

(RESEARCH ARTICLE)



Pyrolytic conversion of waste plastics using African apple seed-based activated carbon catalyst

Patrick Isicheli ^{1*}, Akuma Oji ² Obumneme Okwonna ² and Peter Odiboroghene Muwarure ¹

¹ NLNG Centre for Gas, Refining and Petrochemicals Engineering, Nigeria.

² Department of Chemical Engineering University of Port Harcourt, Nigeria.

Global Journal of Engineering and Technology Advances, 2023, 16(03), 207–218

Publication history: Received on 18 August 2023; revised on 26 September 2023; accepted on 29 September 2023

Article DOI: <https://doi.org/10.30574/gjeta.2023.16.3.0199>

Abstract

This research aimed to conduct a pyrolytic conversion of waste plastics using an African seed-based activated carbon catalyst. The process description to produce activated carbon from African star apple includes removing and drying seed husks, grinding, and preparing activated carbon (AC). The plastic waste materials used for the catalytic pyrolysis process were waste Low-Density Polyethylene (LDPE) and High-Density Polyethylene (HDPE) plastic, which were sourced from Liberation Stadium Road, GRA Phase IV, Port Harcourt, Rivers State. The effects of activated carbon (AC) as a catalyst on fuel production and gasification efficiency were also evaluated. Proximate and ultimate analyses were conducted on the AC to determine its composition. The results showed that the AC had high fixed carbon content and low volatile matter and ash contents. The experiments also showed that the products' density, calorific value, cetane number, and kinematic viscosity were within the range of diesel fuel specifications. However, the water, flashpoint, acid number, ash, and nitrogen content were higher than diesel fuel. The addition of AC catalyst improved the properties of the pyrolyzed products by reducing the water content, acid number, and ash content.

Keywords: Pyrolytic Conversion; African apple seed; Catalyst; High-Density Polyethylene (HDPE); Low-Density Polyethylene (LDPE); Activated Carbon

1. Introduction

Plastics are petroleum-derived from hydrocarbons that can be converted into liquid fuel through pyrolysis. Pyrolysis involves heating plastics to a high temperature in an oxygen-free environment, which causes the plastic to break down into smaller molecules and produce gas, oil, and solid residue. This process is beneficial for the environment as it helps reduce the amount of plastic waste that goes into landfills and oceans. Additionally, it provides an alternative fuel source for transportation and other energy needs. With the rise in human population, rapid economic growth, continuous urbanization, and lifestyle changes, plastic waste production and consumption is growing alarmingly. Furthermore, the short life cycle of plastic hastens the daily processing of plastic waste. Plastic production in the world is estimated to be about 300 million tons per year, steadily growing (Heikkinen et al., 2004). Petrochemical hydrocarbons and biodegradable additives like flame retardants, stabilizers, and oxidants are used to make plastics. Although there are many different methods for recycling plastic waste, open or landfill disposal is common in most developing nations (Bernando, 2011). The plastic waste provides a home for rodents and insects in landfills that can harbour various diseases. Additionally, the price of recycling projects may increase due to the costs of labour, transportation, and maintenance (Prabir, 2010). In addition, the amount of land available for landfills is declining due to rapid urbanisation, particularly in cities.

The issue of energy and environmental pollution has become more prominent in recent years due to population growth, urbanization, and rapid industrialization. These factors have led to an increase in the consumption of fossil fuels and,

* Corresponding author: Patrick Isicheli

subsequently, a rise in pollution levels. To address this problem, significant investments have been made in the search for alternative or elective fuels that can help reduce our reliance on petroleum derivatives (Dogan et al., 2012). One area of concern is the increasing production of waste plastics, which make up a significant portion of solid waste in both developed and developing countries. Cleaning plastic debris from cars is a challenging task, and the production of plastics continues to rise. More than 80% of solid waste is estimated to comprise waste plastics. If not managed correctly, this can have a detrimental impact on the environment (Dogan et al., 2012).

To tackle this problem, waste-to-energy techniques are being explored as a viable alternative to conventional fuels. These techniques involve converting waste materials into energy, which can be used to power vehicles or generate electricity. This approach not only helps to reduce our reliance on fossil fuels but also has the potential to reduce the amount of waste that ends up in landfills (Muwarure et al., 2023).

In addition to waste-to-energy techniques, alternative fuels for internal combustion engines are also being explored. These fuels include alcohol, biodiesel, and plastic fluids. While these fuels are not without their challenges, they offer a potential solution to reducing our reliance on conventional fuels and the environmental impact associated with their use (Park et al., 2012).

The search for alternative fuels and waste-to-energy techniques is an important step towards reducing our reliance on fossil fuels and addressing the problem of environmental pollution. While these approaches are not without their challenges, they offer a glimmer of hope for a more sustainable future. It is up to individuals, governments, and businesses to work together to make the necessary changes to ensure a healthier planet for future generations (Dogan et al., 2012).

Recycling materials that would otherwise end up in a landfill or incinerator can generate energy (Murugan et al, 2008). Because most plastic waste is currently disposed of through landfilling or storage, massive quantities of land area are required. Using these methods, such as landfills and reusing, may pose serious risks to human and environmental health. Only a small percentage of waste plastic is recycled into new products, such as filters for black-top streets or raw materials for producing supplementary goods, such as recovered elastic, phoney reefs, or barriers. As a result, waste plastics can be regarded as an energy asset (Okpanachi et al., , 2023).

