

Characterization of the Heavy Cut Oil Extracted from the Hydropyrolytic Depolymerization of LDPE, LLDPE, MDPE and HDPE type of Polyethylene Mix

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Abstract

polyethylene waste has become one of the major pollutant worldwide. The conversion of the polyethylene waste into useful hydrocarbon products is being studied and investigated. The conversion of the LDPE, LLDPE, MDPE and HDPE type of polyethylene into hydrocarbon products via hydropyrolysis process is carried out. The product comprises of the gaseous and the liquid products. The liquid or the mother liquid product comprises of the naphtha, middle distillate and the heavy cut oil of varied characteristics. The heavy cut fraction is the part of the mother liquid which remains as the semi liquid fractionate. The heavy cut fraction is the part which is difficult to extract by the fractional distillation under atmospheric pressure. Thus this part remains at the bottom of the distillation column. The characteristic property of the heavy cut oil is studied and it is found to be important as it generates a structure with a higher molecular weight that is less easily volatilized. The heavy cut oil extracted from polyethylene mix has temperature greater than 370 °C. Simulated distillation analysis and the mass spectra analysis were carried out to understand the thermo chemical and the structural properties of the heavy cut oil or end use.

Keywords - Polyethylene, hydropyrolysis, heavy cut oil, SIM-DIST, FTIR, GC-MS

I. INTRODUCTION

With the increasing demand of the petroleum and petroleum products and the depleting reserves of the crude oil, the search for an alternative and renewable source of energy is investigated worldwide. Polyethylene, generally have very strong chemical bond that make it durable and resistant to natural activity. Several thermo chemical techniques have been employed to convert waste PP (Polypropylene) and LDPE (Low density polyethylene) into value added products. The thermal degradation of the polyethylene

materials splits the long chain hydrocarbon into gaseous product, which finally produces low molecular weight, gaseous and liquid products.[1][2] Polyethylene to hydrocarbon fuel is a de-polymerization process of converting waste polyethylene into useful hydrocarbon products. The process of converting the polyethylene into useful hydrocarbon product is followed by hydropyrolytic process[3]. Degradation depends on the nature, such as polar groups and structure, for example 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 external stress[4]. The heavy cut oil is the portion of the extracted liquid which has high molecular weight. The heavy cut fraction of the mother liquid is extracted by the fractional distillation of the polyethylene mix. During the random chain scission processes a variety of chemical species were developed. The type and the distribution of the volatile products depend on the relative volatility of the resulting molecule as discussed earlier. Crosslinking reaction occurs after stripping of the substituent's and involves the creation of bonds between two adjacent polymer chains. This process is very important in the formation of the heavy products and the chars, since it generates structure with a higher molecular weight that is less easily volatilized.

II. EXPERIMENTATION AND METHODOLOGY

The fractional distillation of the mother liquid for the extraction of the heavy cut oil is being carried out on the basis of the boiling point range. The fraction of the mother liquid which remains at the bottom of the column and not easy to be distilled, at higher temperature above 370 °C, it is collected at the bottom of the fractionating column. This is the residual portion of the fractionating column carried out at atmospheric pressure. The product so obtained is waxy in nature and is observed to be semi solid at normal room temperature.

Abnormalities may occur from several sources in the synthesis of polyethylene depolymerization. Unsaturated bonds produced from the chain termination by free radical reaction. End chain insaturation results from second order disproportionation reaction and mid chain insaturation often occurs due to chain transfer reaction with subsequent intramolecular hydrogen transfer. Mid chain radicals results in the formation of chain branching. During the process of synthesis, chain transfer reaction may lead to formation of chain radicals which react with monomers or polymers to create branched polymer structure.

The termination of the of the reaction mechanism may result in head to head, that is monomers attached together such that some monomers are oppositely oriented to the remainder of the chain structure. Due to the impurities present in the polymers initiator or catalyst, foreign atoms or groups may incorporate in the polymer chain.

The melting temperature increases with the stiffness of the polymer chain. Polyamides of the aromatic group melts at very higher temperature than their aliphatic analogs due to stiffness effects [5]. Aromatics are useful for chain stiffening as they provides stiffness without bulk which would hinder crystallinity. Moreover the presence of oxygen atom attached to the polyethylene molecule also lowers the melting point temperature. Many aromatic polymers having melting temperature in excess of there decomposition temperature, making these material achieving thermosetting property.

