

Studies of the synthetic diesel fuel extracted from the de-polymerization of waste polyethylene mix

Abstract:

With the increase of the solid municipal waste, the problem of its disposal has become a big problem worldwide. The plastic materials are the commodity materials which have become part of our life. The polymer materials such as LDPE, LLDPE, MDPE and HDPE are the type of polyethylene materials which are being used by us on a day to day basis. For creating a sustainable energy and environment, alternative energy is needed to be developed rather depending on the conventional fossil fuel. The conversion of these types of polyethylene materials in the municipal waste into useful hydrocarbon fuel is one of the key challenges worldwide. The polymers having polyolefin are very useful materials with different applications, but are reluctant to degradation or deterioration. The thermal pyrolytic conversion of the waste polyethylene mix and the extraction of different useful hydrocarbon components were observed to be one of the key areas of study. The study of the different components extracted from the polyethylene mix, preferably the diesel like components were studied in detail. The different studies including the chromatographic study, simulated distillation analysis FTIR study and the cetane analysis of the product were carried out. The different physical and chemical analysis of the product were also investigated to compare its property with the conventional diesel fuel.

Keywords- Polyethylene, De-polymerization, Diesel, SIM-DIST, FTIR, Hydropyrolysis, Boiling point

Introduction:

With the growth of the industry and the ever increasing demand of the human consumption, the use of the polyethylene materials is increasing considerably. On the basis of the human requirement, the polyethylene materials were produced and used in different patterns. Today about 20 percent of the total municipal solid waste is plastic waste. These are generally non-biodegradable materials which are polluting our environment in a very alarming manner. The search for alternative method of using or degrading these solid wastes is studied worldwide. With the fast depleting fossil fuels, mankind has to focus on searching newer and alternative sources of energy. The development of the alternative fuel technology is found to be the replacement of the fossil fuel in the future. The conversion of the waste polyethylene materials into useful hydrocarbon fuel by hydropyrolytic depolymerization is being studied in this paper.

Polyethylene materials are generally made up of long repeating chain large polymers of single or multiple unit monomers. These may be made up of straight, branched or hybrid type of units. Polyolefins a part of these polyethylene materials are saturated polymers which have a broad range of applications. Polyethylene materials such as LDPE (linear density polyethylene), LLDPE (linear low density polyethylene), MDPE (medium density polyethylene) and HDPE (high density polyethylene) which are generally made up of such materials generally have linear or cross linked in nature. Due to this cross linking of polyethylene materials, it forms dense network of high molecular weight structure which further improves its impact strength, crack resistance, creep and abrasion resistance without any influence in density and tensile strength.[1] HDPE and LLDPE are generally made up of coordination catalysts where as LDPE is made up of free radical initiators. LDPE has both long chain branching and short chain branching structure, while polyethylene made by coordination polymerization generally have only short

chain branches. Some polyethylene resins which are made up of specific metallocenes catalyst may also have some long chain branches, but their long chain branch topology is distinct from that of LDPE resins.[2] The thermal degradation of the polyethylene materials produces different types of fuel comprising of the gaseous, naphtha, diesel grade fuel and the heavier cut fuels. The depolymerization of the polyethylene materials is generally the breakdown of the weakly bonded main chain and then successively splitting up of shorter chain units into further shorter chain or monomeric units. Thermal cracking eliminates a side chain of lower bond dissociation in a plastic of the carbonization residue type. Thermal cracking then causes decomposition, cyclization and other secondary reactions of the plastic and carbonizes all of its molecules.[3] The hydropyrolysis process of de-polymerization of polyethylene mix into useful liquid hydrocarbon products is studied and the extraction of the diesel range product from the recovered liquid product is examined.