As a result, plastic waste may be an appropriate candidate for warm removal (Karatas et al, 2013). Because of these properties, they are well-suited for heated cycles such as pyrolysis and gasification (Portofino et al, 2013). Regular elastic (polyisoprene) and polybutadiene elastic (polyisoprene) are the two most common types of plastic (Williams, 2013). In addition to energy and carbon materials, a wide range of materials can be recovered for reuse. In this investigation, traditional pyrolysis units will be used to employ waste plastics that can be converted into gas and fuel oil and evaluate the physiochemical properties of the gas and oil. Pyrolysis is a widely used technique for converting waste plastic into energy in the form of solid, liquid, or gaseous fuels. Pyrolysis is the thermal decomposition of plastic waste in the absence of oxygen at various temperatures (300-900°C) to produce liquid oil gas and solid char (Kukreja, 2009). Pyrolysis is the thermal decomposition of long-chain organic materials in inert atmospheres, with or without a catalyst. The long chains of organic materials treated become smaller and less complex by regulating the process's heat flow and pressure (Masanet et al., 2002). A longer residence time is typically required with less intense heat, and the byproducts of pyrolysis are typically tars (a mixture of aromatic hydrocarbons with a molecular weight 7 greater than benzene), gases, and char (Fakhrhoseini and Dastanian, 2013). Flue gas cleanup is unnecessary for pyrolysis because the released flue gas is frequently processed before use (Bridgwater, 2012). Additionally, it produces essential products for petrochemical and petroleum refining processes, which can jeopardise the dependability of petroleum processing (Heikkinen et al., 2004). Pyrolysis is commonly associated with producing valuable tars (liquid oils and waxes) at temperatures ranging from 500 to 650oC, with yields ranging from 75 to 80 percent. Because it reduces greenhouse gas (GHG) emissions, specifically carbon dioxide, pyrolysis is a more environmentally friendly alternative to landfilling (CO₂). Pyrolysis has more environmental benefits than other municipal solid waste treatment methods. Because pyrolysis occurs in an inert, oxygen-free environment, it does not generate dioxins because of product reactions with oxygen (Abnisa et al., 2014; Zannikos et al., 2013; Hernandez et al., 2007; Heikkinen et al., 2004). Pyrolysis produces a high calorific value fuel readily marketed and can be used in gas engines to generate electricity and heat (Ahmad et al., 2014). Pyrolysis has proven to be a very profitable investment, with internal rate of returns (IRR) exceeding 30% in industrial economies of scale schemes, just like other thermochemical techniques (TCT) techniques like hydrogenation (Park et al., 2012; Hong et al., 1993). The non-condensable fraction of pyrolysis-produced gases has a very high CV and can be used to reduce the overall energy requirement of the pyrolysis plant (Abnisa & Wan Daud, 2014). Since pyrolysis requires fewer feedstock pre-treatment steps than other treatment methods, it is also more affordable. The study's comparative evaluation section will cover the relationship between pyrolysis and other thermal and catalytic plastic solid waste chemical treatment methods in more detail. The type of feeds and catalysts used, along with the process

conditions, greatly impact pyrolysis. To thoroughly understand the process and its major influencing factors on the final products, this study will present and objectively evaluate the pyrolytic conversion of waste plastic using African apple seed base activated carbon as catalyst.

2. Material and methods

2.1. Material

The raw materials (waste Low-Density Polyethylene (LDPE) and High-Density Polyethylene (HDPE) plastic) used for the catalytic pyrolysis process were sourced from Liberation Stadium Road, GRA Phase IV, Port Harcourt, Rivers State.

Below are the list of materials and tools used during the experimental procedure.

- Low-Density Polyethylene (LDPE) plastic
- High-density polyethylene (HDPE) plastic
- Digital Weighing Balance (OHAUS Scout pro-2000 g),
- Mechanical Stirrer (JENWAY 1000 Hot Plate and Stirrer ST15 OSA, UK),
- SVAC2 Compact Vacuum Drying oven,
- 1.7 Cubic Foot, 240 oC, Model SVAC2,
- Model F6018,
- Thermo Scientific Thermolyne A1 Premium Muffle Furnace - 208V-FEI-QUANTA 200.
- African Star Apple seed shell.
- Mercury-in-glass Thermometer (GH Zeal LTD, 76mm 0-360°C),
- Conical Flask (250 mL),
- Measuring Cylinder,
- Beaker (500 mL),
- Retort Stand, Pipette (25mL), Plastic containers for samples, Mortar pestle, Spatula, Stopwatch.
- De-ionized water and Phosphoric acid solution (14.7M, available in the laboratory)

2.2. Process Description for Activated Carbon production

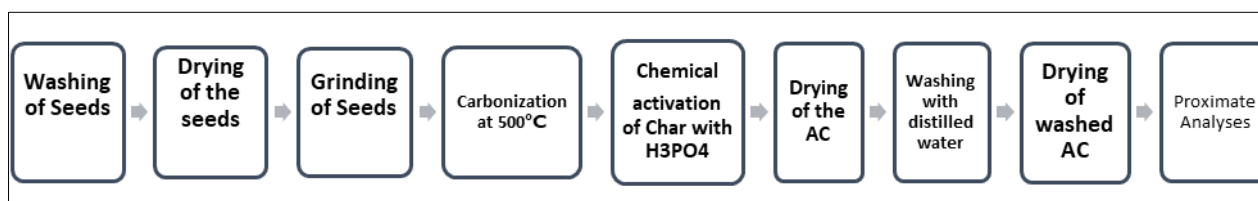


Figure 1 Flowchart of procedures for producing activated carbon from African star apple

- Removal and drying of seed husks: The seed kernels of the African star apple were physically torn apart from fleshy fruit, retrieved, and washed to remove grease and debris and then dried for three days in the sunlight, after which it was dehydrated in an oven at temp 105 °C for 3 hours to ensure all effective removal of all water residue in the seeds.
- Grinding: The dried precursor was separated into three sample shells and ground using mortar and pestle, and then the ground kernels were ground further to make particle size of -6 to +40 mesh.
- Preparation of activated carbon: Accurately weighed samples of dried African Star Apple seed shells were carbonized in crucibles at 500 °C in the furnace. The charcoal product obtained was ground and sieved to 2mm size. A solution of known concentrations of 0.8 M of Phosphoric acid (H₃PO₄) was made. Three separate 10g portions of the African Star apple samples were stirred and left to be soaked separately in 100 mL of 0.8 M H₃PO₄, respectively for 24 hours. The sample was labeled ABD1 before being heated in the oven at 105 oC for 2 hours. The activated product was then cooled to 27 oC and washed with warm distilled water until it reached a pH of 7 to remove any undiluted residue of phosphoric acid after which the precursor was dried in an oven at a temperature of 105 0C for 1 hour. Finally, the dried antecedent was ground and sieved to get a molecule size of 125-150µm. It was stored in plastic containers for further use.

