

# Fuel Oil from Thermolysis of Waste Plastic: A pathway from Waste to Energy

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**Citation:** Somendra Nath Roy, Ananya Pal, Purbasha Saha, Snita Das, Soham Dutta (2022) Fuel Oil from Thermolysis of Waste Plastic: A pathway from Waste to Energy. J Waste Manag Disposal 5: 103

## Abstract

Plastic is an example of a widely used product that is sometimes referred to as one of the millennium's biggest innovations. The day will arrive when the world will be entirely covered in plastics and humanity will live on top of it. Researchers are increasingly resorting to alternative disposal techniques for mounting plastic output. Therefore, reduction of solid waste generated is the need of the present world.

The present work attempts to formulate a commercial petro-diesel like fuel from the waste plastic (LDPE), which is derived from unusable plastic waste materials by the thermolytic reaction [here the product named as waste plastic thermolysis oil (WPTO)]. A thermolysis reactor is fabricated to transform the solid waste into the fuel oil through thermal cracking. Thermal cracking is a high energy endothermic process which requires temperature between the ranges of 350-5000C. The cracking of these polymeric materials was done by heating them to a temperature between 400-4500C by breaking the long polymeric chain into short polymeric chain. A portion of the volatile fraction has been condensed and fuel was obtained, while the remaining is a non-condensable high calorific value gas. The fuel produced has density of about 836 kg/m<sup>3</sup>. GC-MS analysis of the sample has indicated that it is comprising mostly of Bicyclo [2.2.0] hexane-1-carboxaldehyde, 1-Nonene, 1-Decene, 2-Hexene, and Benzene as major components. The other minor components are also present. Physico-chemical properties of WPTO have a higher Cetane index as compared to commercial diesel which makes the product favourable as a substitute fuel.

**Keywords:** Thermolysis; Reactor; GC-MS; Waste plastic; LDPE; Cetane Index

## Introduction

Before examining the various process options for conversion of plastic into oil products, it is important to take the characteristics of these materials into account to identify where similarities exist, and the basic conversion process. The principal similarities are that they are made up of molecules in chains of carbon atoms and are mostly made up of carbon and hydrogen.

Crude oil is a complex combination of hydrocarbons that is separated and purified at an oil refinery by distillation and other procedures. The majority of crude oil is used to make transportation, heating, and power production fuels. These oil products are not single components, but rather a blend of components used to meet the required fuel criteria in the most cost-effective manner possible, given the crude oil composition and refinery setup. These components have a wide range of chain lengths, i.e. gasoline has compounds with a chain length between 3 and 10 carbon atoms, whereas diesel has compounds with a chain length between 5 and 18 carbon atoms, but both contain only hydrogen and carbon.

Due to the extreme fossil fuel crisis, humanity must concentrate on creating alternative energy sources such as biomass, hydropower, geothermal energy, wind energy, solar energy, and nuclear energy. The development of alternative fuel oil technologies has been studied in order to provide a fossil fuel replacement. Bio-ethanol, bio-diesel, lipid derived bio-fuel, waste oil recycling, pyrolysis/thermolysis, gasification, dimethyl ether, and biogas are among the technologies being studied. On the other hand, given the global waste problem, an appropriate waste management strategy is a vital part of sustainable development.

The waste to energy technology is investigated to process the potential materials in waste which are plastic, biomass, and rubber tire to be oil. Pyrolysis process becomes an option for the conversion of waste-to-energy technology to deliver bio-fuel to replace fossil fuel. The increase of petroleum and petrochemical prices opened the ways for industries to invest in decomposition of plastic wastes to petrochemicals [1, 2].

