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CONVERSION OF WASTE POLYMERS INTO HYDROCARBON LIQUID FUEL AND PROPERTY ANALYSIS

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ABSTRACT

Industrialization is the key to development where energy is the driving force. Fossil fuel is not an unending source of energy and hereby can be supported from renewable energy. This paper addresses an experimental study of a new dimension of energy that can be a good support of fossil energy as well as meet the environmental concern. All sorts of municipal plastic waste except PET have been successfully converted into fuel and hereby prevent their unhygienic exposure in environment that might lead emission of carbon-monoxide by burning as well as degrading soil fertility. The majority of plastics are derived from ethylene, propylene, butadiene and benzene. With the presence of Al_2O_3 *and ZnO catalyst, the plastic wastes are heated up to 350°C temperature into a reactor and the gaseous stream were condensed and collected in receiving chamber. Performance and property tests are conducted of the derived fuel. The produced fuel contains long carbon chain lengths C3-C27 determine by GC. ASTM test result showed low sulfur contents resulting high performance and environmentally friendly at the same time. The experiment has been met the highest standards of safety, quality, reliability and environmental sustainability in converting hydrocarbon fuel of this locality.*

Keywords: *Waste polymers; catalytic cracking; gasoline; diesel; distillation; RON*

INTRODUCTION

Plastic is a polymeric compound which is synthesized from monomer whereas the source of monomer is petrochemicals. Polymers are any of various complex organic compounds produced by polymerization, capable of being molded, extruded, cast into various shapes and films, or drawn into filaments and then used as textile fibers.

Plastic is a relatively cheap, durable and versatile material. For these reasons polymers have triumphed in our daily life for its inert features and sustainability of higher tensile strength than its weight and thickness own. It is also emblematic material, transforming our everyday life for over 60 years, delivering unprecedented functionality. As with most materials, global plastics production is estimated to have fallen from 245 Mt in 2008 to around 230 Mt in 2009 as a result of the economic crisis. However, Over the past fifty years, there has been a very steep rise in plastics production, especially in Asia. Plastics global productions, mainly from fossil raw materials, have skyrocketed: from 1.5 million tons (Mt) in 1950 to 288 Mt in 2012 [1]. To this end, globalized trade in waste plastics needs to be focused on more vertical use than recycling.

In Bangladesh the plastic industry has begun with a small industry at 1960's. At present there are 3000 plastic manufacturing units, 98% of which belong to the Small-Medium Enterprises (SMEs) [2]. At present, total consumption of polymers including imported polymers and recycled plastic wastes is 750,000 tons in FY 2010- 2011 [2]. This corresponds to the per capita consumption of plastics in Bangladesh is 5 kg per year against the world average 30 Kg. Per capita consumption in India and ASEAN countries are 8kg and 17kg respectively. 20-25% of landfill weights are plastics [2]. Landfills are chosen to

dispose of Municipal Solid Waste (MSW) in the Bangladesh, with an overall increase in MSW consistent with increases in the population.

The mushrooming growth of MSW can be understood if we look at the projected quantity of 2025 that will be 50,000 Tons/day according to a survey [3]. The growth rate of waste generation is plotted below as per the survey.