2.3. Gasification of HDPE and LDPE using activated carbon as catalyst

The gasification process consists mainly of a feeding system, two reaction zones, a char separation system, and a quenching system. The reaction zones consist of a bubbling fluidized bed gasifier and a tar-cracking reactor, which are divided by a distributor. The bubbling fluidized bed reactor was designed to have a short freeboard length to induce physical removal of coke formed on the surface of the distributor by impact of the fluidized bed material. The tar-cracking reactor is a packed bed reactor filled with AC. The two reactors have the following dimensions: fluidized bed reactor (height: 380 mm, inner diameter: 160 mm) and tar-cracking reactor (height: 430 mm, inner diameter: 160 mm). The diameter of the tar-cracking reactor is larger than that of the fluidized bed reactor to increase the contact time between the gas leaving the fluidized bed reactor and active carbon bed and prevent the sweeping of active carbon (or reduce the superficial velocity of the gas) from the tar-cracking reactor. Electric heaters, which cannot be easily adopted in commercial processes for economic reasons, are used to heat both reactors in the current bench scale set-up because of simple construction and high controllability. Because reactions for tar cracking are endothermic, energy supply for the reactions should be demanded. Most of the energy supply for tar cracking in the UOS two-stage gasification process can be provided from the energy coming out from the fluidized bed gasifier which is directly connected to the tar-cracking reactor. When air or oxygen is used as a gasifying agent, oxygen from the fluidized bed gasifier can also be used for tar cracking. In the real applications of the UOS two-stage gasification process, a dual loop gasification system can be adopted for energy supply for the steam gasification of the fluidized bed gasifier. The char separation system consists of a cyclone and a hot filter to remove particulates in the syngas larger than 10 and 2 μm , respectively. The quenching system consists of a series of water-cooled condensers. Finally, an EP can be used additionally to remove tar in some runs.

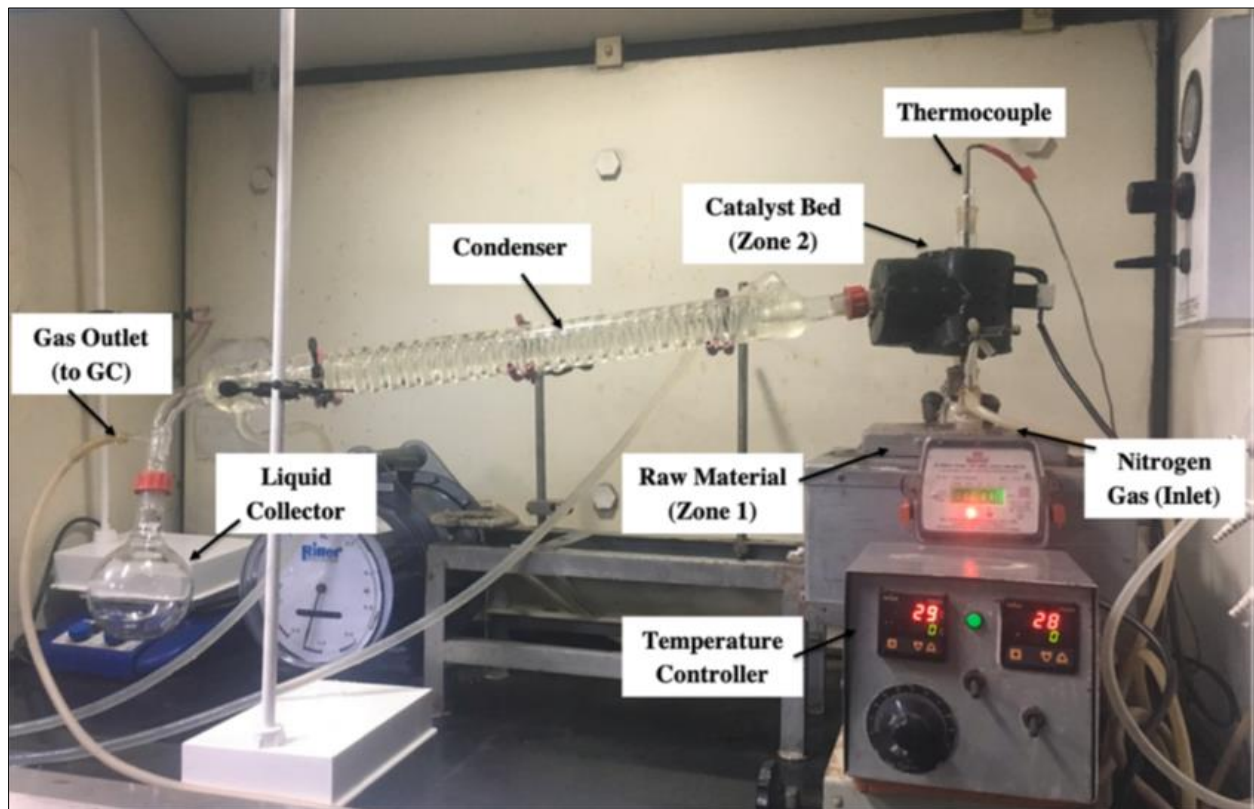


Figure 2 Pictorial representation of the pyrolysis set up

2.4. Physicochemical properties of the pyrolysis oil

Some parameters were analysed from the diesel fuel obtained via pyrolysis of the waste plastics (HDPE and LDPE) in comparison with the diesel fuel, following various ASTM methods as shown in Table 1.

Table 1 Test method for LDPE and HDPE

Parameter	Method
Density	ASTM D4052
Calorific value(mJ/kg)	ASTM D240
Cetane number	D613-84
Water content (mg/g)	ASTM D6304
Flash point	ASTM D93
Acid number (mg KOH/g)	IP 139
Kinematic viscosity @ 40	D445-04E02
Ash content	IP 391
Aromatic content (%)	IP 391
Pour point	D97-05A
Carbon content (wt.%)	ASTM D5291
Hydrogen content (wt.%)	ASTM D5291
Oxygen content (wt.%)	ASTM D5622
Sulphur content (wt.%)	ASTM D5453
Nitrogen content (mg/kg)	ASTM D4530
Carbon residue (wt.%)	ASTM D4530
LHV (MJ/kg)	ASTM D240

