

Catalytic pyrolysis of low density polyethylene and polypropylene wastes to fuel oils by N-clay

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Abstract. Dealing effectively with plastic wastes has been a major global challenge. Different methods have been previously employed to proffer solution to plastic wastes problem however, all showed their energetic, economic and environmental implications. In this research, catalytic pyrolysis of low density polyethylene and polypropylene wastes was carried out to proffer solution to the problem. The plastic materials were collected and appropriately prepared after which ultimate and proximate analysis was carried out on them. The clay was collected from Naka, Gwer West Local Government Area of Benue State, Nigeria, thereafter, referred to as N-clay and was appropriately prepared, then analyzed by a BET analyzer for the following properties: the surface area, which was found to be 85.418 m²/g, pore size 2.100 nm and pore volume of 0.042 cc/g. Also, the XRF determination of the chemical composition of the N-clay was done and the SiO₂/Al₂O₃ ratio was found to be 70.81/29.19. The N-clay and the plastics were then pyrolyzed in a chemical vapor deposition (CVD) reactor in the ratio 1:3 respectively, at 500 °C with residence time of 30 min using nitrogen as purge gas. The polypropylene yielded 70.34 % liquid oil, 6.43 % char and 23.23 % gas. The liquid was analyzed for functional groups, using Raman spectrometer. Physicochemical analysis was also done on the oil and it was determined that the oil had properties consistent with commercial-grade gasoline. The low density polyethylene yielded wax, instead of liquid, char and gas. Finally, it was concluded that the N-clay was suitable as catalyst for the pyrolysis of plastics and the fuel oil obtained from polypropylene pyrolysis is comparable to gasoline fuel.

Keywords: N-clay; polyethylene; polypropylene; plastic-wastes; characterization; fuel oils pyrolysis.

1. Introduction

Plastics are long chain organic compounds, containing carbon, hydrogen and few other elements, which are synthesized from petroleum products and are solid in the finished state [1, 2]. Since the 1950s when the first plastics were made, there has been a dramatic increase in the world's annual plastic consumption from around 2 million tonnes to over 200 million tonnes with a 10 % increase yearly [3]. The increment in the use of plastics over time may be attributed to its ease of use as plastics and since they are durable, versatile, low weight, resistant to corrosion, excellent thermal and electrical insulators, energy efficient, low susceptibility to chemical reactions, and low production costs; making them serve as key components for different sectors [3-5]. The properties which describe the usefulness of plastics, the life duration of plastics, and the fact that plastics are non-biodegradable in nature, pose great challenges when considering the end of the life phase of plastics, causing significant problems for waste management [4, 6].

A lot of methods were used to convert plastic wastes based on local regulations and social acceptability [7, 8]. Methods like reusability, land filling, incineration, mechanical, biological recycling and other chemical recycling approaches. All these methods showed limitations to effectively manage plastics wastes [6, 8-

10]. For instance, non-biodegradable plastic last very long, therefore, polymers manufactured nowadays will persist for decades or centuries, if not more. Even the degradable plastic has very long life span based on local environmental factors, like the extent of ultraviolet light exposure, oxygen and temperature, and the availability of suitable microorganisms for break down, thus resulting in a varying degradable rates considerably between landfills, terrestrial and marine environment. Moreover, the degradation of plastic by weathering may lead to plastic debris or monomers, and the polymers may not necessarily fully degrade in a meaningful timeframe, leaving a substantial quantity of end-time-life plastics accumulating in the landfill and as debris in the natural environment.

Again, recycling of plastics as a method for reducing environmental impact and resource depletion, fundamentally involve high levels of recycling as with reduction in use, reuse and repair or remanufacturing, can allow for a given level of product service with lower or inferior material inputs than would otherwise be required. Catalytic pyrolysis [11] is a chemical recycling method involving the conversion of polymer to recoverable, useful, and valuable chemicals such as hydrocarbon fuels or raw materials (monomers for the polymer industry), may be the appropriate method for dealing with plastic wastes [12-14]. Also, on account of countries increasing desire for energy independence, the

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increase of petroleum and petrochemical prices, and their competitiveness in energetic and transportation applications, cause a growing interest in the search for alternative fuels to fossil fuels and waste plastics pyrolysis oil is identified as one of such good alternatives [15-20].

