy value and ASTM test result showed low sulfur contents resulting high performance and environmentally friendly at the same time. Produce fuel could be use as internal combustion engine, feed for feed stock refinery or electricity generation feed for power plants. By using this technology can be solved waste plastic problem as well as environmental problems and reduce some percentage of foreign oil dependency and boost up alternative energy sector.

Keywords: waste plastic, thermolysis, hydrocarbon, environmental, fuel, LDPE, PP, PS, GC/MS

1. Introduction

Plastics have become an indispensable part in today's world. Due to their lightweight, durability, energy efficiency, coupled with a faster rate of production and design flexibility, these plastics are employed in entire gamut of industrial and domestic areas. Plastics are produced from petroleum derivates and are composed primarily of hydrocarbons but also contains additives such as antioxidants, colorants and other stabilizers [1-2]. Disposal of the waste plastics poses a great hazard to the environment and the effective method has not yet been implemented. Plastics are slowly biodegradable polymers mostly containing carbon-hydrogen, and few other elements like nitrogen. Due to its non-biodegradable nature, the waste plastic contributes significantly to the problem of waste management. According to a nationwide survey which was conducted in the year 2000, approximately 6000 tons of waste plastics were generated every day in India, and only 60% of it was recycled, the balance of 40% could not be disposed off. Today about 129 million tones of waste plastics are produced annually all over the world, out of which 77 million tones are produced from petroleum [3].

Most widely applied methods for waste plastic treatment are landfill and incineration. However, due to non-availability of land space and the danger of additives in plastic being released into soil and air pollutants into soil and air pollutants into air when burnt out in incinerators, alternative treatment options are highly required. With an aid of additional facilities to incinerators for controlling harmful substances released, pyrolysis and gasification of waste plastics is a process being developed around the world that could result in recovery of high energy content of plastics as well as chemical composition of plastics [4-7] given the high calorific value, plastics can be recycled for energy recovery. When mixed and incinerated with municipal solid wastes, plastics contribute to the safe combustion of the mixture and generate energy. In other thermal degradation process, they can replace other fuels in different proportions, saving primary fossil fuels. Fuels derived from specific, separated plastics and important substance because it can perform the activities of commercial gasoline and diesel.

The process described in this paper is a simple thermal degradation process which converts waste plastics to liquid and gaseous hydrocarbons. The degradation process in turn is simpler than pyrolysis and other conversion methods. The waste plastics are obtained from municipalities, and they are converted in an environmentally friendly steel reactor which emits no harmful gases in the environment. The simplicity of the process makes this process a very economic and beneficial conversion system.

2. Materials and Method

2.1 Sample preparation

Waste plastic collected form grocery store in Norwalk and Stamford. Collected waste plastic sample were low density polyethylene (LDPE), polypropylene (PP) and polystyrene (PS). Low density polyethylene was milk container red color cap with ink printed, polypropylene waste plastic was transparent food container cap and finally polystyrene waste plastic was red color drinking glass. Waste plastics collected contained foreign materials such as milk, food and liquid product. Raw waste plastic are cleaned with liquid detergent and water. During waste plastics cleaning period a waste water byproduct is created. This waste water cleaning and treating with coagulations process for reuse. This treatment is a cyclic process. Washed out waste plastics is dried using fan air. Dry waste plastic are cut into small pieces by using scissor for grinder machine. This waste plastic size is 3-4 inch. Waste plastic put into grinder machine at the end collected mixture of grounded waste plastic and size is 3-4 mm. Table 1 and table 2 showing waste plastic mixture percentage ratio for experimental process and carbon (C%), hydrogen (H%) and nitrogen (N%) percentage by Elemental analyzer -2400 equipment and ASTM test method was apply for CHN mode detection ASTM D5291.a. Table-2 EA-2400 results shown C, H and N percentage is less than 100% each raw material. Because of waste plastics has other impurity when plastics making time manufacturing company are use as 4-5 % different types of additives.

Table 1: Composition of the waste plastic mixture

Materials	Wt. %
Polystyrene (PS)	33.33
Low density polyethylene (LDPE)	33.33
Polypropylene (PP)	33.34

Table 2: Raw Materials Carbon, Hydrogen and Nitrogen percentage detected by EA-2400 (CHN mode)

Name of Materials	Carbon %	Hydrogen %	Nitrogen %
PS	78.60	7.21	<0.30
LDPE	85.33	14.31	<0.30
PP	79.93	14.17	<0.30

2.2 Experimental process

A grounded waste plastics mixture was transfer into reactor chamber. A waste plastic to fuel production process thermal degradation process was applied and temperature range was 25 ºC to 390 ºC (Fig.1). During fuel production process vacuum system did not apply and catalyst or extra chemical did not added. Condensation unit was setup with reactor and no water circulation system was added. Reactor temperature capability range from 25 ºC to 500 ºC and experimental temperature controller was watlow system. Experiment was batch process under Labconco fume hood and experiment was fully closed system setup. LDPE waste plastic melting point temperature is 120 ºC, PP waste plastic melting point temperature is 160 ºC and PS waste plastic melting point temperature is 240 ºC. Based on three types of waste plastics melting point temperature experimental temperature profile was setup.

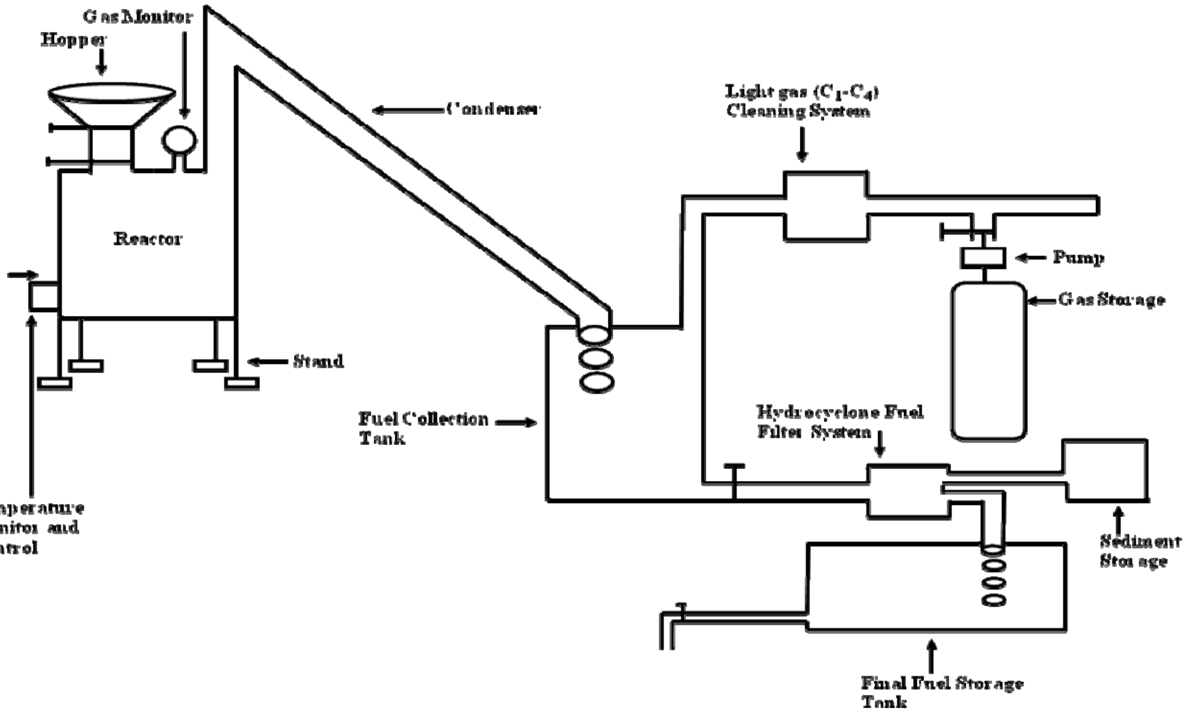


Figure 1: LDPE, PP and PS mixture of waste plastics to fuel production process diagram