The crosslinking structure also increases the melt temperature and chain stiffening which can render infusibility. During the depolymerization process the crosslinking structure created is important as it increases the glass transition temperature in the polyethylene molecules.

Random chain scissions can quickly render a material unusable by affecting its physical properties unless cross linking occurs.

Thus the heavy cut fraction terminates to fuse due to the formation of the complex crosslinking structure and hence remains as a semi solid fractionate. The fractional distillation of the mother liquid extracted from the LDPE (linear density polyethylene), LLDPE (linear low density polyethylene), MDPE (medium density polyethylene) and HDPE (high density polyethylene) mix polyethylene is carried out and the

heavier fraction left at the bottom is extracted. The heavy cut fraction is the part which is difficult to extract by the fractional distillation under atmospheric pressure. Thus this part is remains at the bottom of the distillation column in the fractionation of the heavy cut fraction from mother liquid.

A. Physical properties

The melt stabilization of polyethylenes has primary importance in practice. The nascent polymer is subjected to heat, shear and low level of oxygen already in the pelletizing process. As a consequence, several chemical processes take place simultaneously resulting in considerable changes in the chemical structure of the polymer. The reaction depends on the chemical structure of the polyethylene such as the number of unsaturated groups, long and short chain branching and type of co-polymers.

Stabilizers are chemical substances which are present in the polymers in small amounts (about 1-2 w/w%) and are capable of trapping emerging free radicals or unstable intermediate products such as hydroperoxides in the course of auto oxidation and to transform them into stable end products [6].

Some of the physical properties of the heavy cut fraction extracted from the polyethylene mix are

Colour	yellowish to dark yellow
Carbon residue	0.91%
Solubility	soluble in CCl ₄ , n-hexane, benzene and other Non-polar solvents

B. SIM-DIST Analysis of the Product

The distillation of the fraction is carried out following ASTM method of distillation analysis using the simulated distillation (SIM-DIST) analysis. The different recoveries were observed on the basis of temperature and boiling point. The analysis provides information regarding the different temperature cuts of the fraction on the basis of volume percentage. The SIM-DIST analysis of the product also provides data for the different tentative carbon number distribution based on the boiling point graph. The boiling point yield graph with respect to the different temperature cuts is described below.

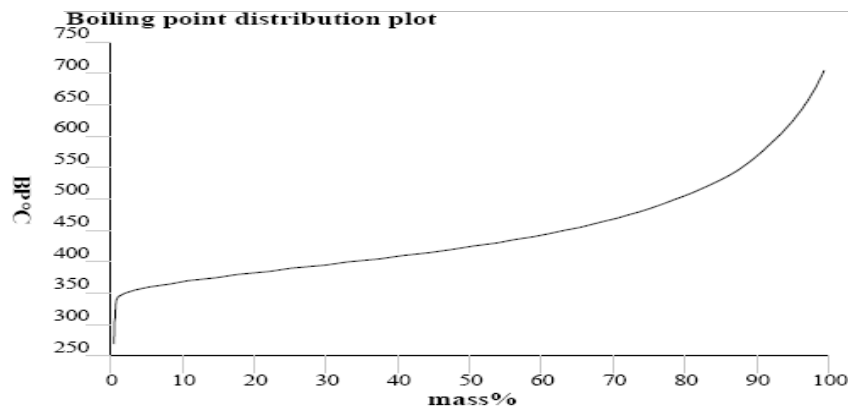


Figure 1. Boiling point distribution graph on the basis of boiling point versus mass percentage