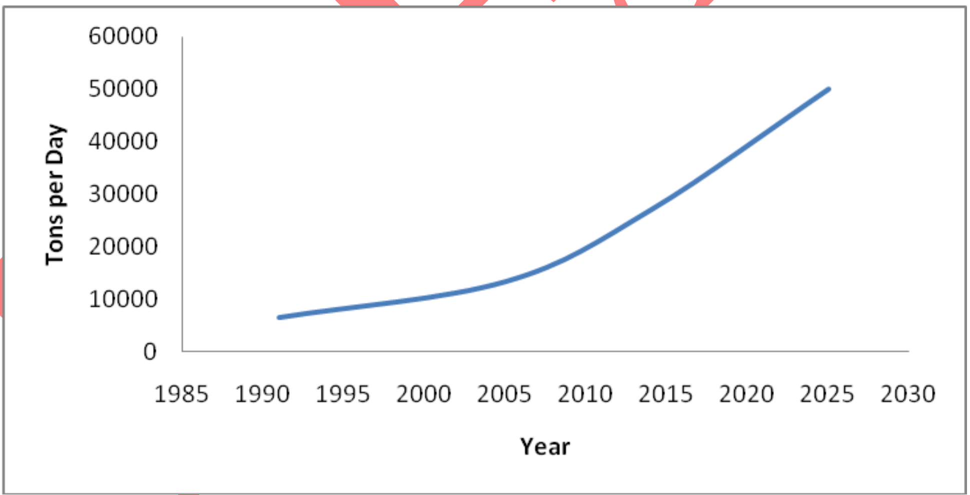

Figure 1: Growth rate of solid waste generation

Plastics made up only 1% of MSW in 1960. This has increased to 12% (30 million tons) in 2008. 43% of this is containers and packaging, 22% are nondurable goods, and 35% is from durable goods. This means that 11.3 million tons of just containers and packaging end up in landfills each year. Total Plastic Waste generation in Bangladesh found 3, 36,000 tons/year and around 17,000 tons/year is going to the landfill [3]. Most people agree that recycling is a preferred method of dealing with plastics. However, only 24% of municipal waste is recycled and 9% is composted, for a total of only 33% of waste that is being recovered [2].

The widespread use of plastic goods and materials lead to the uncontrolled generation of polymeric waste. Again, all plastics are not economically feasible to be recycled. In result, there are some selective polymers are thrown into the landfill. Poly-ethylene can be a good example here that cannot be recycled and used once only. Recycled polymers are also having some problem such as less stiffness, firmness and less durability than virgin polymer products. So it can be utilized by thermal cracking of polymers converting into liquid fuel [4]. Liquid fuel deriving process is based on pyrolysis. Sometimes incomplete combustion of waste plastics in existing recycling methods leads to generate toxic and greenhouse gases. So the fuel making process is eco friendly and profitable both [5]. Moreover the experiment does not allow the emission of carbon-monoxide and focuses on re-using the polymers rather than being recycled again.

METHODOLOGY

A. *Raw materials:*

Raw materials have been selected from waste plastic materials that are being thrown to landfill, namely low density polyethylene (LDPE), high density polyethylene (HDPE), polypropylene (PP), polystyrene (PS) and other thermoplastic polymers. Most prominently the waste plastics were merely used in purpose of recycling. These raw materials have been collected from the first hand buyers to apprehend the most intellectual way to converting the waste plastics into liquid fuel instead of recycling or making environmental pollution.

B. *Catalysts:*

Conversion of waste plastics into liquid fuel has been performed using different catalysts like, Al_2O_3 and ZnO. Each 200g raw polymer batch executed with different percent of single catalyst or both either.

C. *Reactor specification:*

Main reactor has been made by stainless steel having thickness 0.24-inch, 4.25-inch diameter and 9-inch height. The reactor has been totally sealed off by gasket and flange after being fed. Thermocouple used to sense the temperature. Among two 1000W coils, first one has been used in beneath of the reactor to power up the system and another is spiral over the bottom of the reactor supposed to heat uniformly to the charged feed. A discharge tube has been bent and spiraled with copper tube having thickness of 0.5-mm. It has been used to condense the fuel vapor by cooling water circulated by a centrifugal pump. The maximum capacity of the reactor is 3.5kg waste plastics at a time. The full reactor surrounded by concrete chamber having thickness 3.5-inch, length 15-inch, width 15-inch, height 16-inch for a purpose to impede heat loss and high safety region. Two discharge paths used for venting gases and collecting liquid. The long height of discharge tube is to assure high reflux ratio to get low viscous fuel.