Initial raw sample was start heat from 25 ºC and temperature increased gradually up to 390 ºC for fuel production. Waste plastics starts to melt when temperature is increased and turn into liquid slurry after that liquid slurry turn into vapor, volatile vapor passed through condenser unit, at the end collection liquid hydrocarbon fuel. Waste plastics sample melting point temperatures are different range temperature for that reason was used temperature from 25 ºC to 390 ºC. Temperature when goes up from 150 ºC to 260 ºC was notice that fuel was coming droopily and when temperature goes up to 300 ºC fuel production rate was increased and until finished experiment was monitored step by step. During production period vacuum system was not apply to take out moisture for that reason carbon and water is creating carbon dioxide and it's come out with light gas and passed through alkali cleaning system. Also production period are creating some alcoholic group compounds. Ones start experiment heat moisture is come out with some light gas which is present methane, ethane, propane and butane mixture. These types of light gas is not condensing due to negative boiling point are present in this light gas compounds. These light gases pass through collection tank to alkali cleaning process then transfer into storage system for future use or identification by using small pump. Whole production process finished time was 5-5.30 hours. Raw materials were used 3 types of waste plastics (LDPE/PP/PS) to fuel production process equal ratio wise. After finished experiment process produced fuel was cleaned by using RCI technology provided RCI fuel purification system with 35 psi force and micron filter to remove all kind of fuel sediment. At the end liquid fuel was collected as final fuel and fuel density is 0.80 g/ml.

2.3 Thermolysis Yield Calculation

LDPE, PP and PS waste plastic mixture to produce liquid fuel yield percentage is 89.5%; black solid residue percentage is 4.5% and light gas percentage is 6%. Initial raw materials 100 gm of mixed waste plastics to fuel production conversion mass balance showed liquid fuel is 89.5 gm, solid sample conversion into light gas as 6 gm and black solid residue is 4.5 gm left over during conversion.

2.4 Analytical Techniques

Different type of analytic techniques used for pre analysis to liquid fuel analysis purposed. Raw material analysis purposed we used gas chromatography with pyroprobe for raw sample volatile and GC/MS auto sampler used for liquid sample analysis, FT-IR used for raw and liquid sample functional group analysis purposed, EA -2400 used for raw waste plastics CHN percentage analysis, DSC was used for liquid fuel boiling point measurement. GC/MS program set up for liquid fuel analysis initial temperature 40 ºC and hold for 1 minute, final temperature 325 ºC and temperature ramping rate 10 ºC per minute. Final temperature hold 15 minutes, equilibration time 0.5 minute and total experiment run time 45.50 minutes. Carrier gas used Helium and Perkin Elmer Elite 5MS capillary column was used for GC. Column length 30 m, ID 0.25 mm and DF 0.5 um. Column temperature range -60 to 350 ºC. MS method set up for mass scan Ion mode EI +, data format Centroid, start mass 35.00, end mass 528, scan time 0.25 sec and inter scan time 0.15 sec. Perkin Elmer FT-IR (Spectrum 100) used for liquid fuel analysis. Spectrum range is 4000-450 cm^{-1}, number of scan 32 and resolution 4 is setup for fuel spectrum analysis. NaCl cell used for sample holding and cell thickness is 0.25 mm. Differential Scanning calorimeter (DSC) equipment was use for liquid fuel boiling point measuring. Nitrogen gas used for carrier gas at 20 ml /m. Temperature program setup for 0-400 ºC and temperature ramping rate 15 ºC/min use for sample run.

3. Result and Discussion

3.1 Pre-analysis Results

Before start the experiment raw materials were analyzed by ICP-AES (Inductively coupled plasma atomic emission spectroscopy) water and aqueous matrices and ASTM test method (ASTM D 1976) flowed for raw material trace metal detection. After finishing the ICP experiment was found some percentage of trace metal present into raw waste plastics. The experimental process any kind of catalyst did not apply, because ICP analysis result indicate that waste plastic inside has different kind of trace metal those trace metal can react as a catalyst. This type of trace metal is acting as a catalyst and for that reason we do not need to put any extra catalyst or extra any kind of chemical for waste plastic to hydrocarbon fuel conversion process (patent pending). From LDPE, PP and PS waste plastic trace metal table are provided below table 3, table 4 and table 5.

Table 3: Raw LDPE waste plastic trace metal detected by ICP

Name of Method	Name of Trace Metal	Results (mg/L)	Name of Method	Name of Trace Metal	Results (mg/L)
ASTM D1976	Silver	<1.0	ASTM D1976	Molybdenum	<1.0
	Aluminum	197.4		Sodium	45.2
	Boron	2.8		Nickel	<1.0
	Barium	<1.0		Phosphorus	26.7
	Calcium	962.6		Lead	<1.0
	Chromium	<1.0		Antimony	<1.0
	Copper	<1.0		Silicon	90.2
	Iron	6.0		Tin	<1.0
	Potassium	35.4		Titanium	2.7
	Lithium	<1.0		Vanadium	<1.0
	Magnesium	25.1		Zinc	2.6

Table 4: PP waste plastic trace metal detected by ICP

Name of Method	Name of Trace Metal	Results (mg/L)	Name of Method	Name of Trace Metal	Results (mg/L)
ASTM D1976	Silver	<1.0	ASTM D1976	Molybdenum	<1.0
	Aluminum	<1.0		Sodium	5,966
	Boron	<1.0		Nickel	<1.0
	Barium	<1.0		Phosphorus	<1.0
	Calcium	30.5		Lead	<1.0
	Chromium	<1.0		Antimony	<1.0
	Copper	<1.0		Silicon	5.3
	Iron	3.9		Tin	<1.0
	Potassium	<1.0		Titanium	<1.0
	Lithium	<1.0		Vanadium	<1.0
	Magnesium	2.8		Zinc	<1.0

Table 5: PS waste plastic trace metal detected by ICP

Name of Method	Name of Trace Metal	Results (mg/L)	Name of Method	Name of Trace Metal	Results (mg/L)
ASTM D1976	Silver	<1.0	ASTM D1976	Molybdenum	<1.0
	Aluminum	59.8		Sodium	118.8
	Boron	2.8		Nickel	<1.0
	Barium	2.7		Phosphorus	<1.0
	Calcium	33,420		Lead	<1.0
	Chromium	<1.0		Antimony	<1.0
	Copper	<1.0		Silicon	17.2
	Iron	47.2		Tin	<1.0
	Potassium	28.4		Titanium	60.8
	Lithium	16.8		Vanadium	<1.0