The extraction of the diesel like component and their different characteristic properties which enable it to become equivalent to the conventional diesel fuel is studied in this paper. The oils derived from municipal solid waste have high oxygen content due to the presence of cellulosic components in the waste, The oils derived from the pyrolysis of waste materials tend to be chemically very complex due to the polymeric nature of the wastes and the range of potential primary and secondary reactions. Municipal solid waste pyrolysis oils contain hundreds of different chemical compounds, including organic acids, phenols, alcohols, aldehydes, ketones, furans, etc. The product oils derived from pyrolysis of plastic waste produce end-products which are based on the original polymer structure.[4] The different physical and the chemical characteristics of the recovered oil were studied. The FTIR study of the recovered diesel like fuel from the waste polyethylene is studied. The simulated distillation analysis of the fuel is observed. The Cetane analysis of the product and its different characteristics in accordance with the conventional diesel fuel is studied.

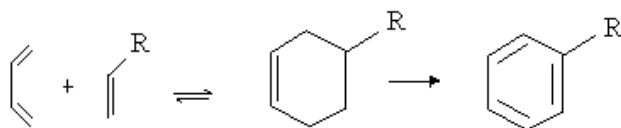
The diesel component extracted at the temperature range 150⁰C to near about 500⁰C is being studied and the characteristic properties of the product at different boiling points with respect to mass and volume percent is observed. The distribution of the carbon number and the different functional group were also observed. The study provides the scope of using recovered diesel oil from polyethylene mix by hydropyrolytic process as compared with the conventional diesel fuel with some changes or modifications. This characteristic property enable the diesel like fuel extracted from the waste polyethylene mix, to be used either directly or with some modifications, in the diesel engines.

Experimental and Methodology:

The degradation of the polyethylenes and different polyolefins into its constituent monomers follows different steps. The experimentation to develop liquid product from the different types of the polyethylene and polypropylene materials is carried out in a batch reactor. The reactor is connected with two adjacent vessels. The vessel containing de-ionized water is connected with the reactor with a connecting pipe or hot water condenser. The vessel is filled with chilled water and is covered with cold water. The secondary vessel is connected with the primary vessel, which is filled with ice water. The reactor is heated gradually. During the process the gases which comes out from the reactor and passes through the hot water condenser, The vessel is filled with chilled water and is covered with cold water. The secondary vessel is connected with the primary vessel, which is filled with ice water. The reactor is heated gradually. During the process the gases which comes out from the reactor and passes through the hot water condenser get quenched in the chilled water in the vessels. During the process some amount of hydrogen is added to the reactor, so that the free radicals so produced get attached with the hydrogen atom to produce monomers and short and very short chain monomers and dimmers.

It was observed that the thermal degradation of the polyethylene and polypropylene in the pyrolysis reactor proceeds via random scission to yield a wide spectrum of hydrocarbon fragments which may contain any number of carbon atoms. The C–C bond is the weakest in the polymer structure and leads to the formation of straight-chain alkanes. In addition, during the degradation process, the stabilization of the resultant radical after chain scission leads to the formation of carbon double bonds in the structure. Therefore, the product oil will consist of mainly alkanes and alkenes. In addition, the pyrolysis oils contain a significant proportion of toluene, xylene and alkylated benzenes, indene and indane and naphthalene.

The thermal degradation mechanism for polyethylene and polypropylene has been shown to be via first chain scission and then random scission, which results in the formation of monomer and also dimer, trimer and tetramer. It is observed that the isoprene monomer is formed via a depropagating mechanism in the polymer chain and that the dipentene dimer is formed either by intramolecular cyclization followed by scission, or by monomer recombination via a Diels–Alder reaction.



Material not undergoing de-polymerization is cyclised and cross-linked to form a residue which is degraded in the second stage. The product of pyrolysis from the second stage is a complex mixture of hydrocarbons[2].

The degradation process mainly follows the mechanism of chain scissions which is generally caused by increase in the temperature and sheer stress and hence decreases the molecular weight. The chain branching and the cross linking have the opposite effect to the chain scission and are caused by the low sheer stress and high residence time. The mechanical degradation of the polymeric material occurs by breaking C-C and C-H bonds. The degradation depends on the nature such as the polar group and structure such as head to head or tail to tail weak linkages, double bonds or branching points of the polymeric chain on the ingredients in the polymer resin and on the type of the stress.