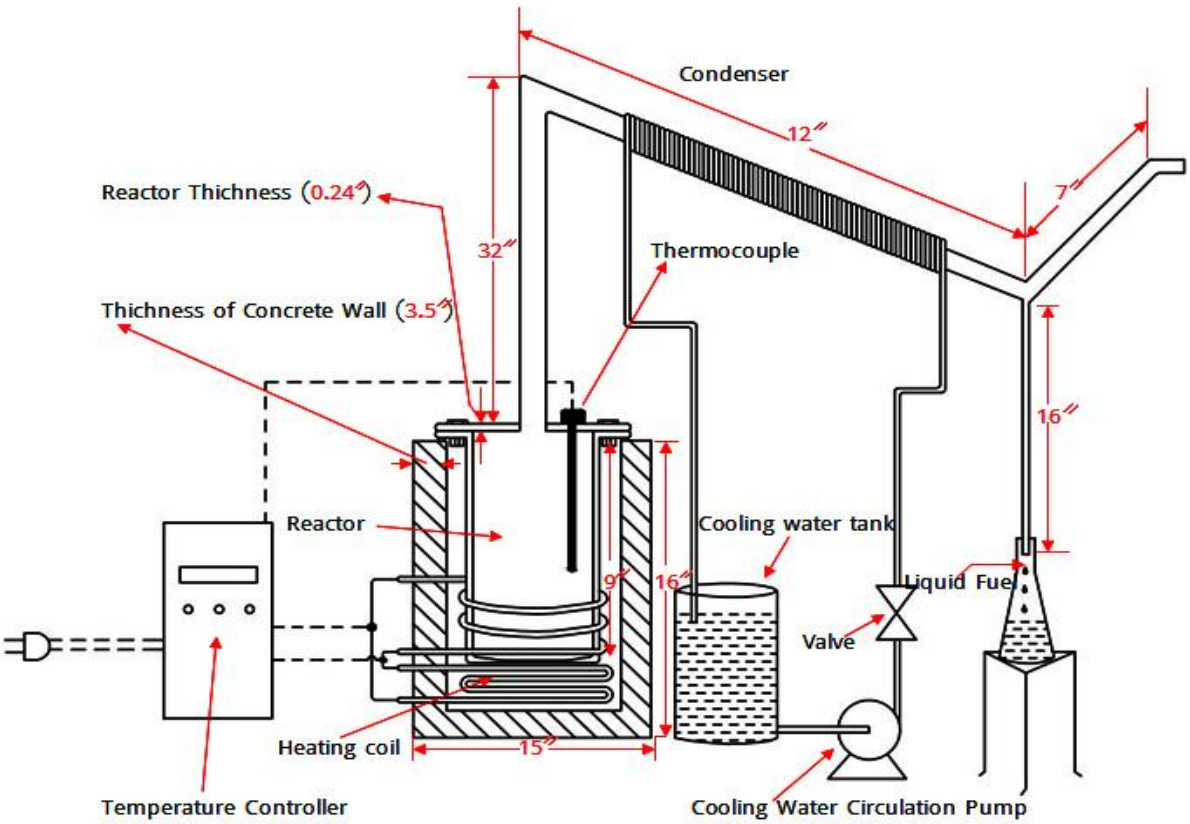

Figure 2: Schematic diagram of the waste plastic to fuel conversion system

D. *Process description:*

After collecting the waste plastics, those were washed to remove the impurities and then also dried to remove remaining water droplets. Finally, they were shredded and cut into pieces for ease of feeding the raw materials and for good heat transfer. 200gram of solid waste plastic was weighed and fed to the reactor and the reactor was properly sealed to protect the gas from leaking. Isolation system was checked carefully prior to start the experiment through bubble test. Then the heater was started and the reaction continued until the last drop of oil was being noticed in the measuring cylinder. The solid waste plastic was first melted and then cracked in the same reactor (converted to smaller units or gases) at different temperatures. Finally, the gas is allowed to pass through the metal tube. The gas from the tube is directly condensed by the continuous circulation of the cooling water pump.