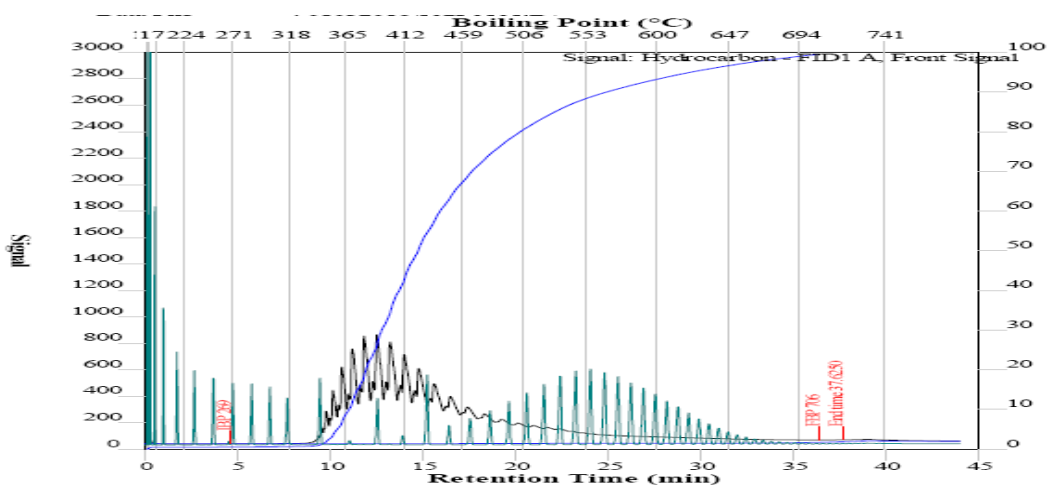


Figure 2. Boiling point distribution of the heavy cut fraction on the basis of retention time versus boiling point

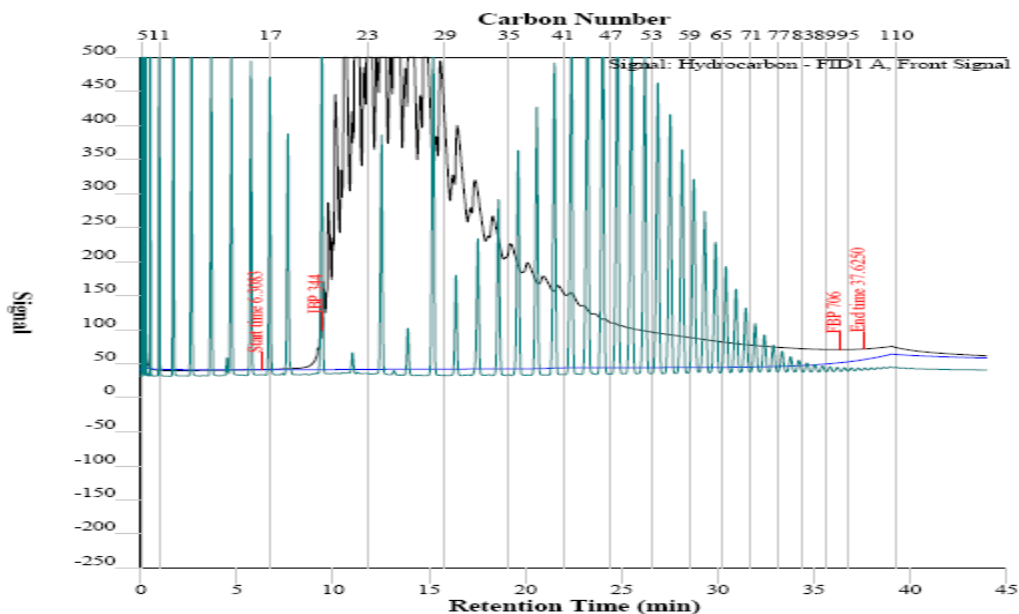


Figure 3. Carbon number distribution of the different fraction on the axis of their boiling points

Based on the above graphs for the determination of the boiling point on the basis of the volume percentage the

different boiling point distribution with respect to recovery is described below

Vol %	Boiling point (⁰ C)
IBP	
5	367
10	378
15	384
20	389
25	394
30	398
35	401
40	405
45	410
50	416
55	424
60	434
65	445
70	457
75	471
80	488
85	513
90	545
95	583
FBP	613

Table 1 Boiling point on the basis of volume percentage of the heavy cut fraction

The distillation of the heavy cut fraction reveals that the heavier fraction from boiling points above >370 ⁰C temperature is present in the fraction with some partial fraction above 350 ⁰C.

C. FTIR Study

The different probable functional groups present in the fraction are also analyzed using the FTIR study of the fraction. The FTIR study produces the evidence of the presence of the different functional groups having different frequencies at different wavelengths, present in the fraction.

