Prospects of pyrolysis oil from plastic waste as fuel for diesel engines: A review

V L Mangesh¹, S Padmanabhan², S Ganesan, D PrabhudevRahul³ and T Dinesh Kumar Reddy³

¹Research Scholar, Faculty of Mechanical Engg, Sathyabama University, Chennai-600119, India.
²Associate Professor, Faculty of Mechanical Engg, Sathyabama University, Chennai-600119, India.
³UG Student, Faculty of Mechanical Engg, Sathyabama University, Chennai-600119, India.
vlmangesh@gmail.com, padmanabhan.ks@gmail.com

Abstract. The purpose of this study is to review the existing literature about chemical recycling of plastic waste and its potential as fuel for diesel engines. This is a review covering on the field of converting waste plastics into liquid hydrocarbon fuels for diesel engines. Disposal and recycling of waste plastics have become an incremental problem and environmental threat with increasing demand for plastics. One of the effective measures is by converting waste plastic into combustible hydrocarbon liquid as an alternative fuel for running diesel engines. Continued research efforts have been taken by researchers to convert waste plastic into combustible pyrolysis oil as alternate fuel for diesel engines. An existing literature focuses on the study of chemical structure of the waste plastic pyrolysis compared with diesel oil. Converting waste plastics into fuel oil by different catalysts in catalytic pyrolysis process also reviewed in this paper. The methodology with subsequent hydro treating and hydrocracking of waste plastic pyrolysis oil can reduce unsaturated hydrocarbon bonds which would improve the combustion performance in diesel engines as an alternate fuel.

Keywords: Waste Plastics, Pyrolysis oil, Catalysts, Hydro treating and Hydro cracking.

1. Introduction

The usage of plastic has exploded worldwide leading to increase in researches to search for an alternate application of used plastics. Plastics are non-biodegradable polymers mostly containing carbon, hydrogen, and few other elements. Due to its non-biodegradable nature, the plastic waste contributes significant problem for waste management. Waste plastics like polyethylene used for domestic and
industry purpose are not recycled for about 43% of its volume. Most of the plastics are recycled and sometimes they are not done so due to lack of sufficient market value and energy consumption. Ever increasing diesel consumption, large outflow of foreign exchange and concern for environment have prompted developing countries like India to search for a suitable environmental friendly alternative to diesel fuel. The countries have to simultaneously address the issues of energy insecurity, increasing oil prices and large-scale of unemployment. This paper deals with an objective to convert plastic waste in to liquid hydrocarbon fuel. The different processes of conversion has been studied and compared. The performance of catalytic pyrolysis waste plastic oil as fuel in diesel engines have been reviewed and compared with thermal pyrolysis fuel. This existing literature is on hydro treating and hydro cracking of waste plastic material for converting in to fuel for diesel engine. The various studies and tests are made to understand the chemical composition of processed pyrolysis fuel from the existing literature work in which, the Bromine test was more advantageous to indicate the unsaturated bonds in the oil. The usefulness of Bromine test as an indicator of unsaturated bonds in the oil has been highlighted.

2. Conversion of Waste Plastic into Fuel Oil.
Chemical recycling is a series of processes in which polymers are broken down by heat and/or chemical agents which produces a large variety of products depending on the process employed. Thermal and catalytic pyrolysis processes are the two processes which are economically used to chemically convert waste plastics into fuel oil. They generate at moderate temperatures a wide variety of products (solid, liquid and gaseous fractions) with a broad range of potential applications.

2.1 Thermal Pyrolysis
It is the process of heating of plastic material in an inert atmosphere, a process that decomposes the organic part of the plastic polymer material and generates liquids and gases that are used as fuels and/or raw materials. This method is suitable for complex polymer waste that contains a number of highly mixed materials and prior separation step is not needed. Thermal pyrolysis is done at temperatures ranging between 400 to 800deg C. J.Walendiewski et al., 2001 shows that fuel oil yield is highest at reaction temperatures between 400 to 450degC.