Heat exchange between cooling water and hot stream was accelerated using icebergs and controlling the circulation flow rate. When the first distillate has been seen in the measuring cylinder, the temperature and time was noted down. The volume of fuel oil produced was monitored with time and temperature. The temperature was sensed by a thermocouple and the whole heating process was controlled and monitored by a temperature controller. Every experiment has been initiated with 200 gm raw materials and catalyst percentage was different. Each experiment temperature profile was same and temperature monitoring was same procedure. Temperature was controlled by temperature controller and temperature range was 300^0 -450^0 C. The 1st experiment was started with 200 gram of waste plastics and 3% of aluminum oxide (Al_2O_3). 2nd experiment was started with 200 gram of waste plastic and 4% of Aluminum Oxide (Al_2O_3). 3rd experiment is started with 200 gram of waste plastics mixture and 5% of Aluminum Oxide (Al_2O_3). All experimental initial raw materials were same and temperatures are same but catalyst percentage is different. The goal of this type of experiment was to determinate the conversion rate and compounds range. The mixture consisting of 5% aluminum oxide (Al_2O_3) and waste plastics found high conversion rate. The procedure is repeated for the Zinc Oxide (ZnO) catalyst also. Same procedure was followed for the mixture of Zinc Oxide (ZnO) and Aluminum Oxide (Al_2O_3) catalyst. The reaction/experiment duration is 50 to 60 minutes. Better result was observed in the mixture of Zinc Oxide (ZnO) and Aluminum Oxide (Al_2O_3) catalyst when the percentage was 5%. Beneath the minimum catalyst percentage production of fuel were significantly low and over the percentage proceeds gum formation and grease type semisolid products.

RESULTS AND DISCUSSIONS

Total reaction has been taken place into a stainless steel reactor. First droplet was found at 340^0C. After attaining the desired temperature, fuel was continuously being supplied by the reactor. The system took 15 minutes around to be heated at the desired temperature. Then the production of fuel started and gradually the rate of production was increased. The time vs. production curve are analyzed to find out the duration time of the reactor and shown at Fig 3:

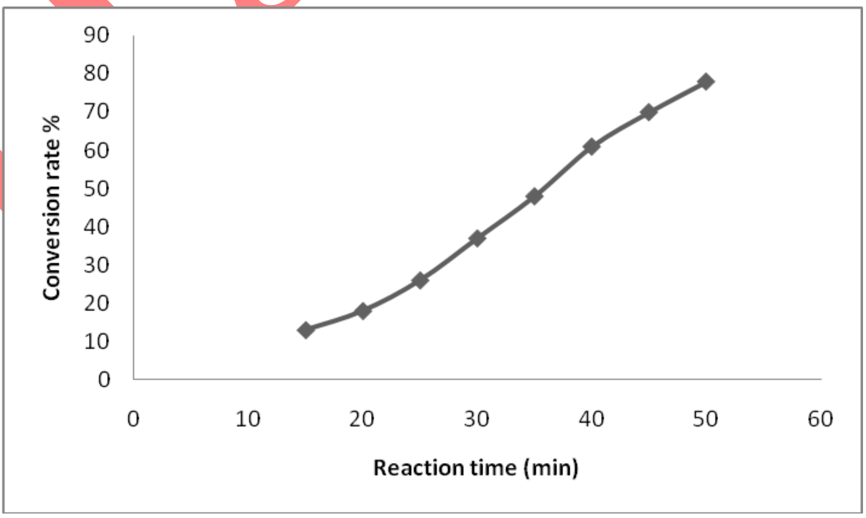

Figure 3: Reaction time vs. conversion plot.

The propagated liquid fuel from waste plastic was analyzed both physical properties and chemical compositions.

A. *Physical properties:*

A.1. ***Density:***

To compose the properties of fuel characteristics, it is exclusively important to study the density and density depended properties like API (American Petroleum Institute) gravity, UOP (Universal Oil Products) Characterization Factor **K**. The density of our fuel is 0.7897 Kg/L at 15^{0}C at (ASTM D 1298). Basically traditional range of density is 0.72–0.78 Kg/L for Gasoline and 0.8-0.89 Kg/L for Diesel for same ASTM standard [6].