Polyethylene as well as other vinyl polymers degrade via a four step free radical mechanism, radical initiation, de-propagation (as opposed to propagation in the case of polymerization), intermolecular and intramolecular hydrogen transfer followed by β -scission (initial step in the chemistry of thermal cracking of hydrocarbons and the formation of free radicals) and, lastly, radical termination. β -Scission and hydrogen abstraction steps often occur together in a chain propagation sequence. That is, a radical abstracts a hydrogen atom from the reactant to form a molecule and a new radical. A bond is then broken to the radical centre (β -scission) to regenerate an abstracting radical and to produce a molecule with a double bond (a molecule with a double bond involving the carbon atom that had been the radical centre). Sample size and surface area to volume ratio of the polymer melt have a significant influence on the rate and relative importance of the various mechanisms of polymer degradation. In pyrolysis, which is normally done on micro-scale, only random initiation and intermolecular transfer were reported to be important. Conversely, on milligram scale of polyethylene charges and samples, intermolecular transfer of hydrogen atoms via abstraction by free radicals was considered to be the predominant transfer mechanism to produce volatiles[5].

The thermal decomposition of polymers often involves the formation of volatile species within a highly viscous polymeric matrix. Transport of these species through the molten polymer mass towards the vapour phase is not a straightforward process, and so the occurrence of mass transfer limitations can be expected. It was observed that the rate of polymer thermal degradation depends on factors such as the surface area and thickness of the polymer sample, showing that the polymer decomposition is controlled by the diffusion and/or the vaporization of the volatile species

On the other hand, polymer thermal decomposition is an endothermic process. At least the dissociation energy of the C-C bond in the chain must be supplied to break down the polymer. Moreover, this is the main factor determining the polymer stability [6].

Thus depolymeriation of the polyolefins via hydropyrolytic process follows the following steps, involves the succession of first bond in the chain yielding two radicals, which may occur at random or end chain position. De-prorogation resulting in the release of the olefinic monomeric fragments from primary radicals. Hydrogen chain transfer reaction may occur as intermolecular or intra molecular processes. This leads to the formation of olefinic species and polymeric fragments. β -cleavage of secondary radicals yields end chain olefinic groups and primary radicals. Branches were observed between two secondary radicals or between secondary and a primary radical. Termination process takes place either in a bimolecular mode, either by coupling of two primary radicals or by disproportion of radicals [7]. The resulting liquid so obtained is then fractionated in a fractionating column. The diesel like component ranging from boiling range 130 °C -500 °C with maximum yield up to 360 °C is extracted. The extracted middle distillate portion of the liquid is tested for various physical and chemical properties. The boiling point distribution graph is prepared according to the different boiling point recoveries at different temperatures. A graph showing the boiling point with different mass percentage is described below in figure 1.