2.4.1. Experiment conditions

In all experiments, feed rates were almost identical at approximately 8.3 g/min, and the gasification time was 60 min, except for Run (240 min). The reaction temperatures of the fluidized bed gasifier and tar-cracking reactor for all runs were maintained at approximately 790 and 840 °C, respectively. The amounts of natural olivine and active carbon were 2200 and 1500 g, respectively. Steam as a gasifying agent was preheated to approximately 600 °C before being fed into the gasifier. The supply rate of steam was varied in the range of 12.5–20.8 g/min, which corresponded to an S/F of 1.5–2.5 and 2.8–4.6 Umf (calculated minimum fluidization velocity). The S/F was calculated according to Eq. (3):

$$\frac{S}{F} = \frac{m_s}{m_f} \dots\dots\dots 2.1$$

Where mS and mF are the mass flow rates of steam and feed material (g/min), respectively. The contact time (t_c) between the syngas and the active carbon bed in the tar-cracking reactor was calculated using Eq. (4):

$$t_c = \frac{V_{ac} \times (1 - \epsilon)}{V_g \times \frac{T_{rxn}}{T_0}} \dots\dots\dots 2.2$$

Where V_{ac} is the volume of the active carbon bed in the tar-cracking reactor (m³), is the voidage of the active carbon bed (0.55 in this study), V_g is the volumetric flow rate of produced gas (m³/s), and T_{rxn} and T_0 are the temperatures of reaction and outlet (K), respectively. The calculated contact time was approximately 1 s. Other reaction conditions are summarized in Table 3. Runs 1 and 2 were conducted without and with AC to investigate the effects of AC on the syngas quality. The results of Run 2 showed the role of AC in tar removal and hydrogen production. Runs 2 to 4 were performed to examine the influence of the S/F on syngas composition and gasification efficiency. In the runs, the S/F was increased from 1.5 (Run 2) to 2.5 (Run 4). Run 5 was conducted without EP. Comparisons between Runs 2 and 5 revealed the difference of quality of the syngas obtained with and without EP. A hook-type distributor, which was located between the fluidized bed gasifier and the tar-cracking reactor, was used in Runs 1–5. In Runs 6–8, a mesh-type distributor was used. When the mesh-type distributor was applied, dolomite grains (800 g) as a guard bed material were applied directly above the distributor to prevent AC from falling through the mesh pores. The main aim for the use of the mesh-

type distributor was to investigate how the distributor resists the formation of coke on it. Illustrations of the hook- and mesh type distributors are presented in Fig. 3. Run 7 was conducted with AC regenerated in situ. The regeneration test was performed simply by stopping feeding at an interval of 20 min. During the in-situ regeneration, the AC was treated with steam for 10 min. Comparisons between Runs 3 and 7 revealed the effects of in situ regeneration of AC on the syngas quality and the textural properties of the AC. In Run 8, a long-term operation (4 h) was carried out with repeated regeneration of AC using steam at an interval of 20 min. Cold gas efficiency (CGE), carbon conversion efficiency (CCE), and condensed tar removal efficiency (CTRE) was calculated for each run to evaluate the performance of the UOS two-stage gasification process as follows:

$$CGE (\%) = \frac{V_g \times LHV_g}{M_f \times LHV_f} \times 100 \dots\dots\dots 2.3$$

All gasification products were divided into four portions: syngas, char, condensate liquid, and condensed tar. The condensate liquid was the liquid product excluding the condensed tar. The difference between the weight of condensers, tubes, and EP before and after gasification was first determined in measuring the amount of condensed tar. Then, to separate condensed liquid from condensed tar, the collected liquid product was evaporated in an oven at 105 °C for 24 h. The weight of the remainder was designated as the amount of condensed tar. The calorific values of char, condensate liquid, and condensed tar were determined using a calorimeter (Model 6100, Parr) to establish the energy balance. Syngas was analyzed using gas chromatography (GC: 7890A, Agilent Instruments)-thermal conductive detector (TCD) and GC-flame ionization detector (FID) for N₂, H₂, CO, CH₄, CO₂, and light hydrocarbons, respectively, with argon as the carrier gas. The types of columns used were Carboxen 1000 (TCD) and HP-plot Al₂O₃/KCl (FID). The tar content in syngas, defined in this study as the sum of hydrocarbons with a molecular weight higher than that of benzene, was analyzed using GC-FID. Additionally, AC's specific surface areas and pore size distributions were measured using a Brunauer–Emmett–Teller (BET) surface area and pore size analyzer (BELSORP mini II).

Table 2 Condition for steam gasification

Parameter	HDPE	LDPE
Activated carbon	1000 g	1000 g
Tar-cracking reactor temp. (°C)	800	800
Steam to fuel ratio (S/F)	2.5	2.5
Gasification time (min)	60	60
Fluidized bed reactor temp. (°C)	790	790

3. Results and discussion

3.1. Proximate and Ultimate analysis of the Activated Carbon produced from the African apple seed and used as the catalyst

Table 3 Features of the activated carbon

Proximate analysis (wt.%)^a			
Fixed carbon	Volatile matter	Moisture	Ash
64.90±1.14	22.56±0.01	0.08±0.01	17.72±0.75
Ultimate analysis (wt.%)^b			
Hydrogen	Nitrogen	Carbon	Oxygen
0.74±0.24	0.34±0.04	77.99±1.01	2.23±0.02

Table 3 presents the proximate and ultimate analysis of the activated carbon used to produce hydrogen via fluidized bed catalyst using LDPE and HDPE as feed materials, respectively. From the proximate analysis, the fixed carbon and volatile matter are 64.90 and 22.56, respectively, with a low moisture content of 0.08. The ultimate analysis result showed that the activated carbon contains elements such as high carbon, hydrogen, oxygen, and Nitrogen. The presence

of high carbon content indicates that it is a suitable catalyst capable of producing a high hydrogen content. The catalyst properties showed that it can produce high-quality diesel fuel from plastic pyrolysis. The carbon and hydrogen content are 77.99 and 0.74, respectively.

3.2. Experimental results of LDPE and HDPE biofuel with diesel fuel

Table 4 presents the experimental results obtained from the pyrolysis of waste plastic materials with and without catalysts for diesel production, and the works were compared with the conventional diesel fuel. Various ASTM methods were used to determine the physicochemical properties of the fuel in terms of density, calorific value, kinematic viscosity, flash, pour and fire point temperature, ash content, residue etc.

The density of pyrolyzed LDPE and HDPE without catalyst are lower with 800 and 797 kg/m³, when compared with the diesel fuels using ASTM D4052. The densities of the plastic materials were very low compared with the works with a catalyst, the effect of catalyst addition increases the density of the plastic oil, which are 809 kg/m³ (HDPE) and 810 kg/m³ (LDPE), which is close to the conventional diesel fuel.

