

Fixed Bed Pyrolysis of Waste Plastic for Alternative Fuel Production

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Abstract

The thermochemical conversion of waste plastic using a fixed bed pyrolysis system has been considered in this paper. Favourable properties for pyrolysis conversion, such as high volatile content, elemental composition and thermogravimetric behaviour of waste plastic were investigated by the characterization study reported in this paper. The waste plastic feedstock was pyrolyzed in an externally heated 7 cm diameter and 34 cm high fixed bed reactor. Nitrogen is used as a carrier gas and to maintain the inert condition in the reactor. A biomass source heater and a gravity feed type feeder were used to heat and feed the feedstock into the reactor bed respectively. The pyrolysis products were oily condensate, solid char and gas. The condensate and the char were collected and the gas was flared. The product yields were influenced by the process condition. At an optimum reaction condition of fixed bed temperature of 550°C, feedstock size of 400-600µm, and 60 min running time the condensate obtained was 70% of the weight of dry feedstock. The condensate obtained at this optimum condition was analyzed for their properties as an alternative fuel and was compared with other petroleum derived products. The fuel properties of the derived oily condensate compared were physical properties, calorific value, elemental (CHNOS) analysis, and chemical composition using Fourier transfer Infrared (FTIR) spectroscopy.

Nomenclature

TGA	thermo-gravimetric analysis
CHNOS	carbon, hydrogen, nitrogen, oxygen and sulfur analysis
FTIR	Fourier transform infrared
ASTM	American Society for Testing Materials
AISI	American Iron and Steel Institute
IP	Institute of Petroleum
cSt	centistoke
pH	negative logarithm of hydrogen ion concentration
kg/m ³	kilogram per cubic meter
kJ/kg	kilojoule per kilogram
O-H	hydroxyl stretching
C-H	carbon hydrogen stretching and bending
C=O	carbonyl stretching
C=C	carbon carbon double bonding stretching
-NO ₂	nitrogen dioxide stretching
C-O	carbon oxygen stretching
wt%	weight percent
cm ⁻¹	per unit centimeter

Introduction

The increasing energy consumption continues to outstrip energy supply from the fast diminishing conventional energy reserves. By the year 2100 the world population is expected to be in excess of 12 billion. It is estimated that the demand for energy will be increasing by five times from what it is now [1]. With declining reserves and fluctuating prices of fossil fuels, the search for alternative raw materials to replace petroleum has been intensified all over the world. Plastics are among the best products of chemical process industry and are extensively used in our lives. It was estimated that the world consumption of plastic in 1989 was about 50 million metric tons [2], and the plastic markets are growing at the rate of 6-8% per year [3]. Also it was assessed that the public discarded as waste 20% of the plastic produced in 1988 [4]. Bangladesh is now entering into an era of petro-chemicals and polymers being produced locally. In Bangladesh the production of plastic and its various products are increasing day by day. After use, these products creates serious waste disposal problem. Plastic waste represents 6% of the total municipal solid waste [5]. Open burning of such waste in an uncontrolled manner leads to harmful emissions and environmental problems. Thus there is a scope for recycling these waste plastic by thermochemical pyrolysis conversion technique to improve products and provide energy.

This paper presents the findings from a characterization study of the condensate obtained from the thermochemical conversion of waste plastic using a fixed bed pyrolysis system.

Materials and Methods

Waste plastic is widely available in Bangladesh. In this study locally available waste plastic is taken into consideration for pyrolysis. The waste plastic sample was collected locally in Rajshahi, Bangladesh. It was ground and sieved to the size of 0-400 μ m, 400-600 μ m and 600-1180 μ m and finally dried for 24 hours at 110°C prior to pyrolysis. Actually the collected plastics are used for making different types of utensils for domestic use. Prior to this, the plastics are processed in plastic factory for its use.