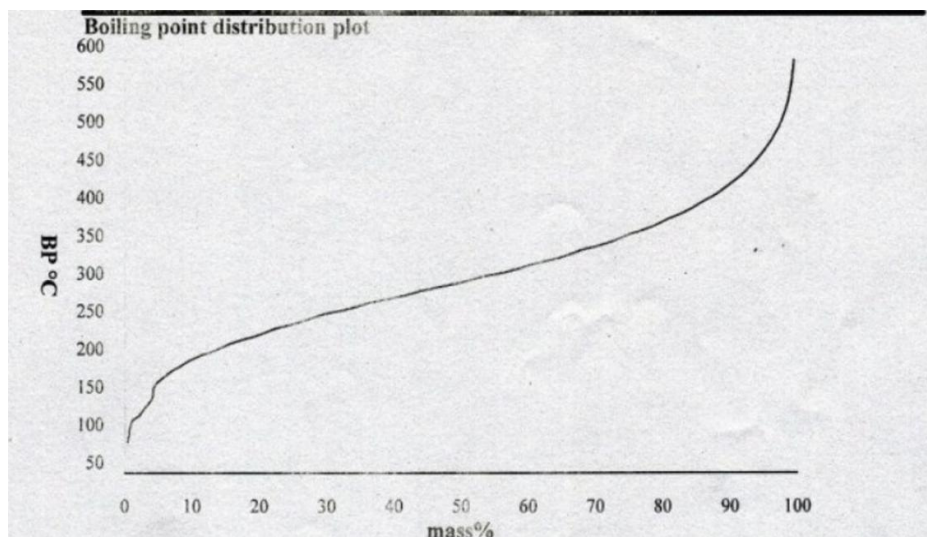


Figure.1. Boiling point distribution plot of the diesel like component extracted from the Hydropyrolytic depolymerization of the waste polyethylene mix

The simulated distillation (SIM DIST) and the DHA(detail hydrocarbon analyzer) analysis of the diesel component extracted from the above depolymerised polyethylene liquid is carried out and the resulting plot between boiling point, retention time and the signal is plotted. Also the plot between the different carbon number with varied retention time is also shown in figure 3. This gives the volume and mass percentage of the components recovered at different temperatures and different retention times. The experiment is carried out in Agilent DHA and SIM-DIST analyzers having single column, FID detector and carrier gas used is helium gas. The above observations are shown in the figure 2 and figure 3 below. The figures showing the reference peaks, the baseline peak, the temperature gradient peak and the sample peak at different boiling points and different carbon number points at different retention times respectively [8][9].

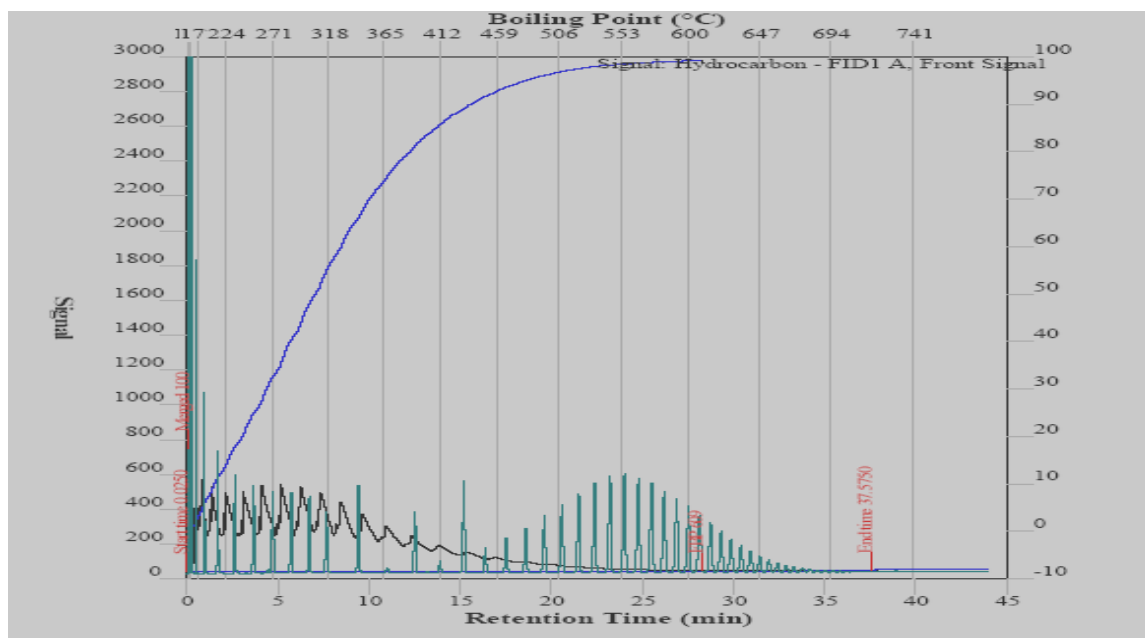


Figure 2. SIM- DIST analysis for Boiling point distribution with retention time of the diesel like component extracted from the hydropyrolytic depolymerization of waste polyethylene mix