API gravity magnifies the specific gravity of fractions. As specific gravity of close boiling cuts usually lies very close to each other, this type of magnification is essential.

$$Deg.\ API = \frac{141.5}{\rho} - 131.5$$

Where,
Deg. API = API gravity index; ρ = Specific gravity of fuel at 15^{0}C

This equation gives us the value of API index is 47.68 which tells us our waste polymer cracked fuel act like paraffin base petroleum. When residue containing more than 5% paraffin and API gravity is more than 40 then the petroleum is called paraffin based petroleum. PONA test at ASTM 1319 refers this fuel have Paraffin 37.5%; Olefin 2.5%; Naphthene 20%; Aromatic 40% whereas Gasoline have Paraffin 57.4%; Olefin 9.2%; Naphthene 21.3%; Aromatic 35% [7].

A.2. ***Pour point and Flash point:***

The pour point of a liquid is the temperature at which it becomes semi solid and loses its flow characteristics. In crude oil a high pour point is generally associated with high paraffin content, typically found in crude deriving from a larger proportion of plant material. At ASTM D97 standard the pour point is less than 3^{0}C which is feasible in Bangladesh perspective.

Flash point is defined as the minimum temperature at which the oil gives a momentary flash when the oil is heated in the standard flash cup as per the specifications and a standard flame is passed over the mouth of the cup. The flash point indicates the volatility of the oil and hence the possible fire hazard during its storage and handling. The Flash point of waste plastic fuel is 20^{0}C in ASTM D93, normally diesel need to be maximum value at 35^{0}C [8].

*A.3. **Indexes:***

Quality of diesel type fuel reclines on various numbers or indexes. Cetane number and diesel index are the most important parameters to signify the fuel properties. The knocking characteristics of a diesel fuel are expresses in terms of cetane number. Cetane $C_{16}H_{34}$ is a saturated hydrocarbon which has a very short ignition lag as compare to any commercial diesel fuel. Hence its number is takes as 100. On the contrary, α-methyl naphthalene $C_{11}H_{10}$ (an aromatic hydrocarbon) has a very long ignition lag as compared to any commercial diesel oil. Hence the cetane number is taken as zero. Then the cetane number of diesel oil is defined as the percentage by volume of cetane in a mixture of cetane and α-methyl naphthalene which exactly matched in its knocking characteristic with the oil under test [9]. At ASTM D 976 the cetane index is 65.5 in case of pure diesel for high speed diesel engine it should be minimum 45.

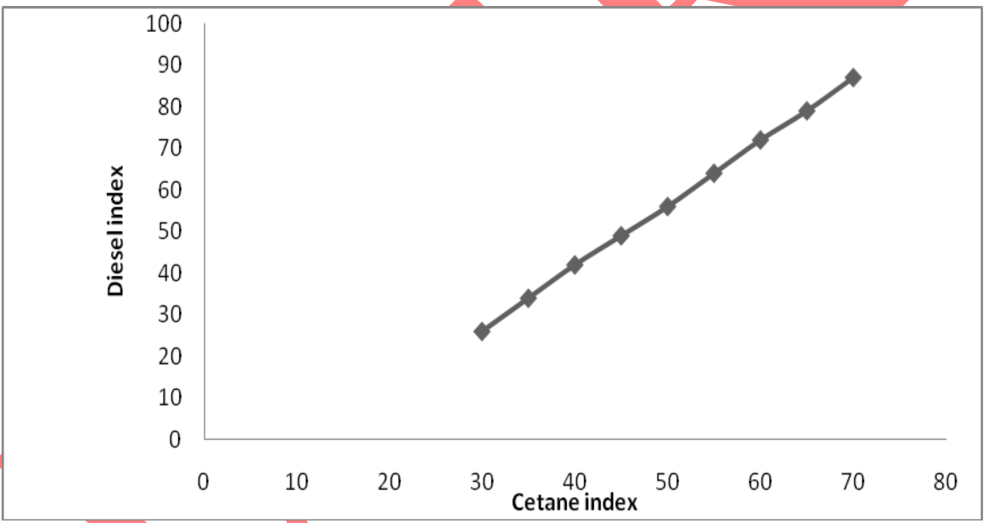

Figure 4: Diesel index vs. Cetane index curve

From the curve [7] at Fig: we have got our diesel index are about 80. This is a satisfactory value. Kinematic Viscosity is 2.6983 Centipoises at 60° F at ASTM D 445. For diesel the range of kinematic viscosity is 2.6-4.1 Centipoises. In case of gasoline the range is 0.37-0.44 Centipoises [10].