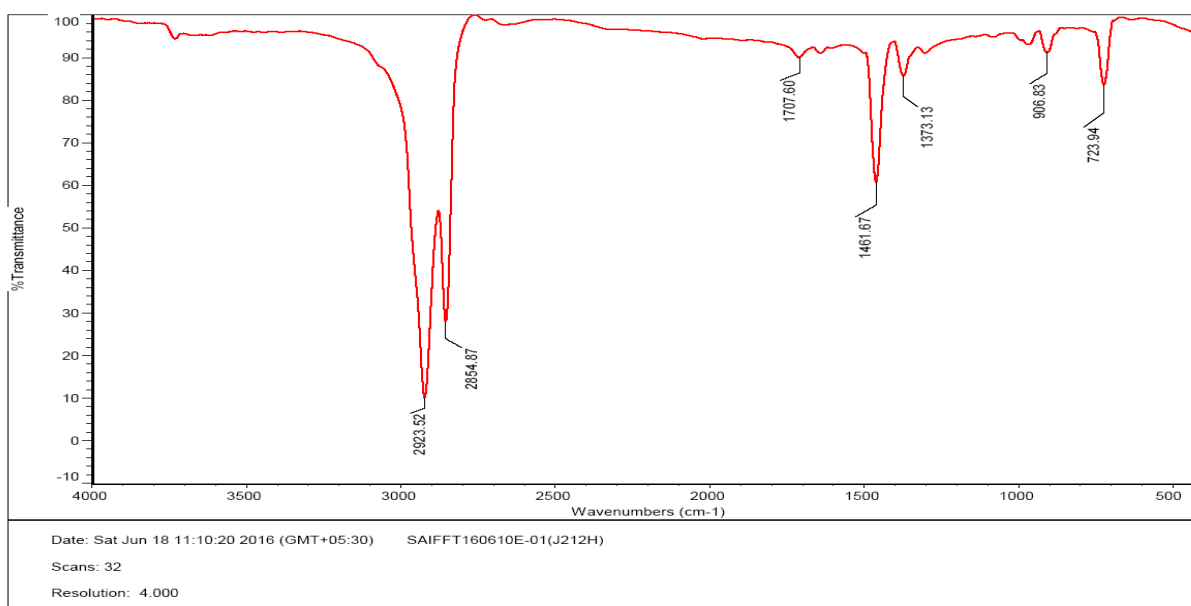


Figure 4. FTIR study of the heavy cut fraction recovered from the fractional distillation of the mother liquid.

The different peaks observed at different wavelengths were described in the above figure. The different peaks at different wavelengths were predicted and their possible bands and functional groups were identified accordingly.

Peak Position/ Wavelength in cm^{-1}	Possible band/ Functional Group	Frequency Strength
2923.52	CH ₂ asymmetric stretching, Alkyl C-H Stretch, R-CH ₂ -OH, R-CH ₂ -OR`	Strong
2854.87	CH ₂ symmetric stretching, Alkyl C-H Stretch, Alkane C-H bond	Strong
1707.60	C=O stretching, aromatic -C=O, Dialkyl ketone	Weak
1461.67	CH ₂ bending, CH ₂ bending vibration, RCH ₂ R` and R-CH ₂ -OR` , R-CH ₂ -OH	Strong
1373.13	CH ₃ bending, CH ₃ COO- group	Medium/ Strong
906.83	CH ₂ Bend, out of plane bending	Weak/ Medium
723.94	Short Chain N-Alkane	Medium, Strong

Table 2. Peak position, possible Functional group/ band and the frequency strength has observed in FTIR study of the heavy cut component from the polyethylene mix from figure 4

D. GC-Mass Spectra Study

The GC-MS with EI-MS spectra analysis provides the exact structure of the compounds present on the basis of the abundance of the compounds versus the charge. With the help of GC-MS with EI-MS analysis the different compounds whether saturated or unsaturated compounds were observed by calculating the mass of the compounds. EI-MS analysis is a hard ionization, and the spectra include molecular ion and

fragment ions that are specific to the target compound. This technique helps in determining the specific compounds with precision.

The possible compounds with different peaks at different time interval and there abundance for possible compound is described below. The different peaks were analyzed and interpreted to get the possible structure of the compounds present in the heavy cut oil extracted from the polyethylene mix.