The cetane number of the pyrolyzed plastics without catalyst (LDPE and HDPE) is far lower compared to the fuel with catalyst. The values of LDPE and HDPE are 49 and 47 respectively. The addition of catalyst, however, increases the cetane number of the fuel which is close to that of the diesel fuel. The HDPE and LDPE properties in relation to the cetane number with catalyst addition are 52 and 53, while that of the diesel fuel is 53, this is an indication of the suitability of the fuel as a replacement with the diesel fuel.

When the fuel viscosity is low, it improves the burning properties of the fuel, thus improves the brake thermal efficiency and low emissions such as CO, NO_x, and hydrocarbon emissions. The kinematic viscosity of the fuel without catalyst is higher than those with catalyst, in other words, the effect of catalyst lowers the kinematic viscosity of the pyro fuel. From table 4.2, the HDPE and LDPE kinematic viscosities are 2.4 and 2.38 (without catalyst) and 2.23 and 2.20 with catalyst. Other properties such as the flash point of the pyro oil, which is very close to the conventional diesel fuel, the values include 73 and 70 °C, while the diesel fuel is 67°C.

Table 4 Experimental results comparing the pyrolyzed LDPE and HDPE with and without catalyst

Parameter	Method	HDPE (without cat.)	HDPE (with catalyst)	LDPE (without catalyst)	LDPE (with catalyst)	Diesel
Density	ASTM D4052	793	809	800	810	811
Calorific value (mJ/kg)	ASTM D240	41880	41790	41850	41700	42000
Cetane number	D613-84	47	52	49	53	53
Water content (mg/g)	ASTM D6304	790	756	762	456	65
Flash point	ASTM D93	97	73	93	70	67
Acid number (mg KOH/g)	IP 139	21	15	9	6	0
Kinematic viscosity @ 40	D445-04E02	2.4	2.23	2.38	2.20	2.33
Ash content	IP 391	0.106	0.104	0.106	0.092	<0.001
Aromatic content (%)	IP 391	35.5	20.4	22.6	30.4	29.5
Pour point	D97-05A	1	-2	-5	1	-4
Carbon content (wt.%)	ASTM D5291	87.9	86.00	86.14	87.27	86.57

Hydrogen content (wt.%)	ASTM D5291	8.5	9.5	9.7	8.9	13.39
Oxygen content (wt.%)	ASTM D5622	1.3	2.1	2.8	2.7	0.05
Sulphur content (wt.%)	ASTM D5453	0.155	0.102	0.125	0.092	0.0014
Nitrogen content (mg/kg)	ASTM D4530	620	527	476	368	44
Carbon residue (wt.%)	ASTM D4530	2.03	1.36	1.98	2.39	<0.01
LHV (MJ/kg)	ASTM D240	38.3	39.5	38.8	39.8	42.9

3.3. Experimental result of steam gasification of LDPE and HDPE plastic materials with and without the AC catalyst

Table 5 shows the gasification results in terms of compositions of identified pyrolysis gases, tar contents and LHVs of all traceable gases, and gasification efficiency. The values for the contents of gas and tar in Table 5 are average values from the gas analysis. As shown in Table 5, all gases obtained at a gasification duration of approximately 1 h with AC contained tar contents less than 25 mg/Nm³ and had LHVs of approximately 12 MJ/Nm³, CGEs within the range of 70–84%, CCEs within 46–55%. The amount of hydrogen present with catalyst is higher without the catalyst as shown in Table 5. Other associated gases from the pyrolysis process from the two plastics include N₂, CO, CO₂, CH₄ etc. The selectivity of hydrogen is quite high, when compared to others. Having a value of 49.29 and 45.28 vol. %.

Table 5 Experimental result of steam gasification of LDPE and HDPE plastic materials with and without the AC catalyst

Parameter	LDPE (without catalyst)	LDPE (with catalyst)	HDPE (without catalyst)	LDPE (with catalyst)
Composition (vol.%)				
CO ₂	6.02	5.39	6.63	6.27
N ₂	5.93	4.95	5.84	4.32
CO	10.38	7.37	10.01	9.24
H ₂	36.93	49.29	34.93	45.28
CH ₄	24.27	19.17	23.93	25.38
C ₂ H ₂	-	-	-	-
C ₂ H ₄	0.88	0.64	0.97	0.73
C ₂ H ₆	0.05	0.01	0.07	0.02
C ₆ H ₆	0.03	-	0.05	0.01
Tar in gas (mg/Nm ³)	-	-	-	-
LHV (MJ/Nm ³)	27.29	11.03	29.20	13.00
Gasification Efficiency (%)				
CGE	57.20	78.20	51.29	72.29
CCE	43.48	44.37	42.93	43.39

3.4. Effect of Active Carbon on gas composition and gas efficiency

The hydrogen production in the LDPE was very high: the hydrogen yield was approximately 150 g/kg, and the hydrogen content in the syngas was approximately 66 vol%. Because hydrogen has the highest energy density per mass of any fuel (approximately 120 MJ/kg) [26], the energy of the hydrogen of LDPE was very high. Figure 3 shows shares of gas components in output energy. As can be seen in the figure, hydrogen occupies about (or above) the half of gas energy in most experiments. The CO, CO₂ and other gases present the associated gas, which is quite low in the reaction as presented in Figure 3. Increase in hydrogen yield, for the LDPE (with catalyst), causes an abrupt reduction of other gases, which may be due to the pores of the activated carbon as well as the morphology of the catalyst in the pyrolysis reactor. For HDPE (with catalyst), the vol. % of hydrogen is quite high, but lower than that of the LDPE, probably due to the morphology of the plastics materials as well as the reaction conditions. Catalyst has great influence on the process reaction. Other factors could be particle size of the feedstock and their respective reaction conditions.