2.2 Catalytic Pyrolysis
It is the process of heating of the material in an inert atmosphere in the presence of catalysts, a process that decomposes organic part of the plastic polymer material and generates liquids and gases that are used as fuels and/or raw materials. This method is done at temperatures ranging between 350 to 550 °C. AguadoJ et al., 2008 states that the catalytic pyrolysis has following advantages over thermal pyrolysis, (a) Reduction of time and temperature of the reaction, with the consequent decrease in energy consumption, (b) Better selectivity to desired compounds depending on the characteristics of the catalyst, (c) Avoiding the formation of undesired compounds, for example, inhibiting the formation of halogenated compounds from samples containing PVC. J. Walendziewskiet al., 2001 had stated the disadvantages of using catalysts as follows (a) cost of the catalysts (b) recoverability of the catalysts (c) reusability of the catalysts.

2.3 Catalytic Hydrogenation Pyrolysis
J.Walendziewskiet al., 2001 has conducted experiments using hydrogen atmosphere along with catalytic conversion to increase saturated compounds in resulting fuel oil.

3. Performance of Thermal Pyrolysis Oil as Fuel in Diesel Engines.
M.Mani et al., 2009 had tried on waste plastic pyrolysis oil obtained from thermal pyrolysis as fuel in diesel engines. The following observation had been given, (a) Ignition delay higher (b) higher heat release rate (c) NOx higher by 25% at peak loads (d) Higher unburnt hydrocarbon and increased smoke levels. OsamiNishsida et al., 2001 had tried waste plastic pyrolysis oil obtained from thermal pyrolysis
as fuel in marine diesel engines. Delayed ignition, Increased exhaust temperature and there by a 19% increase in NOx were observed. Since waste plastic oil has almost nil sulphur, SOₓ production been almost zero compared to Heavy Fuel Oil used in marine engines. M. Ozcanli et al., 2013 carried thermal pyrolysis of waste plastics and subsequently distillate those to observe better performance as fuel. It is found that increase in NOx, even in light phase oil. Viswanath K. Kaimalet al., 2015 made an experiment on waste plastic pyrolysis oil and used silica as catalyst in the production of waste plastic oil. Waste plastic pyrolysis oil was blended with diesel and used as fuel in diesel engine. The Cylinder peak pressure was found higher along with increased heat release rate. The ignition delay was found increasing with higher blending ratios.

4. Performance of Catalytic Pyrolysis Oil as Fuel in Diesel Engines.
Sachin Kumar et al., 2011 had attempted using waste HDPE plastic pyrolysis oil obtained from catalytic pyrolysis as fuel, blended with diesel in diesel engines. Treated Kaolin has been used as catalyst in the experiment. The following observation has been given, (a) NOx is higher by 30% when compared to diesel fuel at peak loads. (b) Unburnt hydrocarbons and smoke were observed at higher levels. Preetham Reddy Churkuntiet al., 2016 used commercially derived fuel (CynDiesel™) made from a blend of waste plastics through catalytic pyrolysis was tested as a blend with Ultra Low Sulphur Diesel. Increased PM emissions and decreased NOx emissions were observed. Better results were attributed to increased saturated bonds in CynDiesel™.

5. Evolution and Developments in Catalytic Pyrolysis Process of Waste Plastics and Conversion to Liquid Fuels.
The thermal degradation process of waste plastics is further enhanced by using suitable catalysts for obtaining commercially valuable products. Common catalysts used in this process are Zeolite, alumina, silica, FCC Catalyst, reforming catalyst etc. Ahmad RahmanSongip and Kenji Hashimoto et al., 1993 conducted catalytic cracking using several solid acid catalysts such as HY, REY, HZSM-5 zeolites and silica-alumina (SA). REY Zeolite was found to be the most suitable catalyst for the reaction having the highest research octane number (RON) of 67 and a highest gasoline yield of 48wt %. A. Marcilla et al., 2008 conducted catalytic pyrolysis of LDPE and HDPE plastic waste with HZSM-5 catalyst in a batch reactor and observed that the yield and composition of the products depends on the type of polyethylene used. HDPE gave higher N-paraffin’s and iso-paraffin’s whereas LDPE gave higher olefins at lower temperatures. Guohua et al., 2000 conducted catalytic cracking of HDPE and PP with Silica/Alumina catalysts in a powder particle fluidized bed. Over 86 wt. % conversion of liquid fuel was obtained. Kyong-Hwan et al., 2003 conducted catalytic cracking of HDPE, LDPE and PP using spent Fluidic catalytic cracking (FCC). It was observed that a yield of 89% yield was obtained and LDPE and PP degraded faster than HDPE. Achyut K. Pandaet al., 2013 conducted catalytic pyrolysis using kaoline and silica alumina as catalysts. Yield up to 91% was obtained and silica alumina was found better as compared to kaolin in liquid yield. Nnamso S. Akpanudoh et al., 2005 conducted catalytic conversion of plastic waste using Y zeolite. The effect of plastic polymer to catalyst ratio-mentioned as the acidity content of the polymer/catalyst system – was studied on the creation of liquid hydrocarbons. J. Shahet al., 2005 used Lead sulphide as a catalyst for pyrolysis. The author observed more than 70% yield of gas and liquid fraction with boiling point up to 350 °C.
6. Hydro Treating and Hydro Cracking of Waste Plastic into Liquid Fuels.
H.S.Joo et al., 1998 carried out on liquid plastic pyrolysis oil the sequential process of hydro treating, hydrocracking and distillation. The gasoline range product produced from upgrading the residual plastics pyrolysis liquid was characterized by higher paraffin’s, lower aromatics, olefins and nitrogen. J. Walendziewskiet al., 2001 carried out thermal pyrolysis using catalyst and hydrogen inside closed autoclaves. The liquids obtained in the presence of hydrocracking catalyst are characterised by lower unsaturated hydrocarbons in comparison to liquid fractions obtained using cracking catalyst of thermal cracking.