In catalytic pyrolysis process, a suitable catalyst is used to carry out cracking reactions involving the breakdown of polymer chains when plastics are heated to high temperatures, between 350 °C and 500 °C, in the absence of oxygen, and useful low molecular weight compounds are formed [20-22]. The reactions of these polymers are due to weak bond chains which are damaged by increasing temperature, followed by the formation of free radical propagating stage. These free radicals will then separate again to form smaller ones which produce stable compounds in the form of paraffin compounds, iso-paraffins, olefins, naphthenes and aromatics with the general reaction mechanism for plastics thermal degradation [21]. From an economic perspective, reducing the cost even further will make this process an even more attractive option. This option can be optimized by reusing the catalysts and the use of effective catalysts in lesser quantities [20].

2. Experimental

2.1. Materials

Low density polyethylene and polypropylene wastes were obtained from the surroundings of the Benue State University, Makurdi, sorted, washed, dried, and shredded to small pieces. The clay, hereafter referred to as N-clay, was obtained from Naka, Gwer West Local Government Area of Benue State. It was air dried and finely ground.

2.2. Methods

2.2.1. Ultimate analysis of low density polyethylene and polypropylene. The ultimate analysis of the LDPE and PP was done according to CEN/TS 15407 and CEN/TS 15408 to determine the elemental composition of the waste plastic materials using a Perkin Elmer elemental analyzer of model, PE 2400 II.

2.2.2. Proximate analysis of low density polyethylene and polypropylene. The proximate analysis of the LDPE and PP was done according to CEN/TS 15402, CEN/TS 15403 and CEN/TS 15414-1.

2.2.3. X-Ray Fluorescence (XRF) analysis of the N-clay. The XRF analysis of the clay material was carried out with an EDXRF analyzer from Thermo Fischer Company Switzerland, model: ARL QUANT'X and serial number 9952120, to determine the N-clay chemical composition.

2.2.4. Brunauer-Emmett-Teller (BET) analysis of the clay. The BET analysis of the N-clay was done with a BET analyzer from QUANTA CHROME, model: NOVA4200e, to determine the surface area, pore size and pore volume of the N-clay.

2.2.5. Pyrolysis of low density polyethylene and polypropylene wastes. The pyrolysis of the waste plastic materials was done in a Chemical Vapor Deposition (CVD) reactor (VACUTEC of model: XD-1200NT) at

500 °C for 30 min using the clay material as catalyst, with catalyst to plastic ratio of 1:3, and nitrogen as purge gas.

2.2.6. Raman spectrometry of the fuel oil. The Raman spectrometry was used to determine the functional groups present in the fuel oil, and the Raman spectrometer was from ENWAVE OPTRONICS, model: NO-ProRAMAN-L-785-815 and serial number 186166.

2.2.7. Physicochemical analysis. The physicochemical analysis of the fuel oil was according to ASTM D1298-99^{e2}, ASTM D445-06, ASTM D92-05a, ASTM D240-02, ASTM D95-99^{e1}, ASTM D129-00 1, ASTM D189-06^{e2} and ASTM D482-03 methods.

3. Results and discussion

The results for ultimate analysis are shown in Table 1.

Table 1. Result from ultimate analysis of LDPE and PP wastes

Elements	LDPE (%)	PP (%)
Carbon	85.68	84.32
Hydrogen	14.20	14.19
Nitrogen	0.05	0.67
Sulphur	0.00	0.06
Oxygen	0.02	0.15
Chlorine	0.05	0.61

Typically, as in polymers of ethylene and propylene only carbon and hydrogen should be expected however, nitrogen, oxygen and chlorine were present in both LDPE and PP, while sulfur was found in the polypropylene sample. The presence of the additional elements in the plastic materials may be attributed to the additives included during production, since additives are usually added to impart some special properties to plastic materials such as color. Nevertheless, the carbon and hydrogen contents in both plastic materials showed higher percentages, and these make both materials suitable feedstock for pyrolysis process.

