

Engine Performance, Emission and Physico-Chemical Evaluation of Waste Plastic Fuel: A Case for Fly Ash Catalyst Pyrolysis

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ABSTRACT: Municipal plastic waste (MPW) as a component of municipal solid waste (MSW) poses significant challenge to stakeholders because of the ubiquity of use, non-biodegradability and the considerable danger it poses to public health. This work accessed the qualitative as well as the quantitative profile of MPW in the target municipality, composed a waste dump fly ash catalyst for catalytic pyrolysis, produced the waste plastic fuel (WPF) and had it tested in a compression ignition (CI) engine test rig. Result obtained revealed the viability of the fly ash with a competitive oil yield, engine test showed good performance as well as pollution emission well within acceptable limits.

KEYWORDS: Municipal plastic waste (MPW), Fly Ash Catalyst, Pyrolysis, Waste Plastic Fuel (WPF), Test rig, Performance, Emission.

I. INTRODUCTION

The municipal solid waste (MSW) is currently one of the chronic environmental, health and economic problems prevalent in most developing countries [1]. About 1.3 billion tons per year of MSW is generated in developing world and, in Africa, only 57% of this waste is biodegradable where a dismal 4% is recycled [2]. This challenge is set to increase because of rapid increase in population, urbanization, and raised living standards [3, 4]. In the last few decades, millions of people have shifted from rural to urban areas in many parts of the world [5]. Currently half of the world's population lies within urban areas [6]. Moreover, according to a United Nation (UN) report, the 3.9 billion current urban population will increase to 6.3 billion by 2050, with a 90% increase only in urban areas of Africa and Asia (UN, 2014). A key component of this challenge is municipal plastic waste (MPW). Indeed, the ubiquity of plastic is considered one of the gauge of uncontrolled urban

growth and the consumer culture it promotes. Plastic products are used widely because of their durability, low cost, versatility and their compatibility with urban lifestyle. Increasing plastic waste generation bears a direct correlation with MSW and the challenge the posed are exacerbated by: population growth, particularly in urban centers, economic growth, absence of effective waste management practice, weak municipal waste governance and, to a large extent, under-funded waste management architecture [2].

Stakeholders have recognized the need to arrest this development because of the associate risk non-biodegradable plastic pose to public health on the longer term. Plastics are mostly non-biodegradable and remain in the environment for hundreds of years [7]. Plastic waste valorization has been identified as one of the sustainable ways by which the environment can be rid of plastic waste [2]. Conventional recycling methods such as sorting and grinding can recycle only 15-20% of total plastic waste [8]. As a result, energy recovery technologies such as thermal and catalytic pyrolysis, gasification and plasma arc gasification are receiving more attention as alternative methods of plastic waste recycling [6, 9]. Plastic waste is a mixture of: low density polyethylene (LDPE), high density polyethylene (HDPE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC) and polyethylene-terephthalate (PET). PE and PS plastics are the main components of most municipal plastic waste [10].

Pyrolysis process converts plastic waste into liquid oil, solid residue (char) and gases at high temperatures (300-900°C) via thermal decomposition mostly in an inert environment. However, there are certain limitations in the conventional thermal pyrolysis, where the whole process is temperature-dependent [11, 12]. The quality of the liquid yield is difficult to control, the

energy requirement is comparatively high and, the liquid oil produced from thermal pyrolysis may contain impurities like residues, chlorine, and sulphur [13]. Moreover, the thermal pyrolysis of PE type plastics such as HDPE and LDPE along with PP are difficult to conduct due to their crossed chain hydrocarbon structures [14]. Therefore, catalytic pyrolysis is being advocated to overcome the problems of thermal pyrolysis [15]. A range of catalysts have been utilized, including Red Mud [15], spent FCC [16], ZSM-5 [15], HZSM-5 [17], Y-Zeolite [16], Fe₂O₃[18], Al₂O₃, Ca(OH)₂ [19] and natural zeolite [20], in catalytic pyrolysis to improve the quality of liquid oil [20]. At the domestic level, available catalyst performance needs to be evaluated and matched with the right process parameter to determine optimal conditions that will facilitate the adoption of the process as a feasible method of dealing with the MPW challenge.

The catalyst increases the lighter fractions in the liquid oil produced, such as gasoline [22], and decreases the overall process energy-inputs [15]. Moreover, the use of the ZSM-5 catalyst decreases impurities like sulphur, nitrogen, and phosphorous in the produced liquid oil [23]. It is also reported that the use of catalysts with a high BET surface area allows more contact between reactants and the catalyst surface, resulting in an increased rate of cracking reaction to produce more gases [20].