Characterization of waste plastic for pyrolysis process

For the purpose of investigating the suitability of waste plastic as feedstock for pyrolysis to obtain value-added liquid product, the following analyses have been considered:

- ◆ Proximate and ultimate analysis
- ◆ Thermogravimetric analysis (TGA)

Proximate analysis gives information about feedstock suitability for pyrolysis process in terms of moisture content, ash content, volatile matter content and fixed carbon. The test was carried out according to the American Society for Testing Materials (ASTM) Standard D3172-73 (1984) test procedures for solid fuel, titled "Standard Method for Proximate Analysis of Coal and Coke". It was conducted in the laboratory of Institute of Fuel Research and Development, Bangladesh Council of Science and Industrial Research (BCSIR), Dhaka, Bangladesh. The amount of volatile matter indicates the suitability of waste as the feedstock for pyrolysis conversion to liquid product where high volatile content is desirable [6]. Fixed carbon content gives information of the amount of char formation in the pyrolysis process. Moisture content is important in determining drying cost and energy content of the feedstock.

The elemental composition by ultimate analysis, in terms of carbon, hydrogen, nitrogen, oxygen and sulfur (CHNOS) content of the selected material is essential for their pyrolysis conversion upon which the pyrolysis product quality depends. The test was carried out by an Elemental Analyzer of model EA 1108 according to the ASTM D3176-84 standard test procedures in the laboratory of Analytical Research Division, BCSIR, Dhaka, Bangladesh. The technique used for the determination of CHNS was based on the quantitative "dynamic flash combustion" method. The oxygen content was determined by difference, knowing the ash content. The test results of the proximate and ultimate analysis for the sample are

presented in Table 1. It is to mention that in elemental compositional analysis only C, H, N, O & S are detected. Other elements are not considered in this analysis.

Table 1 Proximate and elemental analysis of waste plastic

Proximate analysis (wt%)		Ultimate analysis (wt%) Ash free basis	
Moisture content	0.41	Carbon (C)	83.93
Volatile matter	96.88	Hydrogen (H)	12.84
Fixed carbon	0.28	Nitrogen (N)	-
Ash content	2.43	Oxygen (O)	0.80
		Sulfur (S)	-
		C/H	6.53

The thermogravimetric characteristics of waste plastic have been investigated by thermogravimetric analyzer (TGA) study. The instrument used for this purpose was of model SHIMADZU TGA-50 and the test was conducted at the laboratory of Institute of Fuel Research and Development, BCSIR, Dhaka, Bangladesh. TGA gave information about the temperature at which pyrolysis was initiated, when the rate of devolatilization was maximum and finally the temperature at which the process was completed. The TG curve also indicated the fractional weight loss of volatile in the sample with temperature and time. The plot obtained at heating rate of 10°C/min over a temperature range of 0-1000°C for waste plastic is presented in Fig. 1. Around a temperature 600°C devolatilization of solid sample completed and thus, reactor was designed for this temperature