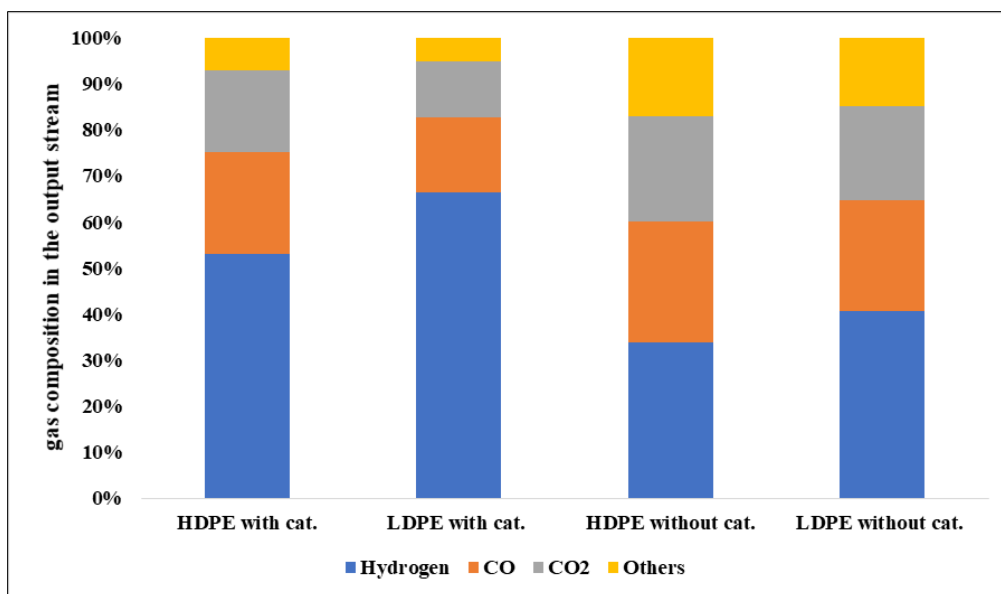
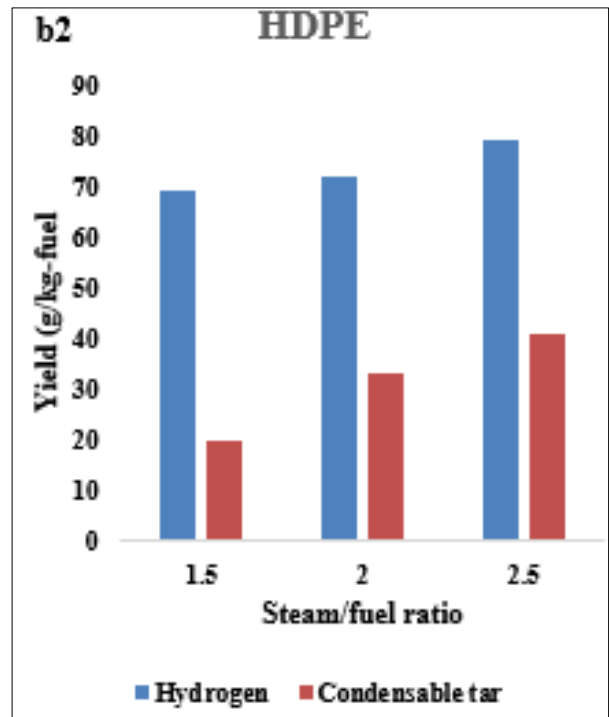
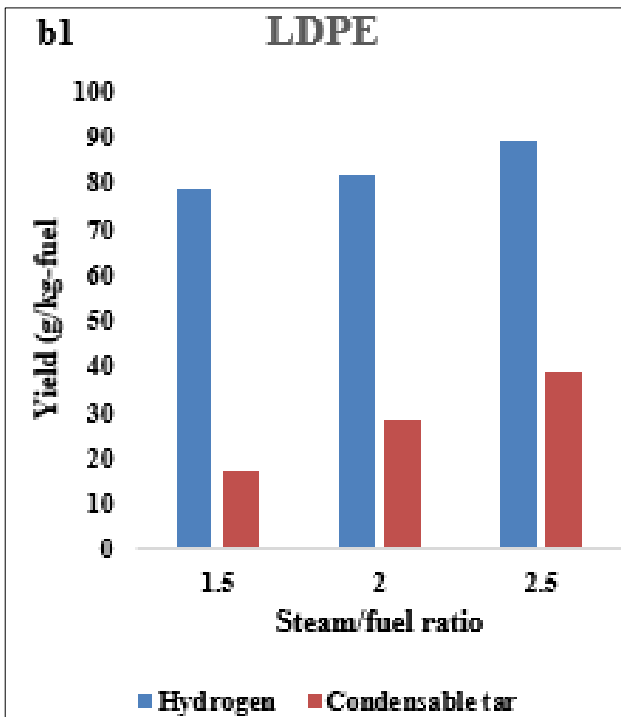
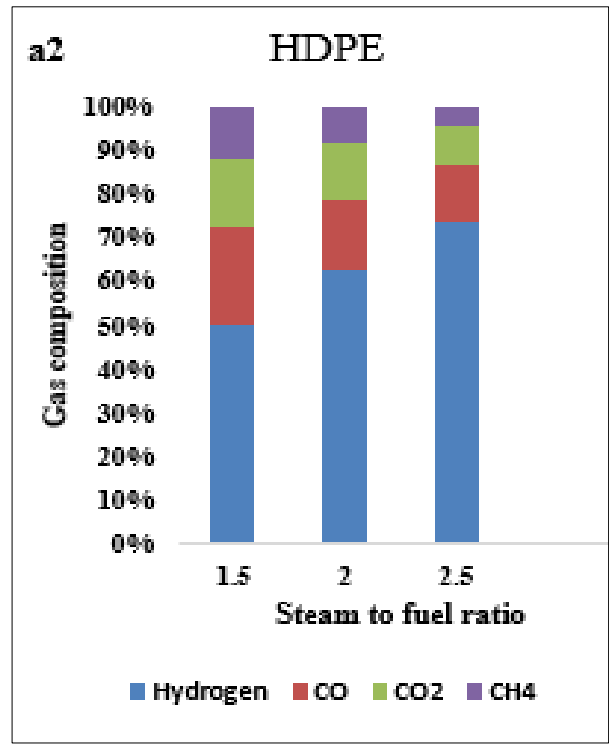
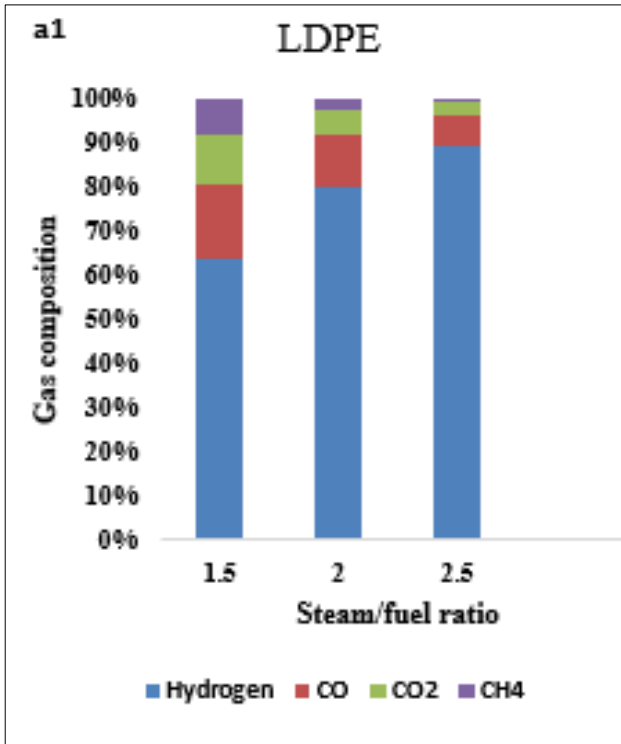