Magnesium	842.7	Zinc	89.9

ASTM (American Standard and Testing Method) analysis of LDPE Waste plastics (**Table 3**) numerous types of trace metal are appeared. In according to analysis of ASTM D1976 LDPE trace metal contents are following such as Silver <1.0 mg/L, Aluminum 197.4 mg/L, Boron 2.8 mg/L, Barium <1.0 mg/L, Calcium 962.6 mg/L, Chromium <1.0 mg/L, Copper <1.0 mg/L, Iron 6.0 mg/L, Potassium 35.4 mg/L, Lithium <1.0 mg/L, Magnesium 25.1 mg/L etc. Again ASTM Method D1976 trace metal analysis found that Molybdenum <1.0 mg/L, Sodium 45.2 mg/L, Nickel <1.0 mg/L, Phosphorus 26.7 mg/L, Lead <1.0 mg/L, Antimony <1.0 mg/L, Silicon 90.2 mg/L, Tin <1.0 mg/L, Titanium 2.7 mg/L, Vanadium <1.0 mg/L and ultimately Zinc trace metal content is 2.6 mg/L etc. In two methods doesn't make any significant change in the trace metal contents of analysis because of same method analysis. In most of cases emerged that trace metal contents are less than <1.0 mg/L are found that make more sense in that point in the terms of trace metal consistency contents. In some metal contents noticed that available metal percentages are very high in the LDPE waste plastic such as Aluminum 197.4 mg/L, Calcium 962.6 mg/L, Sodium 45.2 mg/L, Phosphorus 26.7 mg/L and Silicon 90.2 mg/L etc.

ASTM (American Standard and Testing Method) analysis of PP Waste plastics (**Table 4**) numerous types of trace metal are appeared. In according to analysis of ASTM D1976 PP trace metal contents are following such as Silver <1.0 mg/L, Aluminum <1.0 mg/L, Boron <1.0 mg/L, Barium <1.0 mg/L, Calcium 30.5 mg/L, Chromium <1.0 mg/L, Copper <1.0 mg/L, Iron 3.9 mg/L, Potassium <1.0 mg/L, Lithium <1.0 mg/L, Magnesium 2.8 mg/L etc. Again ASTM Method D1976 trace metal analysis found that Molybdenum <1.0 mg/L, Sodium 5,966 mg/L, Nickel <1.0 mg/L, Phosphorus <1.0 mg/L, Lead <1.0 mg/L, Antimony <1.0 mg/L, Silicon 5.3 mg/L, Tin <1.0 mg/L, Titanium <1.0 mg/L, Vanadium <1.0 mg/L and ultimately Zinc trace metal content is <1.0 mg/L etc. In two methods doesn't make any significant change in the trace metal contents of analysis because of same method analysis. In most of cases emerged that trace metal contents are less than <1.0 mg/L are found that make more sense in that point in the terms of trace metal consistency and also appeared that in PP waste plastic comparatively with other waste plastic noticed that less trace metal contents are found such as Calcium, Iron, Magnesium and Silicon are exist less contents in the PP waste plastic compare with other waste plastics except Sodium which contents much more 5,966 mg/L in the PS waste plastic.

ASTM (American Standard and Testing Method) analysis of PS Waste plastics (**Table 5**) numerous types of trace metal are appeared. In according to analysis of ASTM D1976 PS trace metal contents are following such as Silver <1.0 mg/L, Aluminum 59.8 mg/L, Boron 2.8 mg/L, Barium 2.7 mg/L, Calcium 33,420 mg/L, Chromium <1.0 mg/L, Copper <1.0 mg/L, Iron 47.2 mg/L, Potassium 28.4 mg/L, Lithium 16.8 mg/L, Magnesium 842.7 mg/L etc. Again ASTM Method D1976 trace metal analysis found that Molybdenum <1.0 mg/L, Sodium 118.8 mg/L, Nickel <1.0 mg/L, Phosphorus <1.0 mg/L, Lead <1.0 mg/L, Antimony <1.0 mg/L, Silicon 17.2 mg/L, Tin <1.0 mg/L, Titanium 60.8 mg/L, Vanadium <1.0 mg/L and ultimately Zinc trace metal content is 89.9 mg/L etc. In two methods doesn't make any significant change in the trace metal contents of analysis because of same method analysis. In most of cases emerged that trace metal contents are less than <1.0 mg/L are found that make more sense in that point in the terms of trace metal consistency and also appeared that in PS waste plastic comparatively with other waste plastic noticed that less trace metal contents are found such as Aluminum, Calcium, Iron, Magnesium, Sodium, Titanium and Zinc are exist high percentage contents in the PS waste plastic compare with other waste plastics except Calcium which contents much more 33,420 mg/L of contents.

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, abroad 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 (sterically hindered phenols, organophosphites),UVand 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 [8].

3.2 Characteristic of the Liquid Fuel

FT-IR (Fourier transform infrared spectroscopy, Spectrum 100) analysis of LDPE, PP & PS mixture to produced fuel (fig. 2) according to their wave number and spectrum band following types of functional groups are appeared in the analysis. In the spectrum field we noticed that higher wave number are emerged in the initial phase and middle index of the spectrum and in higher wave number small and bulky both functional groups are available and in low wave number double bond and single bond functional groups are available such as methane group, cis and trans alkenes etc. Hereafter wave number 2965.31 cm^{-1}, 2729.17 cm^{-1} functional group is $C\text{-}CH_{3,}$ wave number 1871.50 cm^{-1},1816.58 cm^{-1},1798.08 cm^{-1}, 1798.08 cm^{-1} ,1744.07 cm^{-1} and 1718.00 cm^{-1} functional group is Non-Conjugated, wave number 1450.05 cm^{-1} and 1378.04 cm^{-1} functional group is CH_3, wave number 1020.53 cm^{-1} functional group is Acetates and ultimately wave number 990.62 cm^{-1} and 904.64 cm^{-1} functional group is $–CH=CH_{2.}$ Energy values are calculated, using formula is $E=h\upsilon$, Where h=Planks Constant, $h=6.626\text{x}10^{-34}$ J, υ= Frequency in Hertz (sec^{-1}), Where $\upsilon=c/\lambda$, c=Speed of light, where, $c=3\text{x}10^{10}$ m/s, $W=1/\lambda$, where λ is wave length and W is wave number in cm^{-1}. Therefore the equation $E=h\upsilon$, can substitute by the following equation, $E=hcW$. According to their wave number several energy values are calculated such as for 2965.31 (cm^{-1}) calculated energy, $E=5.80\text{x}10^{-20}$ J. Similarly, wave number 1871.50 (cm^{-1}) energy, $E=3.61\text{x}10^{-20}$ J, wave number 1378.04 (cm^{-1}) energy, $E=2.73\text{x}10^{-20}$ J and eventually wave number 990.62 (cm^{-1}) functional group is $1.97\text{x}10^{-20}$ J respectively. LDPE, PP, PS mixture to fuel Perkin Elmer library search results .sp / mirlib.dlb Euclidean Search Hit List : 0.557 F37460 2,5-DIHYDROXYACETOPHENONE , 0.448 F54150 2-HYDROXYACETOPHENONE , 0.428 F65155 2-METHOXYPHENYLACETONITRILE, 0.426 F65470 3-METHYLACETOPHENONE, 0.406 F385583,4-DIMETHOXYACETOPHENONE, 0.389 F22850 4- CHLOROACETOPHENONE, 0.333 F65156 3-METHOXYPHENYLACETONITRILE, 0.317 F37450 2,4-DIHYDROXYACETOPHENONE, 0.316 F24110 ETHYL 4-CHLORO-2-CYANOACETOACETATE, 0.312 F91080 TRICHLOROACETONITRILE.