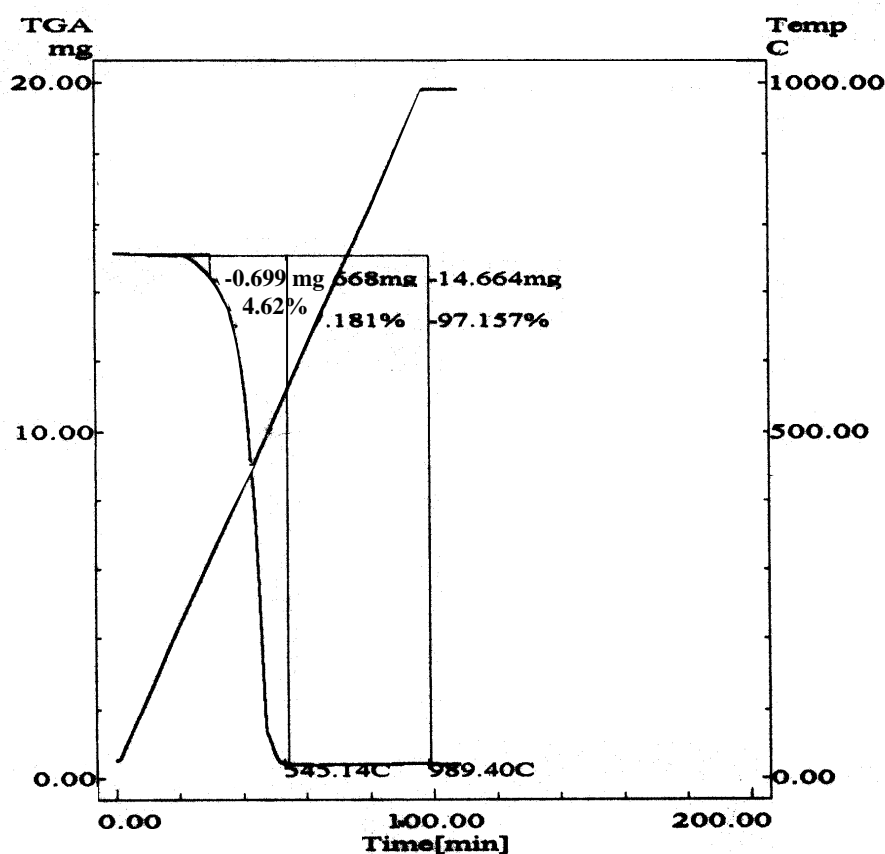


Fig. 1 TG plot for waste plastic in helium at a heating rate of 10 °C/min.

Experimental

Plastic waste was pyrolysed in an externally heated stainless steel fixed bed reactor system with nitrogen as the carrier gas. The system consisted of fixed bed reactor, gas preheating chamber, reactor feeder, condenser, and ice-cooled liquid collectors. The pyrolysis reactor is 340 mm long and 76 mm in diameter. Fig. 2 shows the schematic diagram of the pyrolysis conversion system. For heating purpose a biomass source heater is used. Biomass source heater means that biomass, in this case rice husk is used as a heating fuel instead of other conventional fuel or electricity. The heater supplied the heat to the pyrolysis reactor and the gas preheating chamber. When the desired temperature attained, plastic particles were fed into the reactor from reactor feeder. The reactor temperature was controlled by varying the air supply by the use of an air blower and the temperature was measured by a digital pyrometer. Nitrogen gas was supplied at a constant rate to drive the pyrolysis product out of the reactor and to purge the feed into the reactor. The vapor product and the gases passed through the condenser and the liquid collectors. The pyrolysis products i.e. oily condensate and solid char were collected separately and the gas with the non-condensable vapor was flared. The flow of nitrogen gas was controlled by a gas flow meter. The condensate was characterized for its physical properties followed by elemental analysis and chemical composition analysis by Fourier Transform Infrared (FTIR) spectroscopy

Analysis of Pyrolysis Condensate

Physical and chemical analyses

The condensate obtained at the maximum yield condition was characterized for its physical properties. These properties were determined according to the standard American Society for Testing and Materials (ASTM) test methods. The properties determined were: kinematic viscosity, density, pH value, flash point, pour point and higher heating value. The elemental analysis of the condensate was conducted at Analytical Research Division of BCSIR, Dhaka. The elemental composition of the derived condensate was determined using a Carbon, Hydrogen, Nitrogen and Sulphur (CHNS) elemental analyzer of model EA 1108. Oxygen was calculated by difference.

Compositional analysis

The functional groups of the pyrolysis condensate obtained at a bed temperature of 550°C was analyzed by Fourier Transform Infra-red spectroscopy (FTIR) to identify the basic compositional groups. The FTIR instrument of model SIMADZU FTIR 8400 was used to produce the ir-spectra of the condensate derived from waste plastic. It provided the absorption spectrum in percentage incident intensity, along the wave numbers 4000 to 500 cm^{-1} . The standard ir-spectra of hydrocarbons were used to identify the functional group of the components of the derived condensate. The test was conducted in the laboratory of Department of Chemistry of Rajshahi University, Rajshahi, Bangladesh.

Results and Discussion

Characteristics of waste plastic

Table 1 shows that volatile content was 96.88 wt% of the sample. This higher percentage is usually favorable to obtain liquid by pyrolysis technology [7]. The amount of carbon was 83.93wt% of the sample. Hazardous products creating agents such as sulfur and nitrogen were not found in the ultimate analysis. The TG plot presented in Fig. 1 shows that heat propagated into the solid drove off the inherent moisture at about 110°C, which was less than 4% of the total sample weight. From the plot it was found that at a heating rate of 10°C/min, devolatilization of solid plastic initiated at about 250°C and the rate was maximum between temperature 400°C and 600°C. Around temperature 550°C devolatilization of volatile in the sample completed. From these results an idea was obtained to operate the pyrolysis system at a moderate temperature of around 550°C to obtain maximum percentage of liquid product.