A report from United Nations Environmental Programme on “Compendium of Technologies for converting waste plastics into a resource” stated that the conversion of plastics to liquid fuel is based on the pyrolysis of the plastics and the condensation of the resulting hydrocarbons [3]. They referred pyrolysis which acts as thermal decomposition of the matter under an inert gas like nitrogen. For the liquid fuel production, the conversion of suitable plastics were introduced into a reactor where materials will decompose at 450 to 5500 C. Depending on the pyrolytic conditions and the type of plastic used, carbonaceous matter gradually developed as a deposit on the inner surface of the reactor. After pyrolysis, this deposit should be removed from the reactor in order to maintain the heat conduction efficiency of the reactor. The resulting oil (mixture of liquid hydrocarbon components) was continuously distilled once the waste plastics inside the reactor have been decomposed enough to evaporate upon reaching the reaction temperature. The evaporated oil was further cracked with a catalyst. The boiling point of the produced oil was controlled by the operation conditions of the reactor, the cracker and temperature of the condenser. After the resulting hydrocarbons have been distilled from the reactor, some hydrocarbons with high boiling points such as diesel, kerosene and gasoline have been condensed in a water-cooled condenser. The liquid hydrocarbons were then collected in a storage tank through a receiver tank. Gaseous hydrocarbons such as methane, ethane, propylene and butanes cannot be condensed and were therefore incinerated in a flare stack. This flare stack is supposed to require when the volume of the exhaust gas emitted from the reactor is being expected to be large. Few researchers [4, 5] were investigated in their investigation to make fuel oil through pyrolysis using waste plastic and waste tire as they are the available technology. The pyrolysis process has the advantage of being able to handle unsorted and filthy plastic. These materials are simple to pre-treat. They employ shredded tires, whereas plastic has to be sorted and dried before pyrolysis, presuming that, unlike incineration, this process produces no hazardous or environmentally detrimental emissions.

The pyrolysis of real waste plastics (high-density polyethylene and polypropylene) in a pilot scale horizontal tube reactor at 520°C temperature was investigated in the presence and absence of ZSM-5 catalyst [6]. It was found that the yields of gases, gasoline and light oil could be increased in the presence of catalyst. They also discovered that, depending on the parameters utilized, plastic wastes might be turned into gasoline and light oil with yields of 20–48 % and 17–36 % respectively.

It is evident from the work [7] that the process of converting waste plastic to reusable oil is a current research topic. The preparation of diesel blends with varied quantities of waste plastic oil produced by thermal pyrolysis, as well as the examination of their viscosity and density, were reported. The practicality of waste plastic oils generated from PVC plastics as an alternative transportation fuel is also tested using a single cylinder kirloskar diesel engine with electrical loading at 50% of the engine maximum load, i.e. at 3.7 kW. It has been observed that useful alternative fuel products were introduced [8] from waste plastic (denoted as WPPO) using in a self-designed stainless steel laboratory reactor through completely pyrolyzed at 330–490°C for 2-3 hours to obtain solid residue, liquid fuel oil, and flammable gaseous hydrocarbon products and characterized in detailed and compared with conventional diesel. Their fuel properties included a kinematic viscosity (400C) of 1.98 cSt, density of 0.75 gm/cc, sulphur content of 0.25 (wt%), and carbon residue of 0.5 (wt%), and high calorific value represented significant enhancements over those of conventional petroleum diesel fuel.

The objective of the present work is to synthesize fuel oil by the process thermolysis using waste plastic of LDPE. Physico-chemical properties of WPTO are comparable with the commercial diesel by having a higher Cetane index which makes the product favourable as a substitute fuel. Qualitative analysis utilizing Gas Chromatography and Mass Spectrometer (GC-MS) has been done for the produced fuel.

## Materials and Methods

### a. Materials

The plastic used in this study was waste plastic bags of low-density polyurethane (LDPE) collected from the local municipality vat. Waste plastics were cleaned with detergent and water to remove contained foreign materials such as mud and oil followed by proper drying. These dried waste plastics were shredded into small pieces in the range of 5 to 10 mm by using shredder as shown in figure 1.