Octane rating of the fuel is also satisfactory. The research octane number (RON) is 85.9 at ASTM D 2699. It is a property of gasoline fuel. Unleaded fuels carry a RON (Research Octane Number) rating. Simply, RON determines petrol's 'anti-knock' quality or resistance to pre-ignition; or in another way, the Octane Number denotes its resistance to detonation.

*A.4. **Distillation properties:***

Distillation curves provide a breadth of information about the crude oil or the petroleum fuel. In certain respects, the boiling point distribution is representative of the composition of the petroleum fraction. Therefore, in principle, by determining the presence and volume percent of the components in a conventional hydrocarbon fuel solution, the overall physical properties can be determined. ASTM Distillation tests for gasoline, naphtha (A naphtha is a volatile petroleum fraction, usually boiling in the gasoline range), and kerosene (D86). The comparison of the distillation curve between waste plastic foil and Arabian light crude oil is described [11] at following Fig 5 & 6:

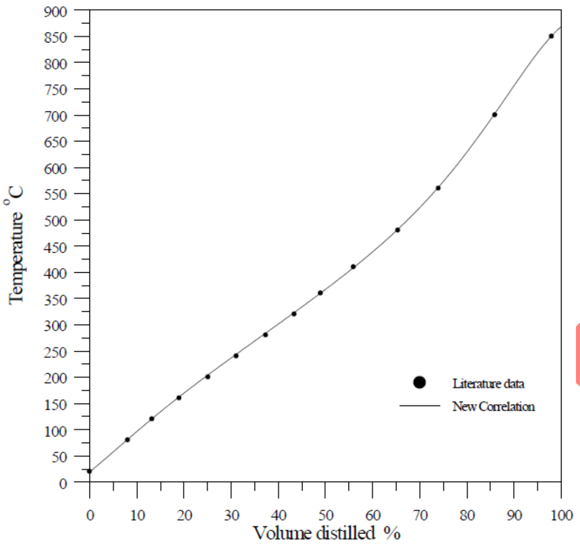

Figure 5: ASTM Distillation profile for Arabian light crude oil

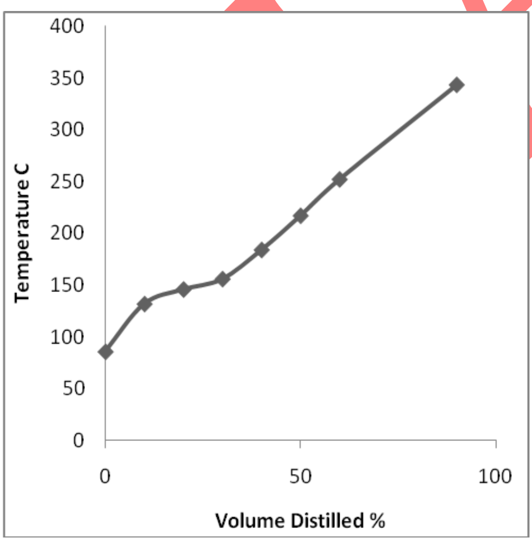

Figure 6: ASTM distillation profile for waste polymer liquid fuel

The data [7] of distillation curve was given bellow at table: which was carried out at ASTM D 86 at Table: 1.

Table 1: Volume distillation vs. Temperature

Volume distillation %	***Temperature ^0C***
0	86
10	132
20	146
30	156
40	184
50	217
60	252
90	343

*A.5. **Calorific Value:***

The GHV (Gross Heating Value) of our fuel is measured 10780.7309 Kcal/kg at ASTM D 3177-89; Colour grade 3 at ASTM D 1500; Total Acid No. 1.01 at ASTM D 664; Ash content 0.0029 at ASTM D 482; Copper Strip Corrosion No. 1 (3 hours at 100^0c) (ASTM D 130); Carbon residue on 10% bottom, 0.1%wt at ASTM D 189; Water content 1.36 %wt at ASTM D 95; Sediment 0.009 %wt (ASTM D 473); Residue On Evaporation 22.876 g/100 ml at ASTM D 381; Oxidation stability >300 minutes at ASTM D 525; Doctor Test negative result announces no sulfur content at ASTM D 4952. Those tests was performed in Petromax Refinery Ltd, Bangladesh.[12].