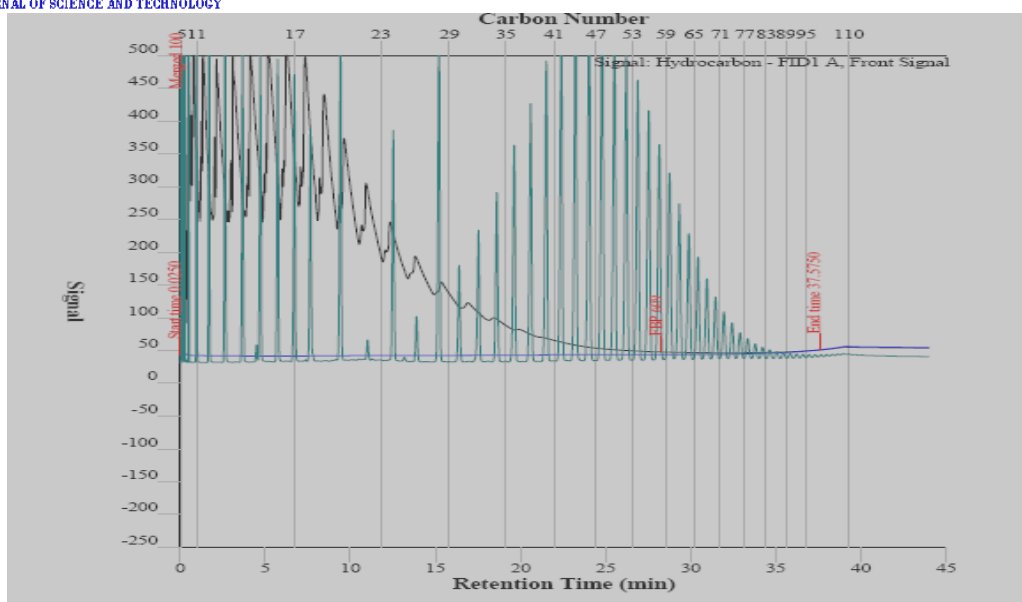


Figure 3. SIM –DIST analysis for carbon number distribution of the diesel component extracted from the hydropyrolytic depolymerization of polyethylene mix

Another observation is carried out between the volume percentage and the boiling point of the liquid for correlation with the boiling point analysis as per ASTM D86 for the diesel like liquid at standard temperature and pressure. This graph is shown below in figure4