Figure 1: Shredded Clean Waste LDPE Plastic

### b. Devices Used

#### (i) Condenser

It cools the entire heated vapour coming out of the reactor. It is made up of stainless steel with special design (patent pending). It has an inlet and an outlet for cold water to run through its outer area. This is used for cooling of the vapour (figure 2). The gaseous hydrocarbons at a temperature of about 400-450°C are condensed to about 15 – 20°C.

## (ii) Reactor

It is a stainless steel (SS316S) cylindrical body of 5 litre volume capacities whose bottom portions is flat of length 300 mm, internal diameter 140 mm, outer diameter 200mm. A conical convergent lid (SS316S) attached with an exhaust chute acts as a cover which directs the pyro gas through a SS316S pipe connected with the condensation chamber. The reactor is placed under the variac controlled electric heater for external heating with the placed feed stock inside. The reactor is heated to a temperature of about 400-450°C. The thermolysis reaction takes place between 275°C and 450°C for used waste plastic. The experimental set up of the thermolysis reactor is shown in figure 2.

### Photo of Experimental SetUp

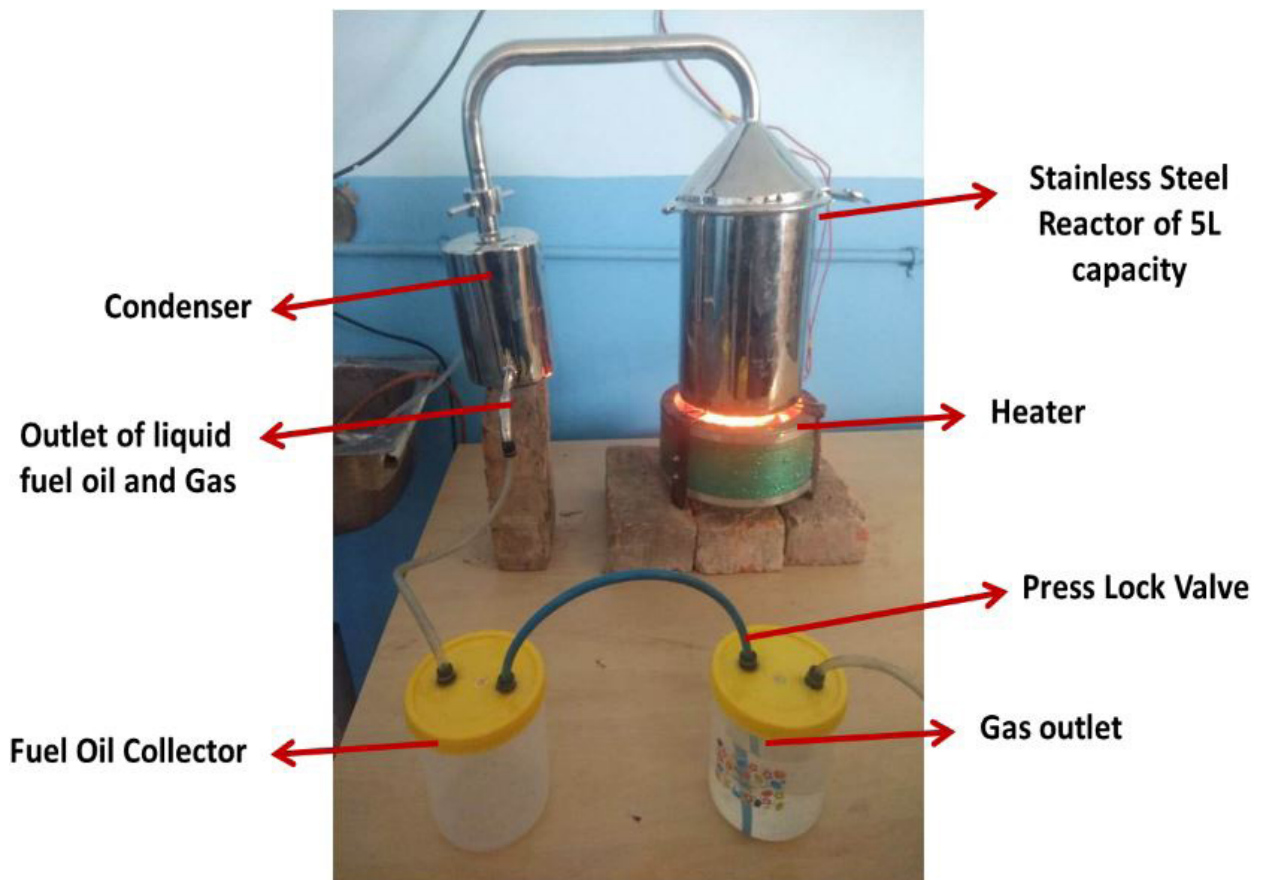


Figure 2: Experimental Set-up for Thermolysis

## (iii) Fuel Oil Characterization

The characterization of the oil which is obtained as a fuel and has been analysed using Gas Chromatograph (Model: G3440B-7890B) and Mass Spectrometer (Model: G7077B- A) of M/s Agilent, USA employed with a higher resolution. Calorific value of the liquid oil was determined using Bomb Calorimeter (Model: KAC2000). Specific gravity, Baume and API gravity were determined using a density meter (Model: DOM2911- Rodolph Research Analytical).

## Results and Discussion

### Product recovery from LDPE thermolysis (WPTO)

The production of the liquid oil, residue (char) and the gaseous products recovery from the thermolysis of 4.5 kg of LDPE at a temperature of 400-450 °C for 1 hr is as shown in figure 2. The probability of yielding gases like hydrogen, methane, etc. may be present. Liquid content obtained in the form of fuel oil and the above-mentioned gases may also be present. Graphene may be present within the solid residual.