MPW is clearly a challenge in almost all municipality in Nigeria but, it could also be an opportunity to create a new business that generate economic value, create employment and effectively deal with the risk posed by indiscriminate disposal of plastic waste. There exists sufficient incentive to explore this technology within the local context, namely, vast mineral resources that could serve as catalyst in the pyrolysis process and the abundance of the feedstock. But, the grand challenge is twofold: identification and characterization of locally available catalyst that could yield optimal outcome and, the conceptualization of a catalytic pyrolysis process that can be domesticated. To overcome these challenge, factors affecting the catalytic pyrolysis process, such as temperature, retention time, feedstock composition, and the use of catalysts, need to be evaluated. The effect of different catalysts on the quantity and quality of pyrolysis products need to be examined in detail against characteristics of catalyst. Furthermore, catalyst reforming and the regeneration and exploration of new cheaper catalysts also need to be focused upon in order to make the catalytic pyrolysis process more economical and sustainable within the domestic environment. Available data on the waste management challenge in Africa indicates

that on the average, only 57% of MSW are biodegradable. In addition, only about 55% of generated waste are collected and greater than 90% of the collected waste are disposed in mostly unregulated landfills. It further state that of the total waste collected, only about 4% is recycled [2]. These figures reflect a dismal failure in waste governance and the evidence are there for all to see in every municipality on the continent. These challenge subsist on a continent that is set to undergo a major transformation in the foreseeable in: population explosion, faster level of urbanization and, a changing consumer purchasing habits. The convergence of these factors will invariably leads to exponential growth in waste generation [2]. This narrative can be changed if the right approach in waste governance are deployed. This will start by seeing waste as a resource, collecting relevant data and instituting the right mechanism. Historically in Nigeria, there exist a death of data on waste generation, characterization and management. On a more specific note, data available indicates that about 80% of plastic waste generated in Nigeria is mismanaged. Available data on the waste management challenge in Africa indicates that on the average, only 57% of MSW are biodegradable. In addition, only about 55% of generated waste are collected and greater than 90% of the collected waste are disposed in mostly unregulated landfills. It further state that of the total waste collected, only about 4% is recycled [2]. These figures reflect a dismal failure in waste governance and the evidence are there for all to see in every municipality on the continent.

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For most municipality in Nigeria and, particularly for Bauchi municipality, the prevailing problem of plastic waste management includes: a lack of actionable data on MPW characterization and composition, a lack of advocacy and domestication of waste valorization scheme that feeds into the local economy, scant identification

and study of technically feasible catalyst available locally for plastic pyrolysis, and the study on a suitable reactor design that meets local condition while giving optimal yield. The aim here is to qualitatively and quantitatively characterize MPW with the stated aim of determining the optimal parameter for its catalytic pyrolysis into usable Internal Combustion Engine (ICE) fuel. The overall aim of this study is to determine, using research based approach, a technically feasible and commercially viable pathway to the production of Internal Combustion Engine (ICE) fuel from the catalytic pyrolysis of Municipal Plastic Waste (MPW) obtained from the target municipal area (Bauchi municipality). The objectives include following: To quantitatively and qualitatively characterize Municipal Solid Waste (MSW) obtained in the target area with the stated aim of determining the averaged MPW composition; To identify, prepare and determine key properties of locally available pyrolytic catalyst that could be used in the catalytic pyrolysis of MPW collected from the target municipality; To determine, using lab. Size reactor, the optimal mix of catalyst and reactors operating parameters that will yield desirable oil output from the characterized MPW; To produce waste plastic oil (WPS) from the plastic sourced from the MSW obtained from the pilot area; To characterize and test the quality of fuel produced with the aim of establishing if it meets the internationally acceptable benchmark for ICE grade fuel or, if there are quality gaps, to suggest remediation strategies.

II. BACKGROUND

Pyrolysis is a recycling process in which organic compound are converted into liquid oil, char and gas at high temperature via thermal decomposition [24]. The process can be conducted at different temperature, however, for plastic waste, the optimal temperature range is about 500 – 550oC [24]. Furthermore, the heating rate and retention time are an important parameter in pyrolysis processes. Several studies have been conducted using heating rate that ranges between 4 oC/min – 25 oC/min [25-27]. With regards to retention time, Lopez et al [15] carried out pyrolysis of plastic waste at retention time of 0 – 15, 15 – 30 and 120min. other studies showed retention time of 40 – 70min [27], 120min [25] and 45min [28]. Most studies showed that increase in temperature results in reduction of retention time. It has also been proven that a further reduction in retention time and process temperature can be achieved via the introduction of catalyst, hence the need for catalyst pyrolysis.