The results for proximate analysis (Table 2), showed ash (the incombustible residue) and moisture (water) contents.

Table 2. Result from proximate analysis of waste LDPE and PP

Parameter	LDPE	PP
Ash content (%)	0.83	3.34
Volatile matter (%)	95.59	94.73
Moisture content (%)	0.76	0.00
Fixed carbon (% wt)	2.82	1.93
Calorific value (MJ/kg)	46.99	46.52

Although, they were present in very small quantities, it is an indication of the presence of impurities in the samples. The observed volatile matter contents of the two plastics are very high, and this is expected since, the volatile matter content indicates the components of the plastics that are readily burnt in the presence of oxygen. The calorific values of the plastic materials are both around 47 MJ/kg, and is comparable to that of natural

gas (48 MJ/kg). The calorific value is an indication of its efficiency as fuel. The calorific values obtained are high when compared to other solid fuels like coal. Coal has calorific value of about 28 MJ/kg, and paper and wood approximately 15-16 MJ/kg.

The XRF analysis (Table 3), showed that N-clay is rich in mineral composition and the major components are silica (SiO_2) and alumina (Al_2O_3). Therefore, N-clay was a good catalyst since the presence of silica and alumina in a material makes it a suitable catalyst for pyrolysis [16, 18].

Moreover, the ratio of silica to alumina has effect on the catalyst action of the clay. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio for the N-clay is calculated to be 70.81/29.19.

Table 3. Chemical composition of N-clay

Compound	Concentration (%)
Fe_2O_3	8.25
CuO	0.01
ZnO	0.02
F	1.88

Compound	Concentration (%)
MgO	3.55
Al_2O_3	15.01
SiO_2	36.42
P_2O_5	0.21
SO_3	0.37
Cl	0.08
K_2O	1.06
CaO	0.23
TiO_2	0.88
V_2O_5	0.31
Cr_2O_3	0.01
MnO	0.13
CeO_2	0.61
Rb_2O	0.01
SrO	0.74
ZrO_2	0.02
Nb_2O_5	0.01
PbO	0.01

Barrett-Joyner-Halenda (BJH) was used to interpret the BET analysis (Figure 1).