*B. **Chemical properties:***

Liquid fuel sample was collected in purpose of testing its quality as a fuel. Physical properties which were discussed before were done at ASTM standard. PETROMAX REFINARY LTD. Khulna, Bangladesh provided us all reports of physical properties [12]. Chemical composition is the most important property of fuel. Gas chromatography (GC) has been conducted in the Bangladesh Council of Scientific and Industrial Research (BCSIR), Dhaka, Bangladesh and hereby ensured about the fuel chemical composition[13]. GC chromatogram of the plastic fuel was described in Fig 8:

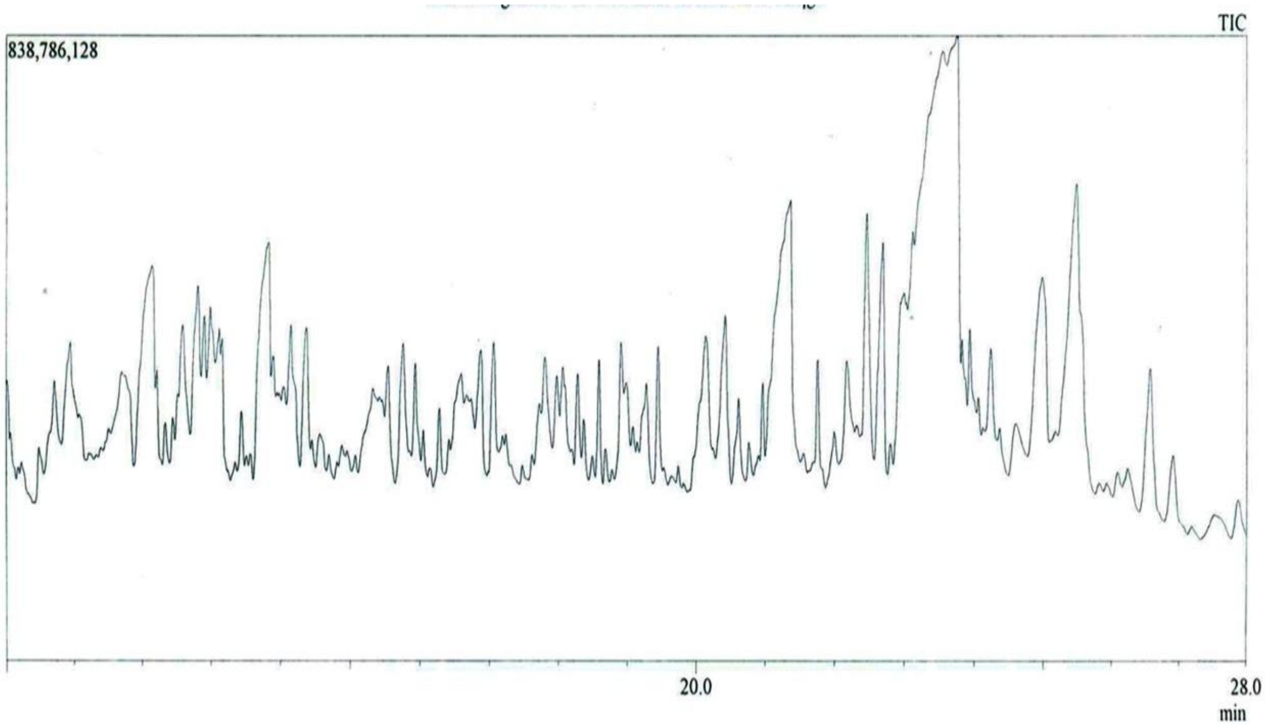

Figure 7: GC chromatogram of waste polymer to fuel by using stainless steel reactor

Chemical compositions are arranged in molecular weight order and mentioned in table-2.