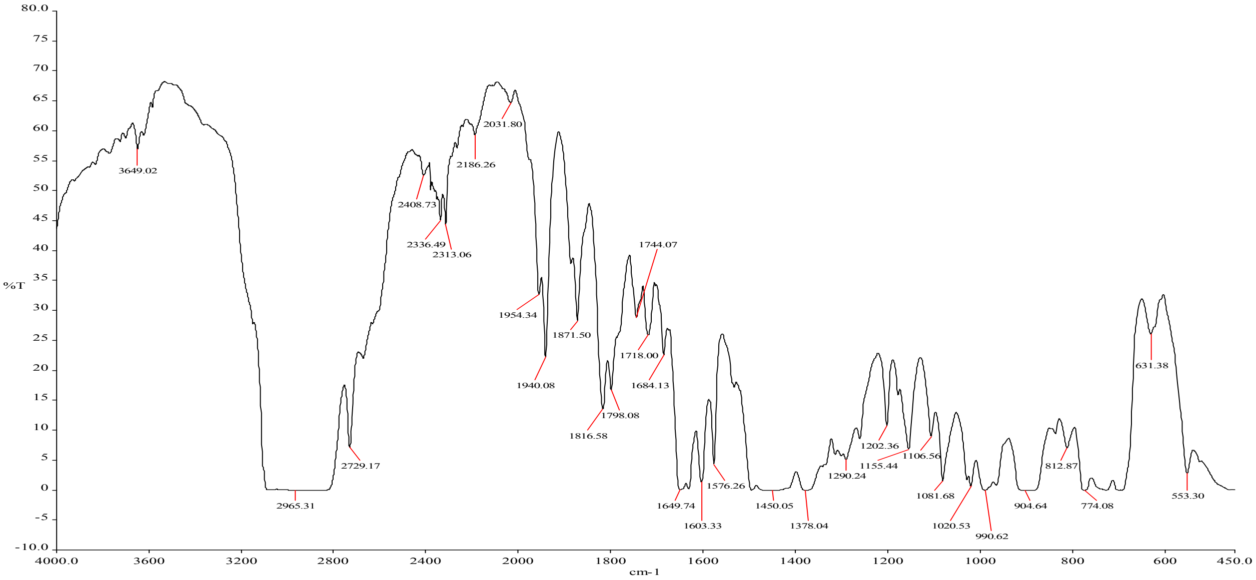


Figure 2: FT-IR spectrum of LDPE, PP and PS mixture to produce fuel

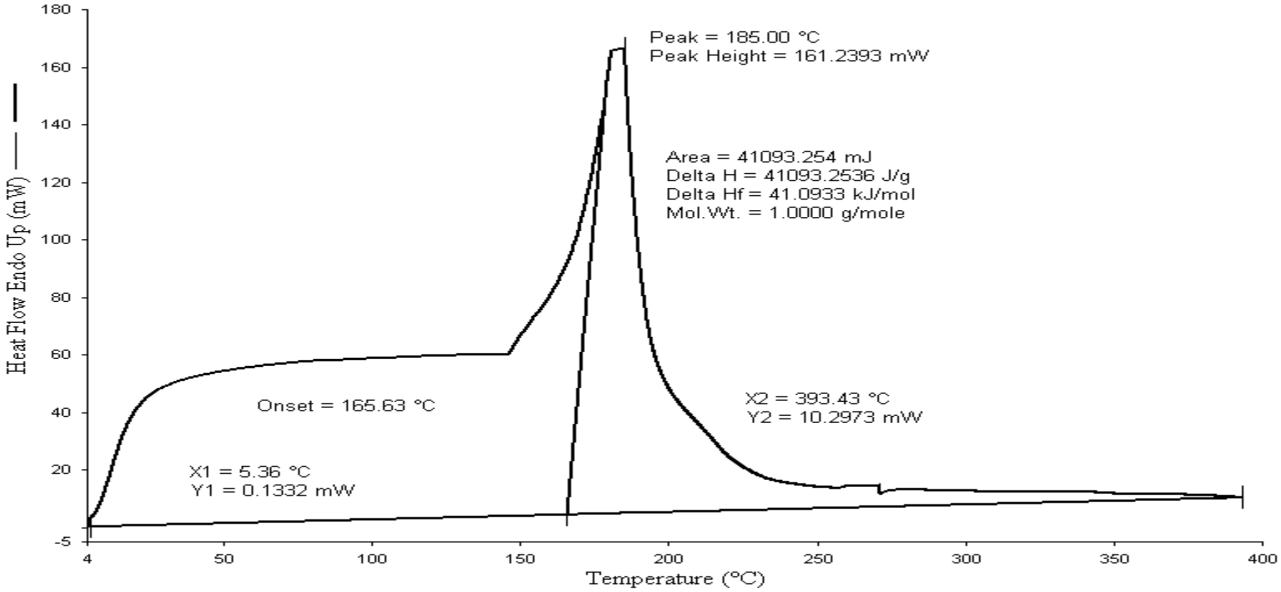


Figure 3: DSC graph of LDPE, PP and PS mixture to produce fuel

DSC (Differential Scanning Calorimeter) equipment was use for produce fuel analysis shown fig. 3. Fuel was used 50 µL for DSC analysis and aluminum pan was used for sample holding. After analysis fuel sample we notice that fuel start boil at 5 ºC and temperature raise up to 185.00 ºC. Fuel boiling point peak showing 185.00 ºC and peak height 161.2393 mW. Peak area 41093.254 mJ and enthalpy delta H value is 41093.2536 J/g. Fuel start boiling X1= 5.36 ºC which is need Endo heat up Y1=0.1332 mW and finished X2 = 393.43 ºC which is go down heat Endo up Y2= 10.2973 mW. Fuel peak point heat flow Endo up showing 161.2393 mW. This fuel has long chain aliphatic hydrocarbon compounds and also benzene compounds because we used polystyrene waste plastic for that reason this fuel has aromatics compounds and boiling point is high.