Product yields

Three products were obtained from the pyrolysis of plastic. These were oily condensate, solid char and gas. The condensate was collected in two ice-cooled collectors in series. The char was collected from the reactor. The gas was flared to atmosphere and measured by difference.

Effect of operating temperature

The influence of operating temperature on the pyrolysis product of waste plastic is shown in Fig. 3. From the plotted result it is found that there is a fairly sharp optimum temperature at which the maximum yield of condensate is achieved. The condensate yield rises approximately to 40 wt% of the feed at a low temperature of 400°C to the maximum value of 70 wt% at 550°C before it drops again to about 54 wt% at 600°C. The char yield is very low and decreases steadily at around 10 wt% at the operating temperature range.

Effect of feedstock size

The studies on the effect of feedstock size on the pyrolysis products were conducted with feed size of 0-400 μm , 400-600 μm and 600-1180 μm . The effect of variation of feed size on the pyrolysis product yield is shown in Fig. 4. From the plotted result it was found that the condensate yield was not affected much by feed size variation. The highest condensate yield is found from the middle size particles (400-600 μm) for the operating temperature range.

Effect of running time

The running time of the study influenced the product yield. The variation of condensate yield with running time is shown in Fig. 5. The yield increases with time. It is found to be pyrolysed in 60 minute time after which there was no more condensate yield.