Figure 3 Gas composition of all tested plastics type

3.5. Effects of steam-to-fuel ratio

For all plastic materials (with and without catalyst), the effects of steam to fuel ratio (S/F) was examined between 1.5–2.5 as shown in figure 4.2. Various gas compositions were analyzed by the GCMS in terms of the S/F ratio of the feed material. Properties analyzed include the gas compositions, yields of gases and condensed tar, and gasification efficiency. The compositions of gas changed significantly within the S/F range (Fig. 4.2). With increasing the S/F ratio, CO₂ was slightly decreased, and CO varied within a narrow range. The hydrogen concentration increases above 65 vol%. According to Nipattummakul et al., (2010), the yield of H₂ improved with increasing S/F because H₂ was produced directly through steam reforming reactions, such as the water gas reaction.

Due to the increased amount of steam with increasing S/F, H₂ production was increased (Fig. 4.2(c)). The maximum H₂ production was approximately 80 g/kg in the LDPE at the S/F of 2.5. The slightly decreased hydrogen content at the S/F of 2 in Fig. 4.2(b) was mainly due to increases of other gases, such as N₂ and CO. The H₂ contents in the gases of LDPE (67–80 vol.%) were higher than that of the HDPE (64–72 vol.%) from the dual fluidized bed gasification and that (68 vol.%) from the spouted bed gasification, both of which were also performed with activated carbon as catalytic material in the fluidized bed. The yield of condensed tar increased at higher S/F ratios (Fig. 4.2(b)). Some of the tar on AC appeared to be swept away at high steam flow rates. However, the maximum condensed tar yield was very low (22.9 g/Nm³). The S/F affected the product yield as well. Gas yield increased from 2.45 to 2.95 Nm³/kg with increasing S/F (Fig. 4.2(b)). With increasing amount of steam, the cold gas efficiency increases as shown in figure 4.2 (c), for both plastic materials, while the CCE decreases. The porosity of the catalyst as well as the steam to fuel ratio may have influenced these properties. Other properties may be the particle size as well as temperature of reaction.



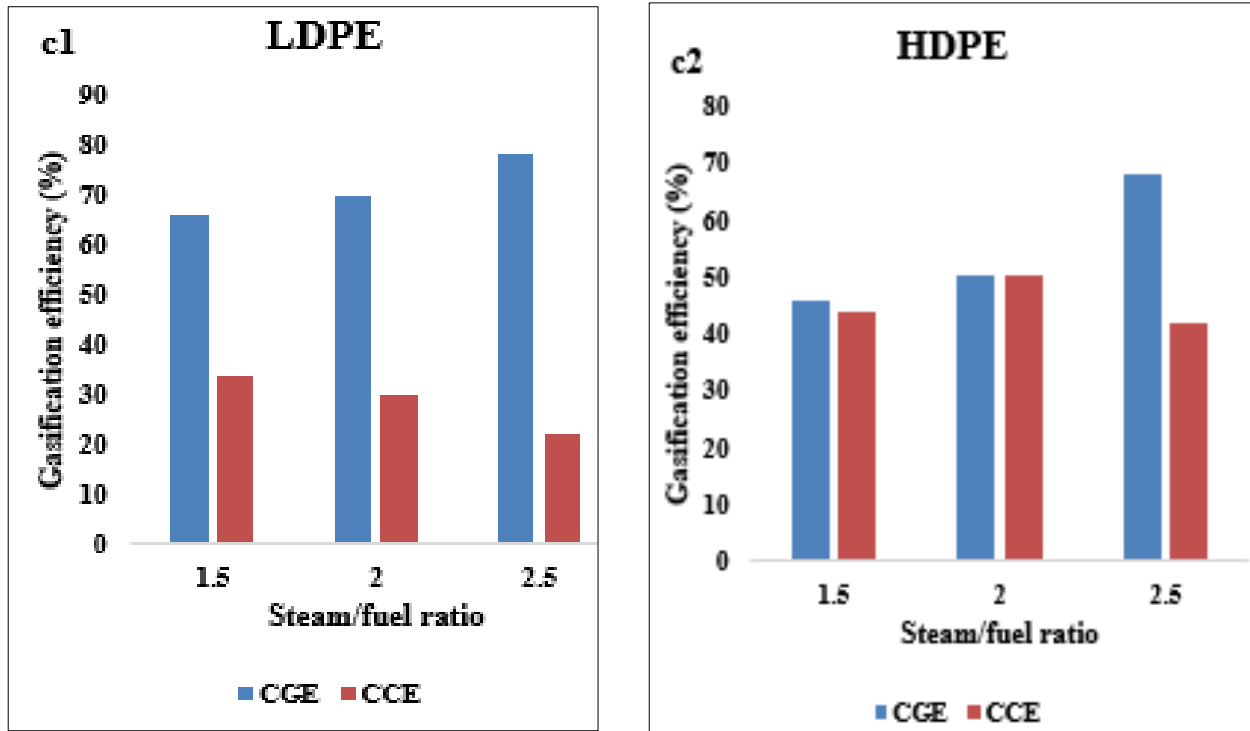


Figure 4 Effects of steam to fuel ratio (a) gas composition (b) yield of H₂ and condensed tar (c) gasification efficiency for HDPE and LDPE, respectively

4. Conclusion

In conclusion, the use of activated carbon as a catalyst in the pyrolysis of waste plastics has been shown to improve the physicochemical properties of the resulting fuels. Adding the catalyst increases the density, cetane number and reduces the kinematic viscosity of the fuel. The steam-to-fuel ratio also affects the process's gas composition, yield, and efficiency. The H₂ yield was significantly improved with increasing S/F ratios. The activated carbon also showed a high selectivity for hydrogen production. Overall, these findings suggest that the use of activated carbon as a catalyst in the pyrolysis of waste plastics is a promising approach for producing high-quality fuels with desirable properties.