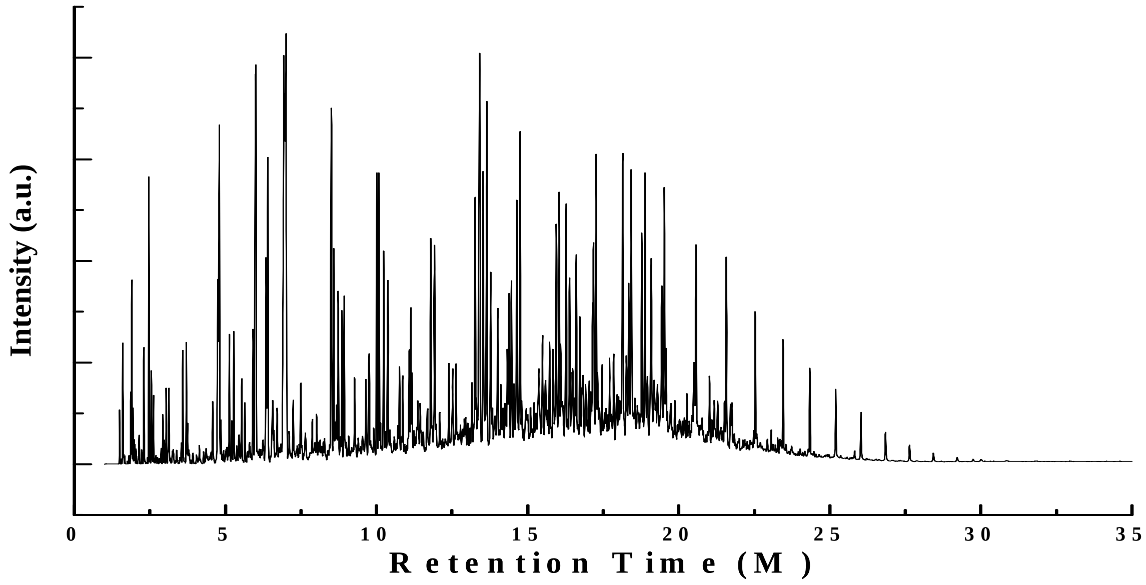


Figure 4: GC/MS chromatogram of LDPE, PP and PS mixture to produce fuel

Table 6: GC/MS chromatogram compound list of LDPE, PP and PS mixture to produce fuel

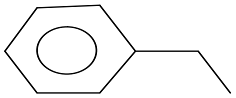
Number of Peak	Retention Time (min.)	Trace Mass (m/z)	Compounds Name	Compound Formula	Molecular Wight	NIST Library Number
1	1.49	41	Cyclopropane	C_3H_6	42	18854
2	1.60	41	1-Propene, 2-methyl-	C_4H_8	56	18910
3	1.87	42	Cyclopropane, ethyl-	C_5H_{10}	70	19072
4	1.90	72	2-Buten-1-ol, (E)-	C_4H_8O	72	53333
5	1.94	55	2-Pentene, (E)-	C_5H_{10}	70	291780
6	2.30	43	Pentane, 2-methyl-	C_6H_{14}	86	61279
7	2.46	42	Cyclohexane	C_6H_{12}	84	291493
8	2.55	41	Hexane	C_6H_{14}	86	61280
9	2.62	69	2-Pentene, 4-methyl-, (Z)-	C_6H_{12}	84	19318
10	2.87	56	Cyclopentane, methyl-	C_6H_{12}	84	114428
11	2.93	67	2,4-Hexadiene, (Z,Z)-	C_6H_{10}	82	113646
12	3.04	56	1-Pentene, 2,4-dimethyl-	C_7H_{14}	98	114435
13	3.13	81	2,4-Dimethyl 1,4-pentadiene	C_7H_{12}	96	114468
14	3.54	56	1-Hexene, 2-methyl-	C_7H_{14}	98	114433
15	3.59	41	Cyclopentane, 1,2-dimethyl-, cis-	C_7H_{14}	98	114027
16	3.71	43	Heptane	C_7H_{16}	100	61276
17	4.14	83	Cyclohexane, methyl-	C_7H_{14}	98	118503
18	4.58	41	3-Heptene, 4-methyl-	C_8H_{16}	112	114150
19	4.75	42	Heptane, 4-methyl-	C_8H_{18}	114	113916
20	4.80	39	1,5-Heptadien-3-yne	C_7H_8	92	142710
21	5.13	41	1-Octene	C_8H_{16}	112	1604
22	5.21	95	1,4-Hexadiene, 2,3-dimethyl-	C_8H_{14}	110	1482
23	5.28	41	Octane	C_8H_{18}	114	229407
24	5.54	69	Cyclopentane, 1,1,3,4-tetramethyl-, cis-	C_9H_{18}	126	27589
25	5.65	43	Hexane, 3-ethyl-	C_8H_{18}	114	113940
26	5.79	67	1-Methyl-2-methylenecyclohexane	C_8H_{14}	110	113437
27	5.91	111	Cyclohexane, 1,3,5-trimethyl-, (1α,3α,5α)-	C_9H_{18}	126	2480
28	5.99	42	2,4-Dimethyl-1-heptene	C_9H_{18}	126	113516
29	6.01	83	2H-Pyran-2-one, 4-ethenyltetrahydro-	$C_7H_{10}O_2$	126	190012
30	6.35	69	Cyclohexane, 1,3,5-trimethyl-, (1α,3α,5β)-	C_9H_{18}	126	2480
31	6.40	91	Ethylbenzene	C_8H_{10}	106	158804
32	6.57	109	Cyclohexene, 3,3,5-trimethyl-	C_9H_{16}	124	114765
33	6.94	77	1,3,5,7-Cyclooctatetraene	C_8H_8	104	1259
34	7.24	82	3-Octyne, 2-methyl-	C_9H_{16}	124	62452

35	7.50	105	Benzene, (1-methylethyl)-	C_9H_{12}	120	228742
36	7.64	43	2,4-Undecadien-1-ol	$C_{11}H_{20}O$	168	136410
37	7.88	117	Benzene, 2-propenyl-	C_9H_{10}	118	114744
38	8.02	91	Benzene, propyl-	C_9H_{12}	120	113930
39	8.59	41	1-Decene	$C_{10}H_{20}$	140	118883
40	8.73	43	Decane	$C_{10}H_{22}$	142	114147
41	8.86	57	Decane, 4-methyl-	$C_{11}H_{24}$	156	5261
42	9.08	41	2-Decyn-1-ol	$C_{10}H_{18}O$	154	53366
43	9.27	117	Benzene, 2-propenyl-	C_9H_{10}	118	114744
44	9.75	91	2-Cyclohexen-1-ol, 2-methyl-5-(1-methylethenyl)-	$C_{10}H_{16}O$	152	114684
45	10.01	41	1-Dodecene	$C_{12}H_{24}$	168	34718
46	10.08	70	Cyclooctane, 1,4-dimethyl-, cis-	$C_{10}H_{20}$	140	61409
47	10.24	55	1-Undecene	$C_{11}H_{22}$	154	34717
48	10.38	57	Undecane	$C_{11}H_{24}$	156	114185
49	10.87	43	Ethanone, 1-(1,2,2,3-tetramethylcyclopentyl)-, (1R-cis)-	$C_{11}H_{20}O$	168	186082
50	11.09	91	Benzene, (3-methyl-3-butenyl)-	$C_{11}H_{14}$	146	113578
51	11.14	69	1,12-Tridecadiene	$C_{13}H_{24}$	180	7380
52	11.18	69	2-Isopropenyl-5-methylhex-4-enal	$C_{10}H_{16}O$	152	191046
53	11.80	69	1-Dodecene	$C_{12}H_{24}$	168	107688
54	11.92	71	Dodecane	$C_{12}H_{26}$	170	291499
55	12.40	43	Decane, 2,3,5,8-tetramethyl-	$C_{14}H_{30}$	198	149589
56	12.63	43	Tetradecane, 2,6,10-trimethyl-	$C_{17}H_{36}$	240	11556
57	13.42	71	1-Decanol, 2-methyl-	$C_{11}H_{24}O$	172	185011
58	13.78	92	Benzene, heptyl-	$C_{13}H_{20}$	176	118464
59	14.38	55	7-Octadecyne, 2-methyl-	$C_{19}H_{36}$	264	114518
60	14.46	118	Benzene, (3-methyl-1-methylenebutyl)-	$C_{12}H_{16}$	160	64019
61	14.64	83	Cyclotetradecane	$C_{14}H_{28}$	196	114117
62	14.75	56	Benzeneacetic acid, 4-tetradecyl ester	$C_{22}H_{36}O_2$	332	282026
63	15.36	43	Tetradecane, 2,6,10-trimethyl-	$C_{17}H_{36}$	240	11556
64	15.84	43	1-Dodecanol, 3,7,11-trimethyl-	$C_{15}H_{32}O$	228	22776
65	15.94	83	1-Pentadecene	$C_{15}H_{30}$	210	232902
66	16.04	85	Pentadecane	$C_{15}H_{32}$	212	107761
67	17.18	55	1-Hexadecene	$C_{16}H_{32}$	224	118882
68	17.27	56	Hexadecane	$C_{16}H_{34}$	226	107738
69	17.46	55	2-Dodecen-1-yl (-) succinic anhydride	$C_{16}H_{26}O_3$	266	76110