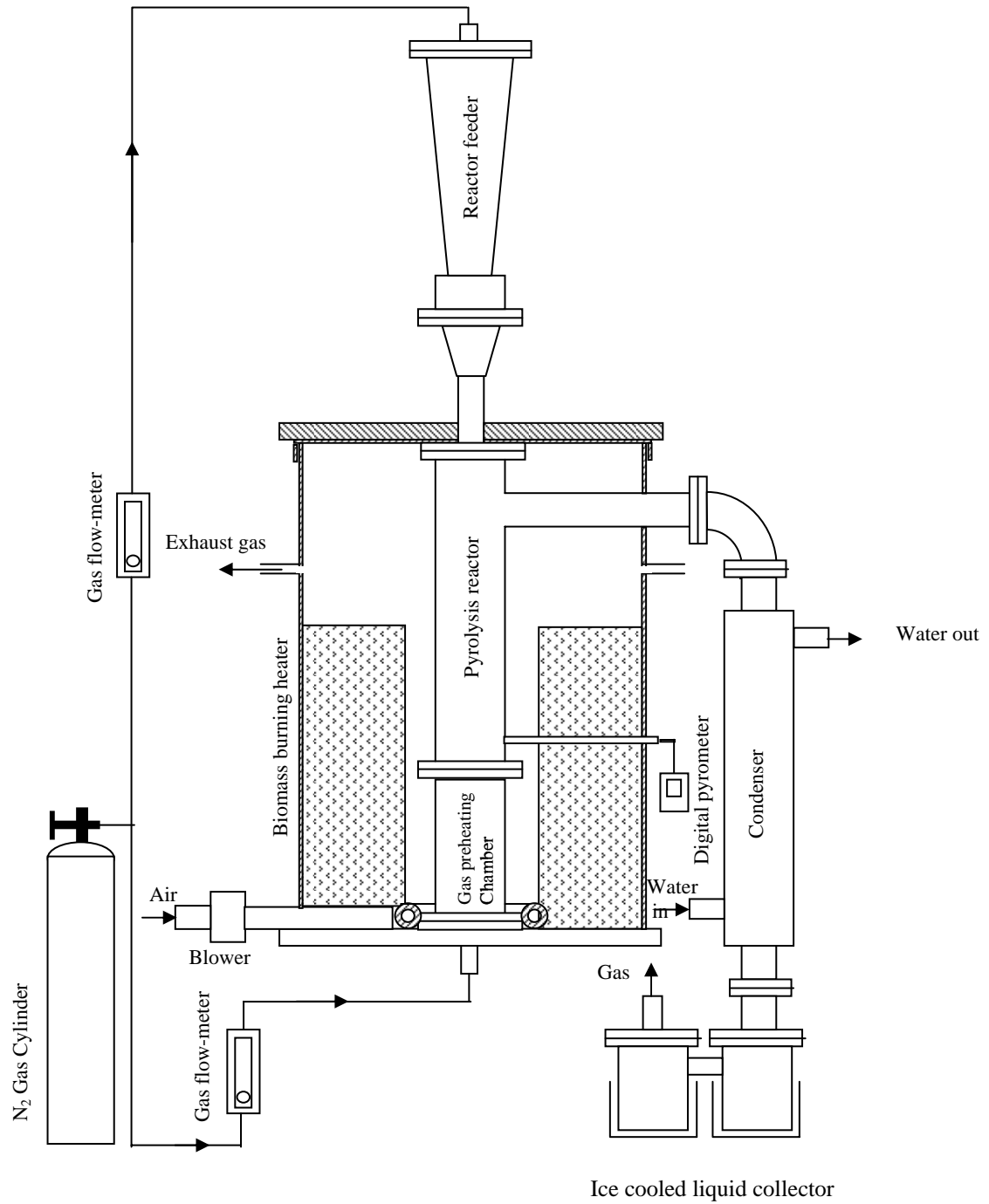


Fig. 2 Schematic diagram of fixed bed pyrolysis system

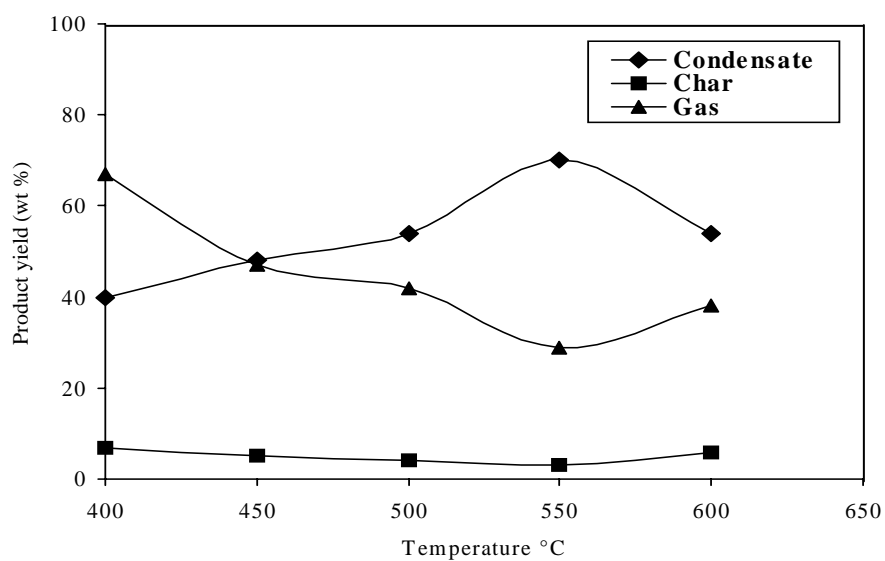


Fig. 3 Operating temperature effect on product yields for particle size of 400-600 μm.