Compliance with ethical standards

Acknowledgments

I am incredibly grateful to my Supervisors, Dr. A. Oji (Director, CGRP) and Dr. O.O. Okwonna, who guided me through this task to completion. Their experience, counsel, consistent contribution, correction, and patience in supervising this task are greatly appreciated. I am grateful to the Management of the Centre for Gas Refining and Petrochemical (CGRP), University of Port Harcourt, particularly Prof. J. Otaraku, Prof. K.M. Oduola, and Prof. J. Ogbonna, for providing a meaningful atmosphere and informative inputs. I also appreciate the Africa Centre for Excellence in Oilfield Chemicals Research, Mope Consult, Indorama Petrochemicals, and Notore Chemicals Plc's assistance with this programme. I am beyond grateful for the unwavering support of my Zonal Director and Pastor, Highly Esteemed Pastor Linda Okocha, my sisters Theresa and Philomina, and all the 2021-2022 M.Sc. students of CGRP who have been instrumental in the success of my research. Their cohesive support has been nothing short of amazing, and I feel humbled by their unwavering encouragement.

Disclosure of conflict of interest

No conflict of interest to be disclosed.

References

- [1] Abnisa F, Daud WMAW, Sahu JN (2014). Pyrolysis of palm shell and polystyrene mixtures: an optional method to produce a high-grade of pyrolysis oil. *Environ Prog Sustain Energy*; 33:1026–33.
- [2] Abnisa F, Wan Daud WMA, (2014). A review on co-pyrolysis of biomass: an optional technique to obtain a high-grade pyrolysis oil. *Energy Convers Manage*; 87:71–85.
- [3] Ahmad I, Ismail Khan M, Ishaq M, Khan H, Gul K, Ahmad W., (2014). Catalytic efficiency of some novel nanostructured heterogeneous solid catalysts in pyrolysis of HDPE. *Polym Degrad Stab*; 98:2512–9.
- [4] Anaele, J. V., Paulinus, U. C., & Muwarure, P. O. (2023). Comparative study of ultrasonic processor to blending kettle for production of lubricants. *Global Journal of Engineering and Technology Advances*, 16(2), 240–255. <https://doi.org/10.30574/gjeta.2023.16.2.0164>
- [5] Bernardo M., (2011). Physico-chemical characterization of chars produced in the co-pyrolysis of wastes and possible routes of valorization. Portugal: Chemical Engineering. Universidade Nova de Lisboa; p. 27–36.
- [6] Bridgwater AV., (2012). Review of fast pyrolysis of biomass and product upgrading. *Biomass Bioenergy*; 38:68–94.
- [7] Dogan PJ, Kaminsky W, Buzeto F, Yang W. (2012). Pyrolysis of polyolefins for increasing the yield of monomers' recovery. *Waste Manage*; 32:840–6.
- [8] Fakhrhoseini SM, Dastanian M., (2013). Predicting pyrolysis products of PE, PP, and PET using NRTL activity coefficient model. Hindawi Publishing Corporation; p. 1–5.
- [9] Hong S-J, Oh SC, Lee H-P, Kim HT, Yoo K-O., (1999). A study on the pyrolysis characteristics of poly (vinyl chloride). *J Korean Inst Chem Eng*; 37:515–21.
- [10] Isicheli, P., Akuma, O., Okwonna, O., & Muwarure, P. (2023). Pyrolytic Conversion of Waste Plastics Using African Apple Seed-Based Activated Carbon Catalyst.
- [11] Kukreja R., (2009). Advantages and disadvantages of recycling. *Conserve Energy Future*.
- [12] Masanet E, Auer R, Tsuda D, Barillot T, Baynes A., (2002). An assessment and prioritization of “design for recycling” guidelines for plastic components. In: *Electronics and the environment, IEEE international symposium*; p. 5– 10.
- [13] Muwarure, P.O, Otaraku, I.J, Iriakuma, E. (2023). Simulation of the Recovery of Boil-Off Gas at LNG Storage Section and Exporting Terminals. *Global Journal of Engineering Science and Research Management*, 10(2)
- [14] Okpanachi, T., Oji, A., Okwonna, O. O., & Muwarure, P. (2023). Inhibition of Calcium Carbonate (CaCo3) Scale using Plant Scale (Raffia Gum and Orange Mesocarp). Zenodo (CERN European Organization for Nuclear Research). <https://doi.org/10.5281/zenodo.7997940>
- [15] Park SS, Seo DK, Lee SH, Yu T-U, Hwang J., (2012). Study the pyrolysis characteristics of refuse plastic fuel using a lab-scale tube furnace and thermogravimetric analysis reactor. *J Anal ApplPyrol*; 97:29–38.
- [16] Park, Y., Namioka, T., Sakamoto, S., Min, T., Roh, S., Yoshikawa, K., (2003). Optimum operating conditions for a two-stage gasification process fueled by polypropylene by means of continuous polyethylene by hydrocarbon group type analysis. *J Anal ApplPyrol*; 70:383–98.
- [17] Prabir B., (2010). Biomass gasification and pyrolysis. Practical design and theory. USA: Elsevier Inc.; 2010. reactor over ruthenium catalyst. *Fuel Process. Technol.* 91,951–957
- [18] Williams PT, Williams EA., (1998). Fluidized bed pyrolysis of low-density polyethylene to produce petrochemical feedstock. *J Anal ApplPyrol*; 51:107–26.
- [19] Williams PT, Williams EA., (1998). Interaction of plastics in mixed-plastics pyrolysis. *Energy Fuel*; 13:188–96.
- [20] Zannikos F, Kalligeros S, Anastopoulos G, Lois E. (2013). Converting biomass and waste plastic to solid fuel briquettes. *J Renew Energy*; 2013:9.