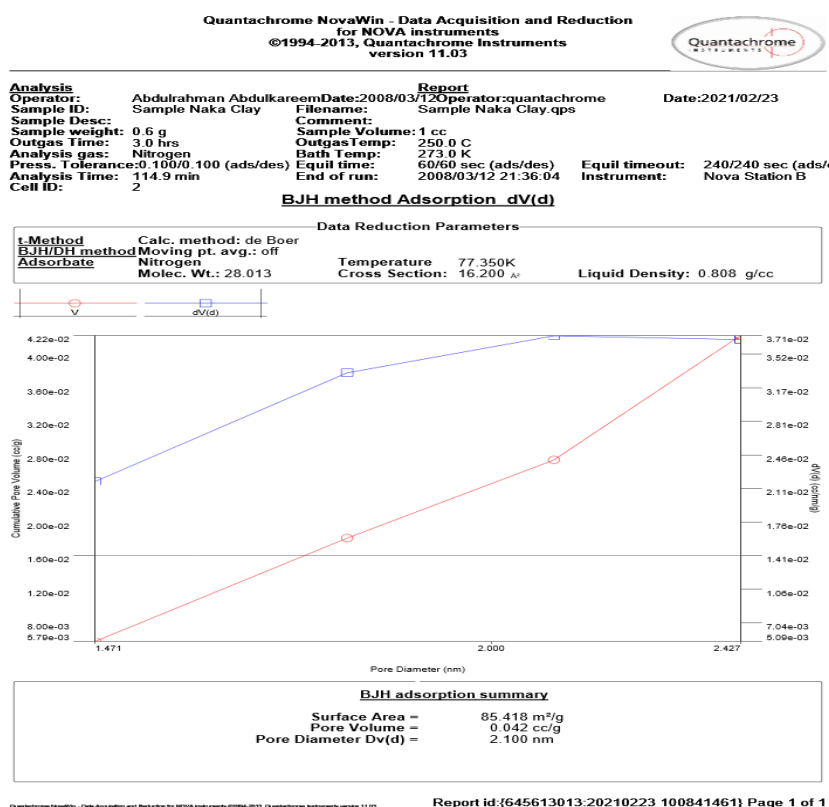


Figure 1. BJH adsorption plot for N-clay from the BET analyzer.

It is observed that the specific surface area of the N-clay catalyst is 85.418 m^2/g , the pore volume is 0.042 cc/g and the pore size is 2.100 nm. The specific surface area is relatively high when compared with the values obtained for some other clay materials (usually between 15 and 65 m^2/g), even after some modification.

Char, gas and wax instead of liquid were the products obtained from the pyrolysis of LDPE, and because at the CVD reactor, there is no possible way to collect the gas products for analysis, hence no further analysis was done on the LDPE products.

The polypropylene liquid yield (Table 4) was 70.34 wt% and it was observed that the liquid yield from catalytic pyrolysis of polypropylene under similar reaction conditions were reported to be around 65-75 wt% even with catalysts modification [23].

Table 4. Yield of pyrolysis products from LDPE and PP

Products	LDPE (%)	PP (%)
Liquid	18.50	70.34
Solid	3.17	6.43
Gas	78.33	23.23

Unfortunately, there was zero liquid yield with the pyrolysis of low density polyethylene under the same reaction conditions as the polypropylene. Rather a waxy substance was obtained with a yield of 18.50 wt%. The type of reactor used for the pyrolysis may likely account for the deviation from the expected, as chemical vapor deposition reactor, has not been reported for LDPE pyrolysis, although further study is suggested to

ascertain the cause of this observation. Also, in Table 4, the char content reported for both LDPE and PP were comparable to values reported in the literature for similar samples.

The functional groups present in the polypropylene fuel oil were determined using Raman spectrometry (Figure 2).

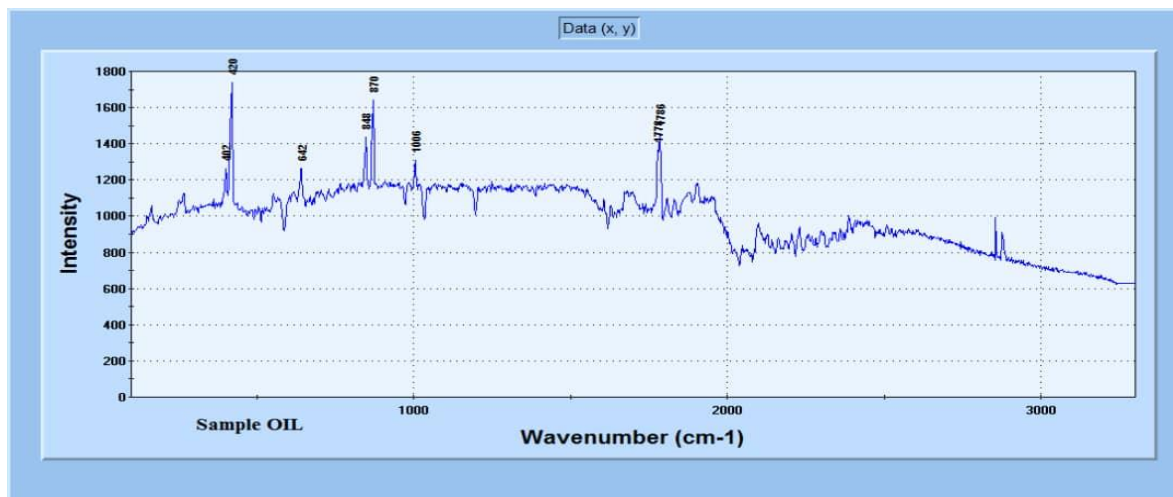


Figure 2. Raman spectra for the polypropylene fuel oil

Table 5. Functional groups present in the PP fuel oil (cm^{-1}) [24]