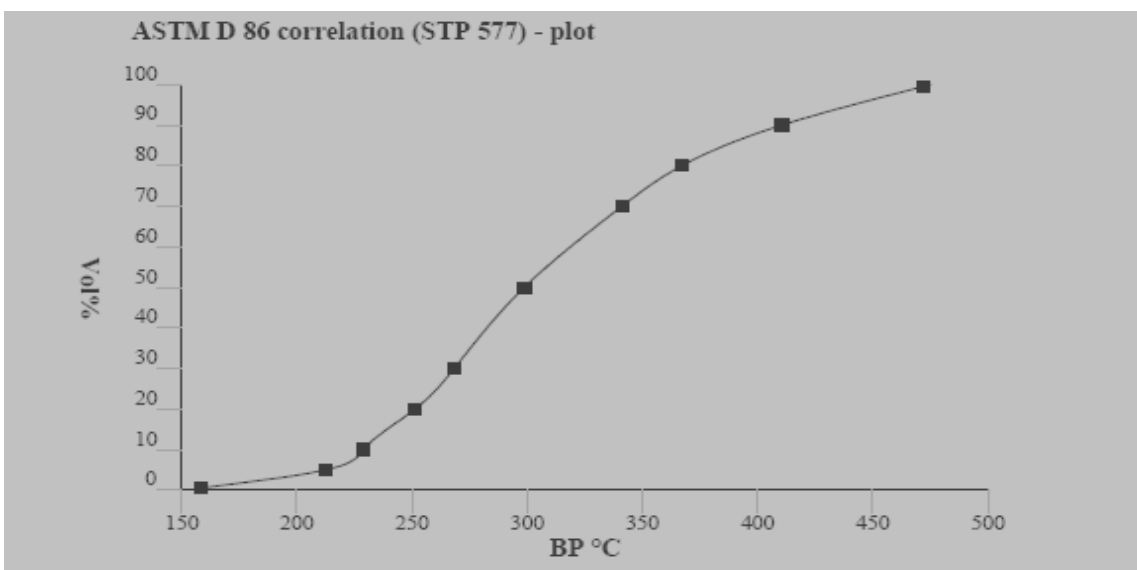


Figure 4 ASTM D86 graph showing boiling point with different volume of the liquid recovered in percentage

The boiling point distribution on the basis of the mass percentage and the volume percentage is described in the table 1 and table 2 below. The Boiling point temperature so recovered is in accordance to the distribution of the different components observed at different carbon number distribution present, as shown in the figure 3. The distribution of the different boiling point is in accordance to the ASTM D86 process [10].

BP ($^{\circ}\text{C}$)	Mass%
120	IBP
148	5
179	10
218	20
241	30
264	40
295	50
310	60
321	70
348	80
367	90
383	95
408	FBP

Table.1. Boiling point versus mass percentage distribution of the component recovered as described in the figure 1, 2, 3 and 4

BP	Vol%
101	IBP
132	5
176	10
213	20
232	30
253	40
271	50
288	60
296	70
328	80
349	90
369	95
399	FBP

Table 2. Boiling point versus volume percentage distribution of the component recovered as shown in the figure 1,2,3 and 4.

The distillation of the diesel like component describes the varied hydrocarbon components having different carbon numbers having different carbon numbers. The FTIR study of the component is carried out, which provides the evidence of the different functional group present in the component. The FTIR study of the component and thick film is being carried out. The different peaks observed with different wavelength having different functional group is shown below.