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File       :D:\GAUTHAM KUMAR ROY\J213H.D
Operator   :
Acquired   : 19 Nov 2016  16:36   using AcqMethod GENERAL.M
Instrument  : GCMS
Sample Name: J213H
Misc Info  :
Vial Number: 3
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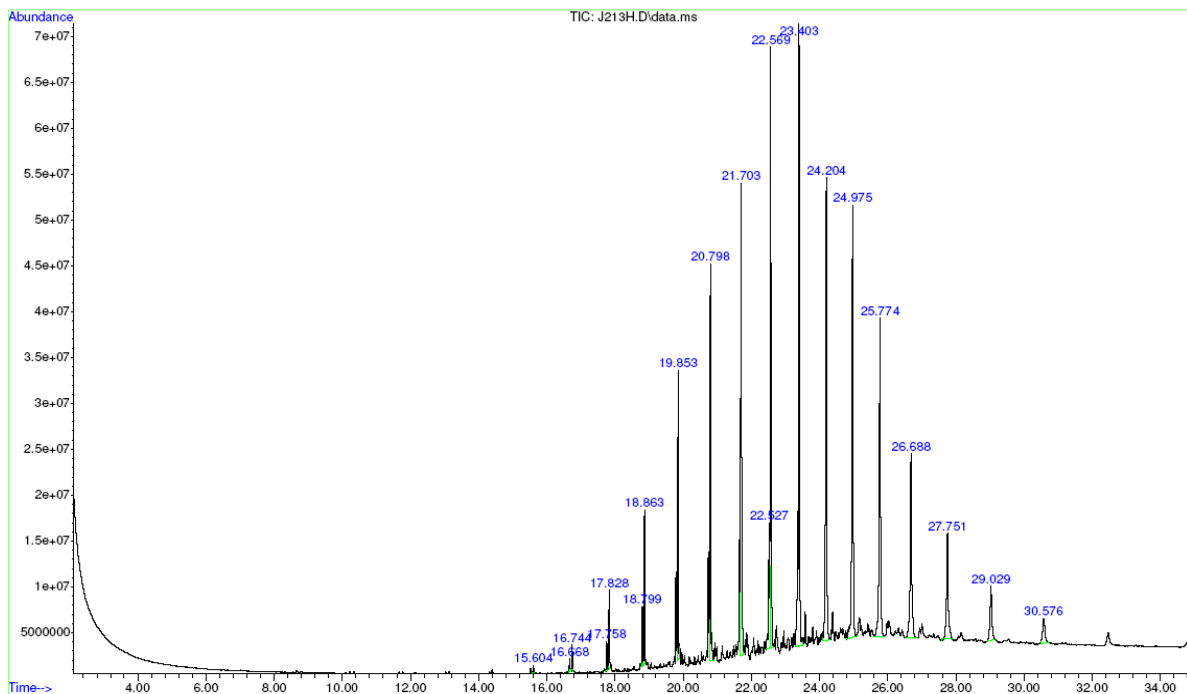


Figure 5. Mass spectra analysis of the heavy cut oil component extracted from polyethylene mix

The characteristic properties of the heavy cut oil were investigated and it was found that the fraction can be used as equivalent to the heavy cut oil extracted from the conventional crude oil. The formation of the long chain and medium chain hydrocarbon components were observed from GC-MS data. The chain structure are mostly of straight chain innature with some cyclic and aromatic attached to the straight chain structure. From the above mass spectra study it was observed that many higher polymeric components were present in the heavy cut oil. These higher polymeric components are produced either due to the crosslinking structure formed during the reaction or strong bond between the compound structure.

Some of the compounds were observed to form cyclic and aromatic structures. This is analyzed by the HPLC (high performance liquid chromatography). In this process the heavy cut oil (in semisolid form) is dissolved in particular non-polar solvent and is injected in the column. The analysis provides the peaks of the monoaromatic, di-aromatic and the polyaromatic peaks [7][8]. This indicates the presence of the different types of the aromatic structures present in the heavy cut oil. Though found in small amount but these are formed during the depolymerization process.

Some high molecular weight linear aliphatic hydrocarbons mainly C8-C23, the formation of light aromatic and of poly aromatic hydrocarbon by gas phase tar re-polymerization reactions during the pyrolysis of polyethylene at high temperatures has been observed.

III. CONCLUSION

The heavy cut oil fractionated from the LDPE, LLDPE, MDPE and HDPE type of polyethylene mix provides a component of the higher fractionate which can be used as grease or lubricant with certain modifications. The heave cut oil fractionated from the polyethylene mix consists of higher polymeric component either in the form of long chain or medium chain structures. The presence of the cyclic and the aromatic ring structure is also observed from the GC-MS analysis. The complex structure does not break because of the crosslinking structure and the presence of the oxygen induced atom in the polymeric chain. this can be revealed by the FTIR data observation. The C=O stretching in the FTIR data provides information about the presence of the oxygen in the polymeric structure. This results in the lowering of the temperature of the melt. The component has a varied structure with boiling range greater than 370 °C to near about 600 °C which is observed by SIM-DIST analysis of the extract. The product is of high importance and can be utilized as an alternative of the heavy cut oil from the conventional crude.

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