This result may be because LDPE has more branching that result in weaker intermolecular force, thus lower tensile strength and hardness and causes the structure to be less crystalline and easy to be thermal break-up to oil products. This result agrees with the previous results [9, 10] using batch reactor at 430 °C. It has been observed that the colour of the fuel oil (figure 3) is dependent on the temperature of water (15 - 20 °C) which was circulated within the condenser.



**Figure 3:** Fuel from Waste LDPE Plastic by Thermolysis Process

### Physico-chemical properties

Table 1 compares the physio-chemical properties of waste plastic thermolysis oil (WPTO) with commercial diesel. It observes that the gross calorific value of commercial diesel is higher than WPTO. The kinematic viscosity at 40 °C of WPTO lies close to commercial diesel. The flash and fire points of WPTO is lower than the commercial diesel. It can be noticed that the density at 15 °C for WPTO is 836 kg/m<sup>3</sup> which is very close to commercial diesel. Sulphur content of WPTO has been obtained 0.038% which is less than the value of commercial diesel (0.047%). It can also be seen that the ash content in WPTO is also very less and it correlates with the findings [11].

Properties	Units	WPTO (waste plastic thermolysis oil)	Commercial Diesel	Testing Methods	Remarks
Gross Calorific Value	MJ/kg	39.45	44.2	IS:1448 P:6	Using Bomb Calorimeter
Kinematic Viscosity,@40°C	cSt	2.1	1.9	IS:1448 P:25	Measuring the time in seconds for a fixed volume of this fuel to flow a known distance by gravity through a capillary within a calibrated viscometer at a closely controlled temperature.
Flash point	°C	41	52	IS:1448 P:20	Determine with semi-automated Cleveland Flash Point and Fire Point Tester.
Fire point	°C	48	57	IS:1448 P:20	Determine with semi-automated Cleveland Flash Point and Fire Point Tester.
Density@15°C	kg/m <sup>3</sup>	836	832	IS:1448 P:16	Determine using a density meter
Ash content	%	0.002	0.01	IS:1448 P:126	Amount of inorganic non-combustible material after combustion of the oil in air at specific high temperature
Sulphur content	%	0.038	0.047	IS:1448 P:33	Energy-Dispersive X-Ray Fluorescence Spectroscopy
Cetane index	---	58	46.4	IS:1448 P:126	Calculated based on the fuel's density and distillation range