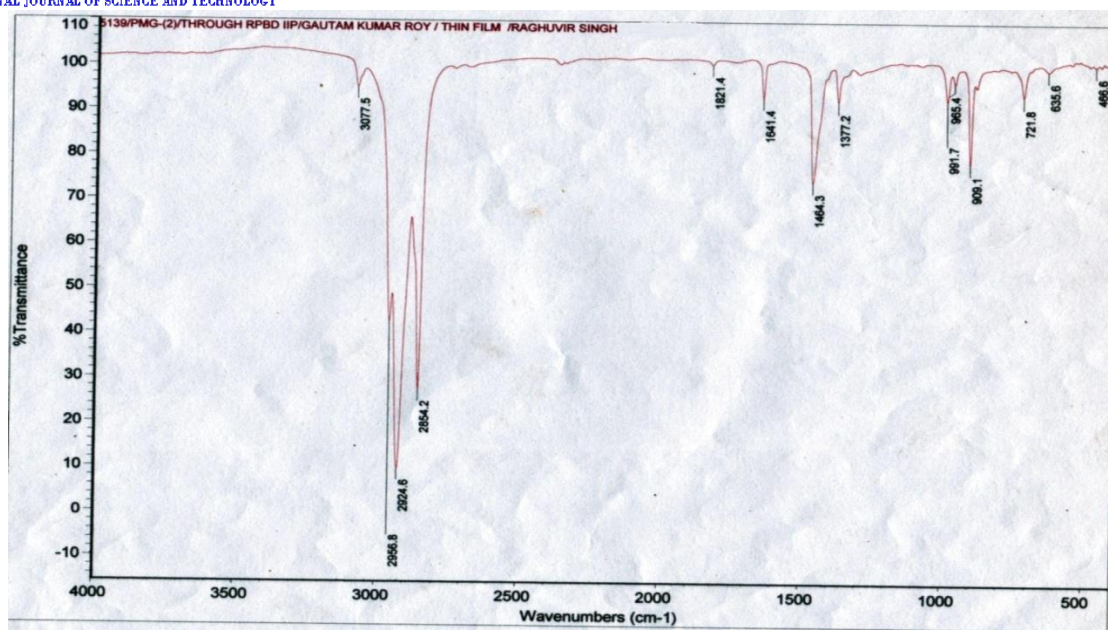


Figure 5. FTIR study of the diesel like component extracted from polyethylene mix using thin film

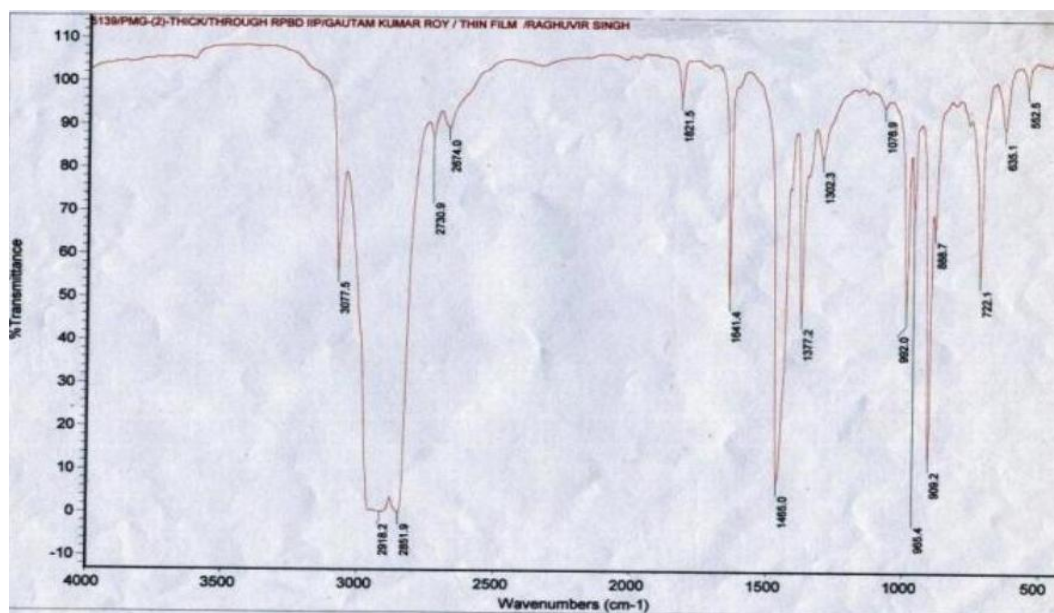


Figure 6. FTIR study of the diesel like component extracted from polyethylene mix using thick film

Peak Position/ Wavelength in cm^{-1}	Possible band/ Functional Group	Frequency Strength
3077.5	-C=C-H	Weak
2956.8, 2924.6, 2854.2	Alkyl C-H Stretch, Alkane C-H bond	Medium/ Strong/ Weak
1821.5	-C=O Stretching	Weak
1641.4	Unsaturated olefins, (C=C stretch isolate/ conjugate)	Strong
1465	CH ₂ bend	Strong
1377.2	CH ₃ bend	Strong
1302.3	C-H vibration	Weak
992, 965.4	Vibration from CH ₂ , CH ₃ group	Strong/Medium
909.2	C-H bend	Strong
888.7	C-H bend	Weak
722.1	Short chain n-alkane	Medium
635.7	C-H vibration	Medium
552.5	C-H vibration	Weak , Medium

Table 3. Peak position, possible Functional group/ band and the frequency strength as observed in FTIR study (Figure 5 and Figure 6) of the diesel like component from the polyethylene mix

FTIR spectrum of the above spectra in thick film and thin film respectively is produced in the figure 5 and figure 6 and the results were observed in table 3. The FTIR study produces the evidence of the different possible bands having different functional groups present. The different stretching and bending vibrations of the groups were also observed in the study. The energy value of the above data is calculated using the formula

$$E = h\nu$$

Where h = Planks constant which is equal to 6.62×10^{-34} J and

ν = frequency of photon in Hertz (sec^{-1})

Again $\nu = c/\lambda$ where λ = wave length

$$W = 1/\lambda.$$

Therefore $E = hcW$

Where c = speed of light having value 3×10^{10} cm/sec and W = Wave number .