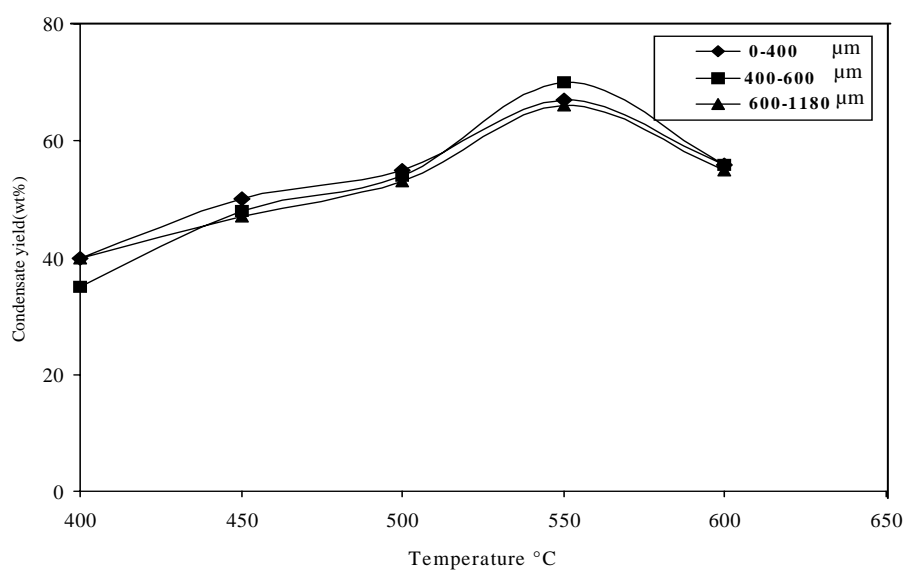


Fig. 4 Effect of feedstock size on the condensate yield at different temperature.

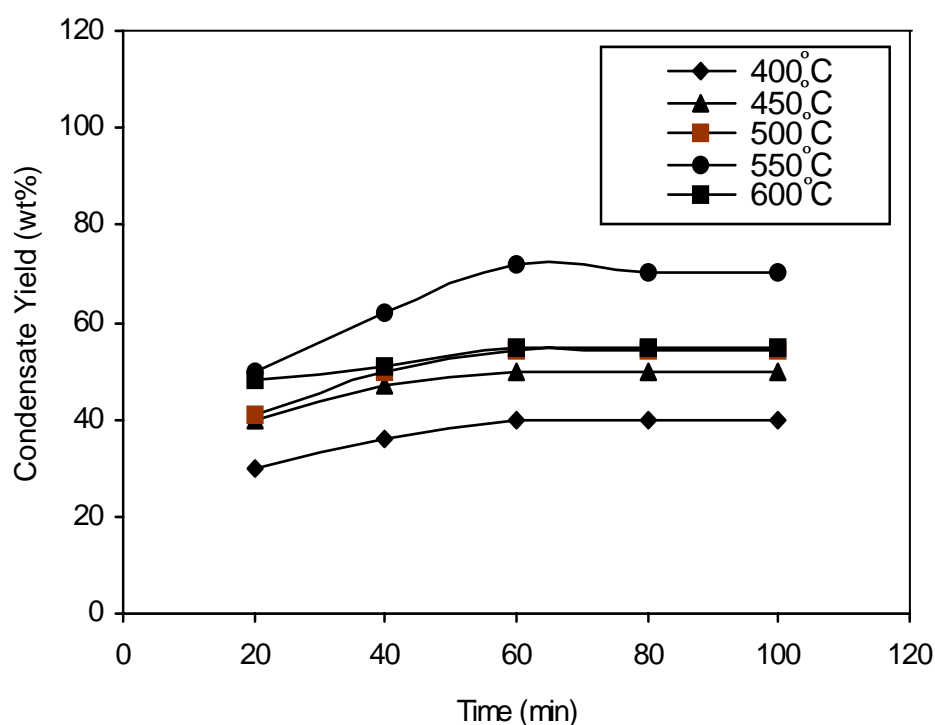


Fig. 5 Effect of running time on condensate yield for pyrolysis of waste plastic.

Physical and elemental characteristics analysis

The condensate derived from waste plastic was analyzed for some physical properties. These are presented in Table 2. The properties determined were elemental composition, higher heating value, pour point and ash content of the pyrolysis condensate at operating temperature of 550 °C.

The elemental analysis of the condensate is an important criterion for the design of a combustion plant. Utilizing this product with the help of the elemental analysis, the combustion calculation can be carried out from which the quantities of combustion air and flue gas and also the composition of the flue gas can be determined [8]. The elemental composition for carbon, hydrogen, nitrogen and sulfur was determined by adopting the standard test method. The carbon content was very high found to be of 72.20% reflecting high potential of the condensate to be a fuel.