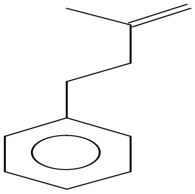
70	17.71	91	Benzene, [3-(2-cyclohexylethyl)-6-cyclopentylhexyl]-	$C_{25}H_{40}$	340	23414
71	18.15	92	Benzene, 1,1'-(1,3-propanediyl) bis-	$C_{15}H_{16}$	196	133399
72	18.34	55	2-Methyl-E-7-hexadecene	$C_{17}H_{34}$	238	130870
73	18.42	56	Heptadecane	$C_{17}H_{36}$	240	107308
74	18.78	69	1-Nonadecanol	$C_{19}H_{40}O$	284	232931
75	18.88	130	Naphthalene, 1,2,3,4-tetrahydro-2-phenyl-	$C_{16}H_{16}$	208	9510
76	19.09	55	1-Nonadecanol	$C_{19}H_{40}O$	284	232931
77	19.52	57	Octadecane	$C_{18}H_{38}$	254	57273
78	20.27	57	Heptadecane, 9-octyl-	$C_{25}H_{52}$	352	15951
79	20.50	55	1-Hexadecanol, 2-methyl-	$C_{17}H_{36}O$	256	36540
80	20.57	85	Eicosane	$C_{20}H_{42}$	282	290513
81	22.53	57	Heneicosane	$C_{21}H_{44}$	296	107569
82	23.06	43	1-Heptacosanol	$C_{27}H_{56}O$	396	16909
83	23.45	57	Heneicosane	$C_{21}H_{44}$	296	107569
84	25.20	57	Heneicosane	$C_{21}H_{44}$	296	107569
85	26.03	57	Pentacosane	$C_{25}H_{52}$	352	150576
86	26.84	57	Heptacosane	$C_{27}H_{56}$	380	79427
87	27.64	57	Heptacosane	$C_{27}H_{56}$	380	79427

Perkin Elmer GC-MS (Gas Chromatography–Mass Spectrometry)analysis of LDPE, PP & PS waste plastic mixture to fuel (fig.4 and table 6) in accordance with the various retention times and trace masses different types of hydrocarbon compound and benzene derivatives compounds appear in the analysis result index. Many compounds emerge on the analysis carbon range C_3 to $C_{27.}$ Based on the retention time and trace mass following hydrocarbon compounds as follows such as at the initial phase of the analysis at retention time 1.49 (min.) and trace mass 41, compound is Cyclopropane (C_3H_6), retention time 1.60 and trace mass 41, compound is 1-Propene-2-methyl-(C_3H_6), retention time 1.87 and trace mass 72, compound is 2-Butene-1-ol,(E) (C_4H_8O), retention time 1.94 and trace mass 55,compound is 2-Pentene,(E)-(C_5H_{10}), retention time 2.30 and trace mass 43, compound is Pentane, 2-methyl-(C_6H_{14}), retention time 2.46 and trace mass 42, compound is Cyclohexane (C_6H_{12}), retention time 2.55 and trace mass 41,compound is hexane (C_6H_{14}), retention time 2.62 and trace mass 69, compound name is 2-Pentene, 4-methyl-,(Z)- (C_6H_{12}), retention time 2.93 and trace mass 67, compound name is 2,4-Hexadiene, (Z,Z)-(C_6H_{10}), retention time 3.59 and trace mass 41, compound is Cyclopentane,1,2-dimethyl-,cis-(C_7H_{14}), retention time 4.58 and trace mass 41, compound is –Heptene-4-methyl-(C_8H_{16}), retention time 5.54 and trace mass 69, compound is Cyclopentane,1,1,3,4-tetramethyl-,cis-(C_9H_{18}), retention time 5.99 and trace mass 42, compound is 2,4-Dimethyl-1-heptene (C_9H_{18}), retention time 6.57 and trace mass 109 compound is Cyclohexene,3,3,5-trimethyl-(C_9H_{16}), retention time 7.24 and trace mass 82, compound is 3-Octyne,2-methyl-(C_9H_{16}) , retention time 8.86 and trace mass 57, compound is Decane, 4-methyl-($C_{11}H_{24}$), retention time 9.27 and trace mass 117, compound is Benzene, 2-propenyl- (C_9H_{10}), benzene compounds are formed because when raw polystyrene are made benzene are added into the reactants. Also at retention time 9.75 and trace mass 91, compound is 2-Cyclohexane-1-ol, 2-methyl-5-(1-methylethenyl)-($C_{10}H_{16}O$), retention time 10.87 and trace mass 43, compound is Ethanone,1-(1,2,2,3-tetramethylcyclopentyl)-, (1R-cis)-($C_{11}H_{20}O$) etc. In the middle phases of the analysis index results in accordance with the retention time and trace masses various kinds of compounds are detected such as at retention time 11.09 and trace mass 91, compound is ($C_{11}H_{14}$), retention time 11.18 and trace mass 69, compound is 2-Isopropenyl-5-methylhex-4-enal ($C_{10}H_{16}O$), oxygenated compound are formed because in the glass reactor chamber much amount of steams are produced and also experiment executed in the presence of air. Retention time 11.80 and trace mass 69, compound is 1-Dodecene ($C_{12}H_{24}$), retention time 11.92 and trace mass 71, compound is Dodecane ($C_{12}H_{26}$), retention time 12.40 and trace mass 43, compound is Decane, 2,3,5,8-tetramethyl-($C_{14}H_{30}$), at retention time 13.78 and trace mass 92, compound is Benzene, heptyl-($C_{13}H_{20}$), retention time 15.84 and trace mass 43, compound is 1-Dodecanol, 3,7,11-trimethyl-($C_{15}H_{32}O$) etc. In the ultimate phase of the analysis index several compound are detected as according to their retention time and trace masses such as retention time 16.04 and trace mass 85, compound is Pentadecane ($C_{15}H_{32}$), retention time 17.71 and trace mass 91, compound is Benzene, [3-(2-cyclohexylethyl)-6-cyclopentylhexyl]-($C_{25}H_{40}$), retention time 18.88 and retention time 130, compound is Naphthalene, 1,2,3,4-tetrahydro-2-phenyl-($C_{16}H_{16}$), retention time 19.52 and trace mass 57, compound is Octadecane ($C_{18}H_{38}$), retention time 20.57 and trace mass 85, compound is Eicosane ($C_{20}H_{42}$), retention time 22.53 and trace mass 57, compound is Heneicosane ($C_{21}H_{44}$), retention time 23.45 and trace mass 57, compound is Heneicosane ($C_{21}H_{44}$), retention time 25.20 and trace mass 57, compound is Heneicosane ($C_{21}H_{44}$), retention time 26.84 and trace mass 57, compound is Heptacosane Heneicosane ($C_{27}H_{56}$) and eventually retention time 27.64 and trace mass 57, compound is Heptacosane ($C_{27}H_{56}$). Some chemical Structure (aromatic group hydrocarbon compound) cited from GC/MS NIST library after liquefaction and produced fuel form 3 types of waste plastic mixture to fuel and structure are shown bellow fig. 5 and aromatic group with hydrocarbon compound mass spectra shown fig. 6. Aromatic compound are present into PS waste plastic this waste plastic when mixed with Low density and polypropylene waste plastic and heat applied for fuel production long chain hydrocarbon breakdown into short chain hydrocarbon and form varieties different structure aliphatic and aromatic group compound. Fig. 5 is showing only aromatic group hydrocarbon compound with different m/z shown number I-VI and different chemical structure. Fig.6 had shown produced fuel some aromatic group hydrocarbon compound mass spectra with relative intensity versus m/z number I-VI.