**Table 1:** Comparison the Physio-chemical properties of commercial diesel and waste plastic thermolysis oil (WPTO)

### Burning of WPTO

One drop of WPTO is placed on a glass petri dish. It burns immediately when lighted which is shown in figure 4. The efficiency of burning test has carried out to show as an example that the sample is highly inflammable.



**Figure 4:** Burning Flame of WPTO on a petri dish



## Gas chromatography mass spectrometry analysis

The qualitative analysis has been used to categorize the different components present in WPTO. With a run time of 3.30 minutes (excluding cooled down time), 1  $\mu$ L of WPTO is inoculated into the spectrometer carefully. The oven temperature of GC was maintained at 2000C. GC/MS fragmentation pattern and mass spectrum (figure 5) revealed the presence of 15 different components in WPTO across the diversified acquisition period between 1.70 min to 3.30 min. It has been noticed that the major components of WPTO are found to be Bicyclo [2.2.0] hexane-1-carboxaldehyde, 1-Nonene, 1-Decene, 2-Hexene, and Benzene. The other minor components present in the sample are 2-Octyn-1-ol, 3-propyl-, (2Z)- 2,4-Pentadien-1-ol, 9-Hexadecyn-1-ol, (E,Z)-3,6-Nonadien-1-ol, 2-methyl 1- Pentene, 2-Pentene, 2-Butene, Cyclopropylcyclohexane, 3-oxiranyl-7-Oxabicyclo [4,1,0] heptane, 1-ethyl-3-methyl-Benzene also found which are given in Table 2. In general, the GC/MS analysis exposed the presence of aromatic and aliphatic compounds in WPTO which must be identify in the further investigation.

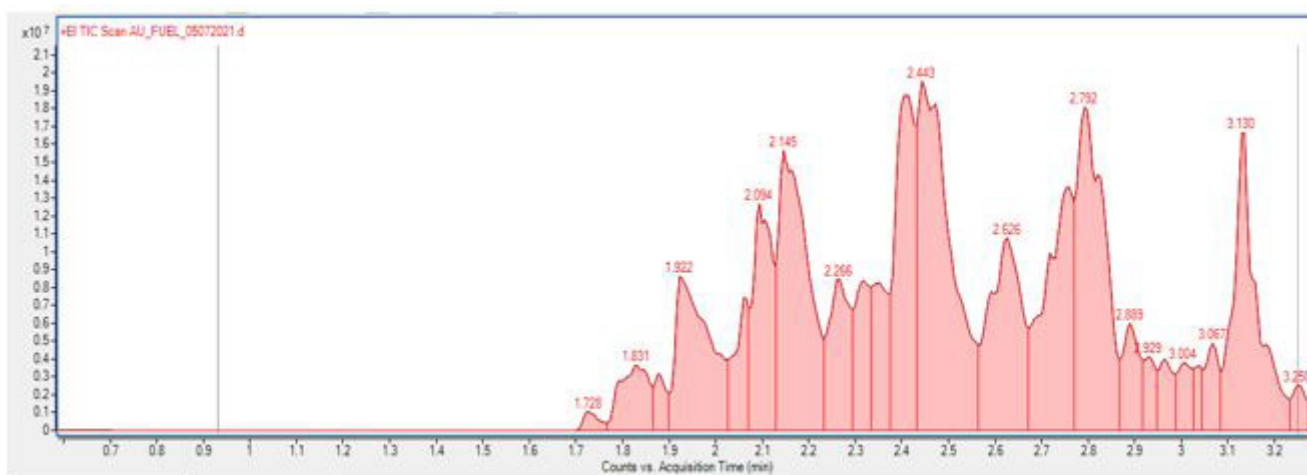


Figure 5: GC-MS Spectrum of Waste plastic thermolysis oil (WPTO)