Functional group	Range	Peaks observed
C-H stretch (methylene group)	2800 – 3000	2854
C-H stretch (methyl group)	2800 – 3000	2876
Carbonyl compound	1750 \pm 150	1786
O-O bond stretch	820 – 890	848, 870
Phenyl substituent	600 -650	648
S-S bond stretch	400 – 500	402, 420

The Raman spectra showed the presence of other functional groups like carbonyl compounds (esters), other than the usual C-H bond stretch for hydrocarbons expected of polypropylene fuel oil (Table 5). These

other functional groups may be due to other elements found in the elemental analysis of the polymers and these compounds are consistent with those reported in literatures for similar work. For instance, the pair of peaks in the 3000-2800 cm^{-1} region are associated one with methylene, the other to the methyl group vibration; together they indicate the presence of linear alkanes (pp. 37-38 in [24]). The band near 1000 cm^{-1} is attributed to cumulated double bond (alkenes) (p. 96 in [25]), 648 cm^{-1} can also be attributed to C-S stretching vibration in diallyl disulfides together with S-S bond stretch identified in 500-400 range.

Table 6 showed the results of parameters from the physicochemical analysis.

Table 6. Physicochemical characteristics of PP fuel oil

Parameter	Value in PP	Kerosene	Diesel
Color	Brown		
Odor	Choking smell		
Density at 25 $^{\circ}\text{C}$ (g/cm^3)	0.74	0.72-0.78	0.82-0.90
Kinematic viscosity at 40 $^{\circ}\text{C}$ (cSt)	2.11	1.0-2.1	2.0-4.5
Flash point ($^{\circ}\text{C}$)	43	37-42	55-80
Calorific value (MJ)	44.73	42.70	45.81
Water content (%)	1.06		
Sulfur content (%)	0.12		
Carbon residue (%)	1.39		
Ash residue (%)	0.07		

The observed density, 0.74 $\text{g}\cdot\text{cm}^{-3}$, of the PP fuel oil is within the range of that of commercial gasoline (0.72-0.78 $\text{g}\cdot\text{cm}^{-3}$). However, it can either be for gasoline or kerosene until ASTM distillation is performed; probably, it is a larger fraction including gasoline and kerosene. The density of the oil influences its rate of consumption as fuel since high density of fuel oil means

low fuel consumption rate. Also, the viscosity of fuel affects the rate of its consumption, engine temperature and load on the engine. The viscosity of the PP fuel oil is 2.11 cSt, and this was observed to be within the kerosene fuel range. Flash point is the lowest temperature at which a fuel can vaporize to form an ignitable mixture in air, and it is used to characterize the

fire hazards of fuels. The observed flash point for the fuel oil was 43 °C and only slightly higher than the maximum flash point of kerosene by one unit. The calorific value observed for the fuel oil is higher than that of commercial gasoline indicating that the oil is of higher efficiency. The water content, sulfur content, ash and carbon residues observed may be due to the presence of impurities in the initial feedstock. Although, they are present in very small and acceptable quantities in the fuel oil however, they are undesirable properties of fuel oil.

4. Conclusions

The results obtained from the ultimate and proximate analysis of LDPE and PP, the BET and XRF analysis of N-clay showed clearly that N-clay is a suitable catalyst abundantly available for the catalytic pyrolysis of polypropylene wastes. The pyrolysis product yield, the Raman spectrometry and the physicochemical analysis of the fuel oil suggests that municipal plastic wastes are suitable for chemical recycling by catalytic pyrolysis using the N-clay. Furthermore, with the reaction conditions employed, good yield was achievable for polypropylene pyrolysis. Therefore, the liquid oil can be used as fuel oil or as a component for gasoline/kerosene formulation.

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Conflict of interest

The authors declare that they have no competing interest.

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