This equation indicates that high wave number light has more energy than low wave number light. Thus accordingly the equivalent wave number and its energy value is given in table 4 below.



Wavelength in cm^{-1}	Energy value (E) in Joule(J)
3077.5	$6.1119 * 10^{-20}$
2956.8,	$5.8722 * 10^{-20}$
2924.6,	$5.8082 * 10^{-20}$
2854.2	$5.6684 * 10^{-20}$
1821.5	$3.6174 * 10^{-20}$
1641.4	$3.2598 * 10^{-20}$
1465	$2.9094 * 10^{-20}$
1377.2	$2.7351 * 10^{-20}$
1302.3	$2.5863 * 10^{-20}$
992	$1.9701 * 10^{-20}$
965.4	$1.9172 * 10^{-20}$
909.2	$1.8056 * 10^{-20}$
888.7	$1.7649 * 10^{-20}$
722.1	$1.4340 * 10^{-20}$
635.7	$1.2625 * 10^{-20}$
552.5	$1.0972 * 10^{-20}$

Table 4. Energy values of the functional group in accordance to the wavelength produced in Table 1.

The experimental study of the diesel like fuel extracted from the polyethylene mix depicts that the product can be used as a diesel fuel directly or with some modifications in its properties either by blending with the conventional fuel or by reprocessing in accordance with the conventional diesel fuel parameters.

The diesel components were compared with the conventional diesel fuel. It was observed that the different parameters observed in the diesel like component extracted from the waste polyethylene mix is quite equivalent to the conventional diesel fuels. The physical and the chemical test of the above samples were carried out, which provides evidence of the fuel like properties of the product with some similarities and dissimilarities.

Conclusion:

The component extracted from the fractional distillation of the product derived from the hydropyrolytic depolymerization of the waste polyethylene mix is compared with the conventional diesel fuel. It was observed that the component so extracted can be used as a diesel fuel with some modifications or can be used as a blended product for the conventional diesel fuel engines. Different analytical techniques were used to compare the product with the conventional fuel. The Simulated Distillation analysis of the product derived from the waste polyethylene mix produces evidence of the different boiling point distribution of the product and the carbon number distribution of the product at different temperatures at different retention times. The distribution of the signal for the extracted diesel fuel also provides the concentration of the fuel at different temperature. The different distribution of the carbon number gives scope for the extraction of the useful diesel component from the synthetic crude mix from waste polyethylene. The SIM-DIST analysis of the diesel like component provides a scope for the extraction of the diesel cut from the mother liquid extracted from the polyethylene mix by hydropyrolysis process. The FTIR study also provides the proof of the presence of the different functional groups and there their corresponding energy values. The paper also helps in understanding the scope for development of an alternative and environmental sustainable and source of energy for our future needs.

Acknowledgement:

The Author Acknowledges the support of Mr. P K Rudra DGM(Technical Services), Mr. A. S. Sarkar, Ex-Deputy Manager(QC), Mr. Bhag Singh, QCO, and Dr. Kajal Ambuj SQCO, Barauni Refinery, Indian Oil Corporation Limited for extending there helping hands in completing this paper. Author is indebted to Dr. I. S. Jha Ex. Dean of Science and professor, University department of chemistry, L.N.M.U. Darbhanga for extending his support and assistance. Author is also thankful to the Scientists of Indian Institute of Petroleum, Deheradun for extending there support in carrying out different experimental studies.

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