Position	Retention Time (min)	Composition	Probable %
POS_1	1.728	2-Butene (C <sub>4</sub> H <sub>8</sub> )	49.1
POS_2	1.825	2-Pentene (C <sub>5</sub> H <sub>10</sub> )	19.5
POS_3	1.928	1-Pentene (C <sub>6</sub> H <sub>12</sub> )	19.7
POS_4	2.094	Benzene (C <sub>6</sub> H <sub>6</sub> )	70.1
POS_5	2.151	2-Hexene, 5-methyl- (C <sub>7</sub> H <sub>14</sub> )	14.2
POS_6	2.266	Cyclohexane (C <sub>9</sub> H <sub>16</sub> )	11
POS_7	2.432	Bicyclohexane-1-carboxaldehyde (C <sub>7</sub> H <sub>10</sub> O)	29.2
POS_8	2.626	2-Octyn-1-ol (C <sub>8</sub> H <sub>14</sub> O)	14.2
POS_9	2.792	1-Nonene (C <sub>9</sub> H <sub>18</sub> )	13.7
POS_10	2.889	2,4-Pentadien-1-ol (C <sub>8</sub> H <sub>14</sub> O)	18.7
POS_11	2.935	9-Hexadecyn-1-ol (C <sub>16</sub> H <sub>30</sub> O)	7.53
POS_12	3.009	3,6-Nonadien-1-ol (C <sub>9</sub> H <sub>16</sub> O)	11
POS_13	3.067	Benzene, 1-ethyl-3-methyl- (C <sub>9</sub> H <sub>12</sub> )	12.3
POS_14	3.13	1-Decene (C <sub>10</sub> H <sub>20</sub> )	14.1
POS_15	3.25	7-Oxabicycloheptane (C <sub>8</sub> H <sub>12</sub> O <sub>2</sub> )	6.47

Table 2: GC-MS qualitative analysis of waste plastic thermolysis oil (WPTO)

## Conclusions

- Based on the study conducted, the following is concluded:
- The thermal decomposition (Thermolysis) of waste plastic leads to the production of fuel oil which is a valuable resource recovery. It also reduces the problem of disposal of waste plastic.
- This study presents an efficient, clean, and highly effective means of recycling the waste LDPE.
- The thermolysis products consist of a mixture of gas, liquid, and solid fractions.
- Proper control of the condensing temperature is needed.
- GC-MS qualitative analysis of WPTO revealed the major components are bicyclo [2.2.0]hexane-1-carboxaldehyde, 1-Nonene, 1-Decene, 2-Hexene, and Benzene. Other minor components are also present within the sample.
- Physico-chemical properties of WPTO are comparable with the commercial diesel by having a higher Cetane index which makes the product favourable as a substitute of fuel.
- FTIR and Thermal analysis of fuel oil obtained from these experiments will be considered as the future scope of this work.
- Further study is required for proper understanding about this product.

## Recommendations

- Avoidance of incineration and land filling will enhance CO<sub>2</sub> emission reduction and have a positive environmental impact.
- The alternative disposal technology is becoming economically and financially beneficial.
- Physico-chemical properties of WPTO have shown higher Cetane index as compared to commercial diesel which makes the product favourable as a substitute fuel.
- Fuel obtained can be utilized for heating transportation and power generation purposes.
- This concept of waste management will open new windows in the field of research for sustainable environment development.

## Acknowledgement

The team would like to acknowledge the Management of the Adamas University to carry out the research. The authors are special thankful to CSIR-CGCRI, Kolkata for the support in fuel testing specially to Dr. Susmita Kundu, Sagnik Das & Raju Manna of FMD Division. Our appreciation also goes to Mrs. Indrani Sarkar, wife of corresponding author, who encouraged us all the time.



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