There was no sulfur and nitrogen in the condensate. This is one of the positive aspects of pyrolytic oil [9]. This property favored that the products are not responsible for SO_x and NO_x emission both of which are undesirable in combustion process. The ash content is 0.1 %. The energy content i.e. the higher heating value is 43.5 MJ/kg. The density of the condensate is 905.0 kg/m³ similar to that of diesel fuel. The flash point of the oily condensate is lower than that of the diesel fuel at the room temperature.

Table 2 The elemental composition and physical characteristics of condensate derived from waste plastic and its comparison.

Analysis	Standard	Condensate *	Diesel [10]	Heavy fuel oil [8]
Elemental (wt%)				
C	ASTM D3176-84	72.20	86.58	85-86
H	ASTM D3176-84	14.04	13.29	11-11.5
N	ASTM D3176-84	Not detectable	65ppm	.03-.065
S	ASTM D3176-84	Not detectable	0.11	1.0-2.6
Ash	ASTM D482-IP 4	0.30	0.00	0.1
O	By difference	13.76	0.01	-
Kinematic viscosity @ 30°C (cSt)	ASTM D445-IP 71	25	2.61 [§]	200 [#]
Density (kg/m ³)	-	905.0	827.1	980
pH value	Digital pH meter	5.5	-	-
Flash point (°C)	ASTM D92-IP 36	48	53	90-180
Pour point (°C)	ASTM D97-IP 15	-14	-	25-30
HHV (MJ/kg)	DIN 51900	43.43	45.180	42-43

@ 50°C; § 20°C; * wet oil basis

Chemical composition

The FTIR spectrum of the derived pyrolytic condensate is presented in Fig. 6 and the FTIR functional groups and the indicated compositions of the condensate is presented in Table 3. The absorbance peak of O-H stretching vibration between 3750- 3120 cm⁻¹ indicates the presence of polymeric O-H in the product. The presence of alkanes is indicated by the strong absorbance peak of C-H vibration between 3100-2800 cm⁻¹, 1180-950 cm⁻¹ and C-H deformation vibration between 1400-1325 cm⁻¹. The stretching vibration of C=O between the peaks 1800-1700 cm⁻¹ indicates the presence of ketones and aldehydes. The possible presence of alkenes are indicated by the absorbance peaks between 1860-1805 cm⁻¹, 1700-1604 cm⁻¹, and 950-880 cm⁻¹ as represented by C=C stretching vibrations.

Table 3 The FTIR functional groups and the indicated compositions of pyrolytic condensate.

Frequency range (cm ⁻¹)	Group	Class of compound
3750-3120	O-H stretching	Polymeric O-H, water impurities
3100-2800	C-H stretching	Alkanes
1860-1805	C=C stretching	Alkenes
1800-1700	C=O stretching	Ketones, Aldehydes, Carboxylic acids
1700-1604	C=C stretching	Alkenes
1625-1550		Aromatic compounds
1520-1400	-NO ₂ stretching	Nitrogenous compounds
1400-1325	C-H bending	Alkanes
1310- 1200	C-O stretching bending	O-H Primary, secondary & tertiary alcohols, phenol, esters, ethers.
1180-950	C-H stretching	Alkanes
950-880	C=C stretching	Alkenes
750-650		Aromatic compounds