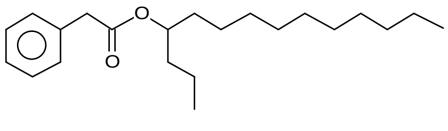
I. Ethylbenzene, C_8H_{10}, m/z =91



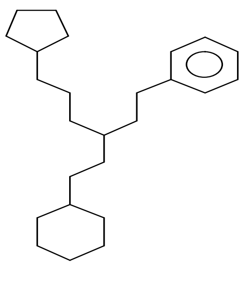
II. Benzene, (3-methyl-3-butenyl)-, $C_{11}H_{14}$, m/z = 91



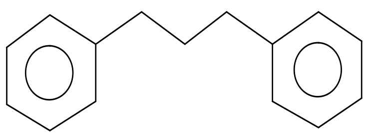
III. Benzeneacetic acid, 4-tetradecyl ester, $C_{22}H_{36}O_2$, m/z =56



IV. Benzene, [3-(2-cyclohexylethyl)-6-cyclopentylhexyl]-, $C_{25}H_{40}$, m/z = 91



V. Benzene, 1,1'-(1,3-propanediyl)bis-, $C_{15}H_{16}$, m/z = 92



VI. Naphthalene, 1, 2, 3, 4-tetrahydro-2-phenyl-, $C_{16}H_{16}$, m/z =130

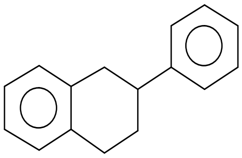
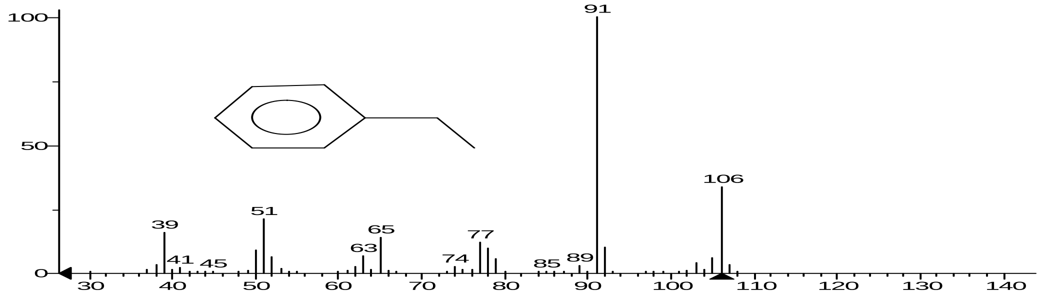
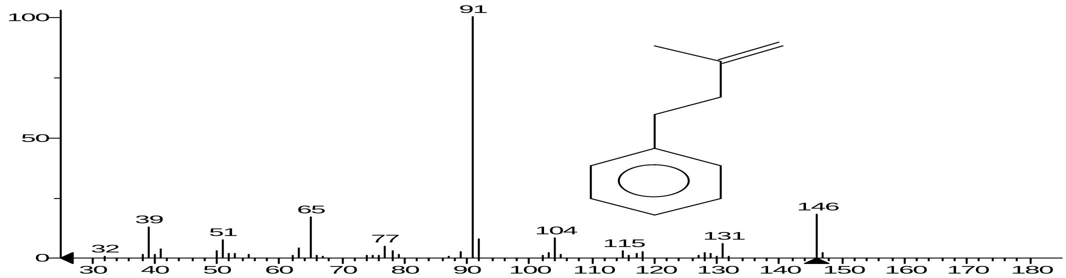


Figure 5: Aromatic group hydrocarbon compound stricture number I-VI cited form GC/MC NIST Library form produced fuel