7. Chemical Composition Tests for Pyrolysis Oil

7.1 FTIR
Sachin Kumar et al., 2011 states that Fourier Transform Infrared Spectroscopy (FTIR) is an important analysis technique that detects various characteristic functional groups present in oil. Upon interaction of infrared light with oil, chemical bonds can absorb infrared radiation in specific wavelength ranges regardless of the structure of the rest of the molecules.

7.2 GC-MS
Gas chromatography–mass spectrometry is a testing method which includes the features of gas-chromatography and mass spectrometry to identify different substances within a test sample.

7.3 Bromine Test
Olefins are unsaturated hydrocarbon bonds and they are of very low presence in diesel. But Olefins are formed during the catalytic and thermal cracking. The presence of excess olefins causes the delayed ignition delay and higher heat release in diesel engines. Hydrocracking can substantially reduce the unsaturated bonds present in waste plastic pyrolysis oil. J.Walendziewski et al., 2004 stated that the presence of higher olefins is the reason for polymerisation and oxidation resulting in production of gums and deposits. Light gas oil obtained by pyrolysis had a bromine number of 88.48 g Br/100g and subsequently reduced to 0.54 g Br/100g by hydrogenation. Bhaskar.M et al., 2001 had observed bromine number for diesel is 4.5 shown in table.1

| Hydrocarbons               | Purity % | Bromine Number |
|---------------------------|----------|----------------|
| Paraffins                 | >99      | 0-0.1          |
| Straight chain Olefins    | >99      | 63-235         |
| Branched Chain Olefins    | >99      | 58-235         |
| Cyclic Olefins            | >99      | 134-237        |
| Diolefins                 | >99      | 185-352        |
| Monocyclic Aromatics      | >99      | 0-0.7          |
| Polycyclic Aromatics      | >99      | 0-12           |

Table 1: Bromine Number of Hydrocarbons and Different Chemistry Olefins

Conclusion
Though, significant progress has been made in chemical recycling of waste plastics its use as fuel in diesel engines is still facing many problems. Catalytic pyrolysis with subsequent Hydro treating and hydro cracking can reduce unsaturated hydrocarbon bonds and thereby improve combustion performance in diesel engines. A literature review of the works in the field of waste plastic pyrolysis oil as fuel for diesel engines is conducted and the results of the review has been presented in this paper. Catalytic pyrolysis has been found by researchers as a better process than thermal pyrolysis with only
the cost and recovery of catalyst as areas of concern. Literature review of performance of fuel derived from thermal / catalytic pyrolysis has been done in this paper. Problems regarding delayed ignition, higher heat release rate and increased NO\textsubscript{x} remains to be addressed to make this fuel suitable for diesel engines. Future research work should focus on reducing the unsaturated hydrocarbons in pyrolysis fuel and thereby improve the combustion performance on par with diesel. Hydro treating and hydrocracking are promising much better results in reduction of unsaturated hydrocarbons.

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