Table 2: Chemical compositions obtained from Gas chromatography

ID#	*Trace mass M/Z*	*Compound Name*	*Compound Formula*	*Molecular Weight*
1	42	Propene	C_3H_6	42
2	55	Butane	C_4H_{10}	58
3	42	Cyclopropane	C_5H_{10}	70
4	72	2-Buten-1-ol	C_4H_8O	72
5	72	Pentane	C_5H_{12}	72
6	51	1-Hexene	C_6H_{12}	84
7	56	1-methyl-Cyclopentane,	C_6H_{12}	84
8	81	2,4-Dimethyl 1,4-pentadiene	C_7H_{12}	96
9	44	1-Heptene	C_7H_{14}	98
10	56	2-methyl-1-Hexene	C_7H_{14}	98
11	44	Heptane	C_7H_{16}	100
12	51	4-ethylene 3,8-Dioxabicyclo[5.1.0.0(2,4)octene	C_8H_{12}	108
13	58	1-Octene	C_8H_{16}	112
14	45	Octane	C_8H_{18}	114
15	30	Cycloheptyl cyanide	$C_8H_{13}N$	123
16	55	1-propenyl Cyclohexane	C_9H_{16}	124
17	30	3-nitroso 3-Azabicyclo[3.2.2]nonane	$C_8H_{15}N$	125

18	69	1,3,5-trimethyl-, (1α,3α,5β)-Cyclohexane	C_9H_{18}	126
19	73	2,4-Dimethyl-1-heptene	C_9H_{18}	126
20	15	Nonane	C_9H_{20}	128
21	81	trans-2,3-epoxyoctane	$C_8H_{16}O$	128
22	55	octahydro-,cis-5H-Inden-5-one	$C_9H_{14}O$	138
23	30	1,2-Epoxynonane	$C_9H_{18}O$	142
24	94	1-(1-cyclohexen-1-yl)Pyrrolidine	$C_{10}H_{17}N$	151
25	17	(1α,2β) Bicyclo[4.1.0]heptane-2-ol	$C_{10}H_{18}O$	154
26	72	hexahydro-3-methyl 2(3H)-Benzofuranone	$C_9H_{14}O_2$	154
27	15	8-Nonynoic acid	$C_9H_{14}O_2$	154
28	30	9,9-dimethyl 3,7-Diazabicyclo[3.3.1]nonane	$C_9H_{18}N_2$	154
29	96	trans-2,3-epoxydecane	$C_{10}H_{20}O$	156
30	43	1-(1,2,2,3-tetramethylcyclopentyl)-, (1R-cis)-Ethanone	$C_{11}H_{20}O$	168
31	71	2-methyl-1-Decanol	$C_{11}H_{24}O$	172
32	43	2,3,5,8-tetramethyl- Decane	$C_{14}H_{3}0$	187
33	55	1-Hexadecene	$C_{16}H_{32}$	224
34	55	2-methyl-7-Octadecyne	$C_{19}H_{36}$	264
35	57	Heneicosane	$C_{21}H_{44}$	296
36	91	[3-(2-cyclohexylethyl)-6-cyclopentylhexyl]-Benzene	$C_{25}H_{40}$	340

CONCLUSION

Waste polymer fuel has been analyzed by its physical properties and chemical compositions. Properties as a standard commercial fuel have been thoroughly discussed. Gaseous product into the discharge vent of the reactor and residuum can be a good potential source of heavy grease type paraffin. Along with the hydrocarbon liquid fuel in GC test, the gases and residuum can also be tested for further upgradation for fuel gas or lubricating agent. Both the product and byproduct of this process can be utilized and will be the more pragmatic use of waste plastics over recycling. Especially in refinery industries, the addition of such a cracking unit can be a potential source of fuel. Over 14 million tons of plastics are dumped into the oceans annually, killing about 1,000,000 species of oceanic life. Though mankind has awoken to this threat and responded to developments in creating degradable bio plastics, there is still no conclusive effort done to repair the damage already caused. In this regard, the study of catalytic thermal cracking presented here can be an efficient, clean and very effective means of removing the debris that we left behind over the last several decades.

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