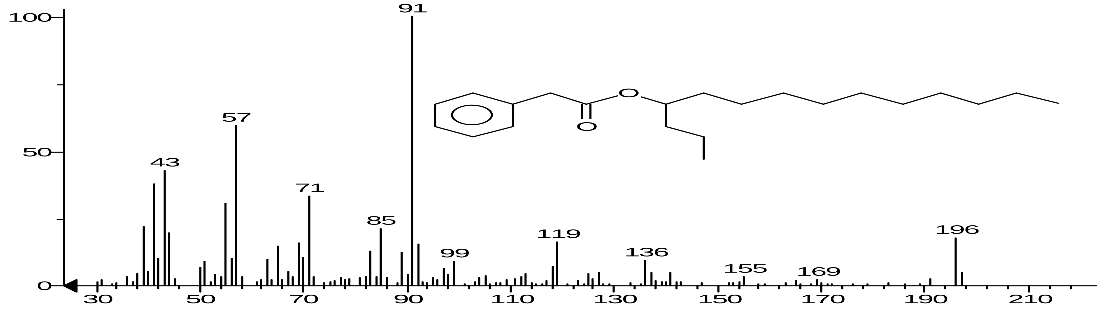


I. Ethylbenzene, C_8H_{10}, m/z = 91

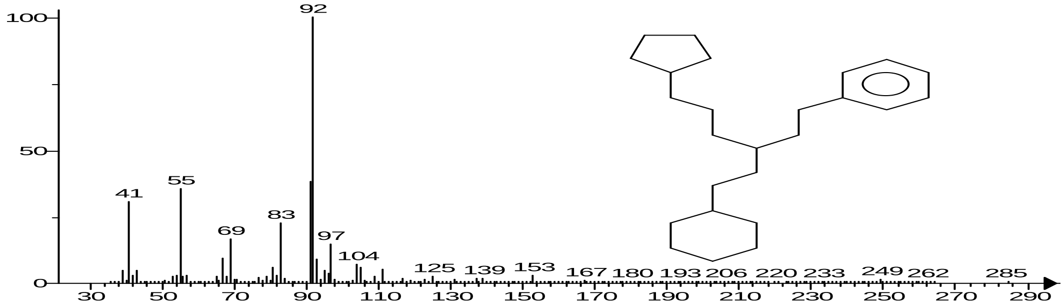


II. Benzene, (3-methyl-3-butenyl)-, $C_{11}H_{14}$, m/z = 91

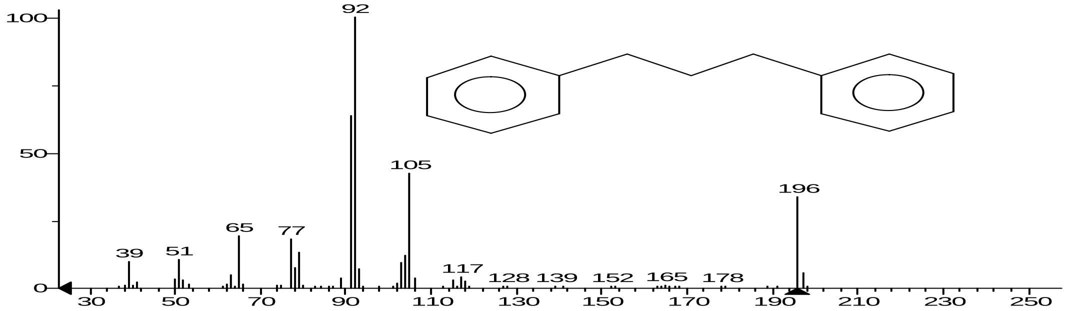
Relative Intensity



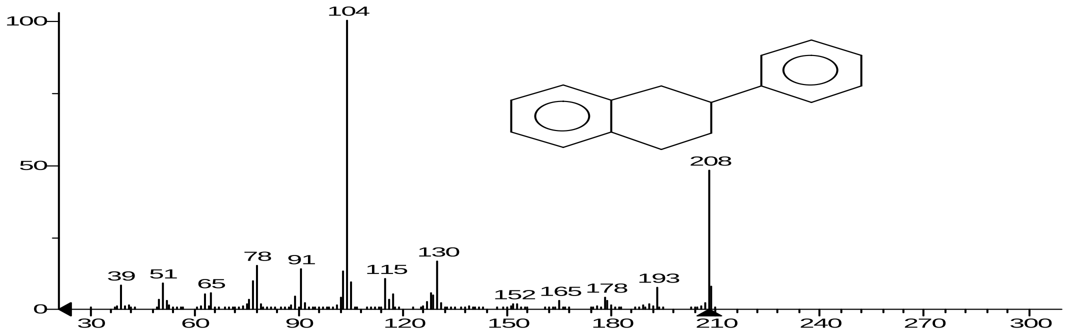
III. Benzeneacetic acid, 4-tetradecyl ester, $C_{22}H_{36}O_2$, m/z =56



IV. Benzene, [3-(2-cyclohexylethyl)-6-cyclopentylhexyl]-, $C_{25}H_{40}$, m/z = 91



V. Benzene, 1,1'-(1,3-propanediyl)bis-, $C_{15}H_{16}$, m/z = 92



VI. Naphthalene, 1, 2, 3, 4-tetrahydro-2-phenyl-, $C_{16}H_{16}$, m/z =130

m/z

Figure 6: Aromatic group hydrocarbon compound mass spectra number I-VI from produced fuel Relative Intensity versus m/z

Produced fuel ASTM test was performed by 3rd party Intertek laboratory in New Jersey, USA. ASTM test method performed for API gravity (ASTM D4052), gross heat of combustion/lb (19218 Btu/lb) and gross heat of combustion/gallon (129242 Btu/gallon) (ASTM D240), IBP and FBP recovery (ASTM D86), residue (ASTM D86), pour point (ASTM D97), cloud point (ASTM D2500), sulfur (ASTM D5453), ASTM color (ASTM D1500), water content (ASTM E203), metal (ASTM D5708_mod), ash (ASTM D482), acid number (ASTM D664), freezing point (ASTM D2386), barometric pressure (ASTM D86) and etc. After finished experiment analysis solid black residue by ICP-AES ASTM test method ASTM D1976 and heat combustion ASTM D240 BTU/lb and bulk density of solid black residue is 0.9331 g/cm^3 test method apply for residue density ASTM D1480. Produced light gas analysis part under investigation and left over residue analysis also under investigation.

4. Conclusion

Waste plastics to fuel production process were used 3 types of waste plastics (LDPE, PP and PS) without adding any kind of catalyst. Without catalyst fuel production yield percentage was almost 90% by wt. %. Waste plastics have different type of metal content because when plastic are made that time manufacturing company production procedure using different kind of additives for plastic shape. This metal content was helping when experimental heat applies on waste plastics to break down long chain to short chain hydrocarbon fuel production. Produced fuel has long chain and short chain hydrocarbon isomer and also benzene group compounds such as Ethylbenzene, 2-propenyl-Benzene, (3-methyl-1-methylenebutyl)-Benzene, Naphthalene, 1, 2, 3, 4-tetrahydro-2-phenyl- and etc because raw materials was mixed with polystyrene (PS). By products of black solid residue percentage also less, the percentage residue is coming out as metal and some carbon and hydrogen because it was presented into pre-analysis trace metal present into the raw waste plastic. Gas Chromatography and Mass Spectrometer (GCMS) analysis also indicated that various kinds of hydrocarbon compounds are present in the obtained fuel including benzene derivatives and styrene compounds named aromatic compound etc. Various aliphatic compounds are also appeared in the GCMS analysis of fuel entities. Fourier Transform Infra-red Spectroscopy (FT-IR) is also performed in order to identified the numerous functional groups including single bond, double bond and triple bonds are present in the fuel such as Alkane, Alkene and Alkyne etc. In carbon-carbon double bonded functional group are divided into cis and trans alkene as well. Differential Scanning Calorimeter (DSC) analysis was determined the onset temperature of obtained fuel that is represents the boiling point of the analyzed fuel. Produce fuel could be use as internal combustion engines, feed for feed stock refinery or electricity generation feed for power plants. By using this technology can be solved waste plastic (LDPE/PP/PS) problem as well as environmental problems and reduce some percentage of foreign oil dependency.

Acknowledgement

The authors acknowledge the support of Dr. Karin Kaufman, the founder and sole owner of Natural State Research, Inc. The authors also acknowledge the valuable contributions NSR laboratory team members during the preparation of this manuscript.

References

[1] S.H. Hamid, M.B. Amin, A.G. Maadhah. Handbook of Polymer Degradation, Marcel Decker, New York, 1992

[2] P.T. Williams, E.A. Williams. Interaction of plastics in mixed plastic pyrolysis, Energy and Fuels 13 (1990) 188-196

[3] Phong Hai Vu, Osami Nishida, Hirotsugu Fujita, Wataru Harano, Norihiko Toyoshima, Masami Iteya, Reduction of NOx, and PM from diesel engines by WPD emulsified fuel, SAE Technical Paper 2001-01-0152

[4] M. Thomas, Novel and innovative pyrolysis and gasification technologies for energy efficient and environmentally sound MSW disposal. Waste Management 2004; 24:53-79

[5] O. Akitsugu, Feedstock recycling of plastics in Japan. Polymer Degradation and Stability 2004; 85:981-8

[6] H. Bockhorn, A. Hornung, U. Hornung, Stepwise pyrolysis for raw materials recovery from plastic waste. Journal of Analytical and Applied Pyrolysis 1998; 46:1-13

[7] F. Pinto, P. Costa, I. Gulyurtlu, I. Cabrita, Pyrolysis of plastic wastes. 1. Effect of plastic waste composition on product yield. Journal of Analytical and Applied Pyrolysis 1999; 51:39-55

[8] Tullo, A. H. Plastic additives. Chem. Eng. News 2003, 81 (46), 36-42