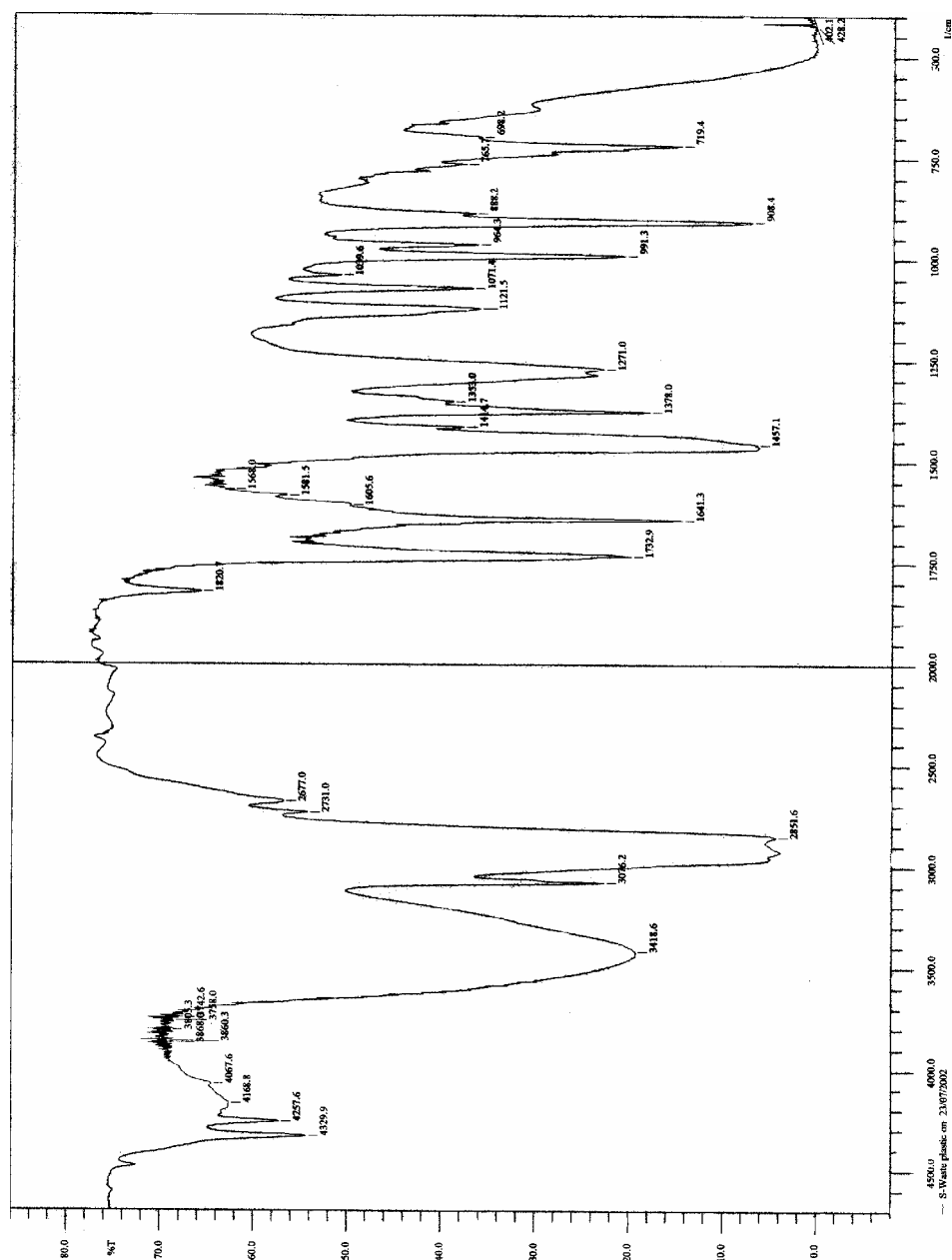


Fig. 6 FTIR spectra of condensate derived from fixed bed pyrolysis of waste plastic at an operating temperature 555°C

The presence of small nitrogenous compound is indicated by the less prominent absorbance peaks between 1520-1400 cm^{-1} . The peaks between 1310-1200 cm^{-1} suggested the presence of primary, secondary and tertiary alcohols, phenols and esters due to the C-O stretching and O-H deformation vibrations of these functional groups. The frequency of 750-650 cm^{-1} and 1625-1550 cm^{-1} , indicate the possible presence of single, polycyclic and substituted aromatics groups. The presence of hydrocarbon groups indicate that the condensate has a potential to be used as fuel.

Conclusions

The characterization study made on the condensate derived from the thermochemical conversion of waste plastic using a fixed bed pyrolysis system, has revealed the following salient points.

- i) Fixed bed pyrolysis of waste plastic has given maximum condensate yield that is 70 wt% of dry feed material at a reactor bed temperature of 550°C. With increasing operating temperature, the char production is decreasing while the gas production is increasing.
- ii) FTIR analysis shows that the condensate is dominant with hydrocarbon species.
- iii) The physical properties analysis shows that the condensate is heavy and slightly acidic in nature. The product possesses favorable pour and flash points.
- iv) The heating value of the condensate is very high and quite similar to that of diesel fuel. This shows the potential that the condensate may be used as a fuel.

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