Thermal pyrolysis (or non-catalytic pyrolysis) is an endothermic process that requires significant heat budget. Extensive study on this has been conducted on the past, these include; PE [29-32]. Thermal pyrolysis of PE (HDPE and LDPE) and PP requires light temperature for degradation, as compared to PS plastic [23]. Furthermore, in the absence of catalyst, PE is converted into wax instead of liquid oil [16]. Where liquid oil is produced by thermal degradation it contains heavy oil compound with large carbon chains as a major compound [15]. A further disadvantage is that the liquid is of low quality due to its low octane number and the presence of high solid residues. It also contains impurities such as sulphur, nitrogen and phosphorus [16].

Catalytic pyrolysis, on the other hand, is the thermal decomposition process that is carried out in the presence of a suitable catalyst. The catalytic process shows high potential for the conversion of plastic waste into liquid oil, it has better product quality, lower temperature and retention time when compares to thermal pyrolysis. These factors make catalytic pyrolysis a more energy efficient and optimal process [33].

As a result, FCC [14], spent FCC [16], HZSM-5 [34] ZSM-5 [23] Cu–Al₂O₃ [35], Co – Mo/Z [36] Zeolite – β [37], Red mud [15] Al (OH)₃ Ca (OH)₂ [19] and Fe₂O₃ [18] have been used to enhance the oil yield and mechanism of catalytic pyrolysis. In addition, hydrocarbon (HC) produced from different plastic waste such as HDPE, LDPE [38], PP [39] and PS [40] contain low carbon chain compound in the gasoline range of HCs when compares with a similar thermal pyrolysis yield [38, 41, 42]. However, the downside to catalytic pyrolysis is that, it produces more gaseous product and reduce the liquid yield, albeit marginally, when compares to thermal pyrolysis [43]. Factors Affecting Pyrolysis are: Temperature [44], retention time [45], feedstock composition, use of catalyst [22], moisture content [24], heating rate and particle size are some of the factors that determine the outcome of catalytic pyrolysis [44].

Temperature is one of the factor that plays important role in the product quality and quantity of catalyst pyrolysis [15]. Temperature affects the cracking reactions that determines the amount of gasses and liquid produced. However, it has little effect on the amount of char produced (Yoshioka et al 2004, Ji et al 2006) at low temperature reactivity is reduced and long chain hydrocarbons are produced but, an increase in temperature results in the production of short chain compounds due to the cracking of C-C bonds. But a further higher temperature results in a diminishing returns as

aromatic compounds are produced due to the triggering of secondary reaction [15, 17].

Retention time has been reported widely to bear no significant effect upon the yield of pyrolysis process. Lopez et al, [15] stated that the same yield of oil is observed at 30 min and 120 min retention time. In a similar study, the aromatic compounds present in liquid oil were found to be the same at different retention times using the same temperature [45]. However, feedstock composition were found to affect the yield of pyrolysis process. According to Miskolczi et al [23], the PE and PP require higher temperatures for their degradation as compared to PS plastic, due to different and complex hydrocarbon structures.

Catalyst plays an important role in catalytic pyrolysis. They serve to improve the quality of the products as well as reducing the process temperature and retention time for overall process optimization. Fe₂O₃, Ca(OH)₂, FCC, natural zeolite and synthetic zeolite are the different types of catalyst that hence been investigated by scientist [19]. The use of catalyst increases the rate of cracking reactions that leads to an increase in the production of gases consequently resulting in the reduction of liquid yield [20]. On a positive note however, the quality of the liquid oil produced is improved. The viability of any given catalyst are determine by characteristics such as Brunauer Emmett and teller (BET) surface area, pore size, pore volume, and acidity. These are the factors that determine the activity of a catalyst. Studies has revealed that thermal cracking occurs at the external surface of the catalyst (in catalytic pyrolysis) the internal porous structure of the catalyst then acts as channels for selective breakdown of larger compound into smaller ones [16]. Hence, small pore size supports the production of gases, whilst wax production occurs due to external cracking on the external site of the catalyst [46]. Catalyst can be applied directly as solid mix with the feedstock or on organic vapour produced in separate chamber. Either way, the cracking will be improved via a reduction of reaction temperature and retention time [15, 24]. However, catalyst recovery is different for direct contact this is because the pores are blocked due to the sticky nature of the plastic feedstock [20]. Only few studies have investigated catalyst regeneration [47]. In addition, direct contact contaminates the catalyst through the deposition of impurities such as chlorine, sulphur and nitrogen on the surface of the catalyst [42]. Vapour phase contact has been investigated using Y-zeolite for PE [48], ZSM -5 for PS [49] and ZSM -5 for industrial packaging waste [15].

Another important point to note in the use of catalyst for plastic waste pyrolysis as it affects the oil yield is the level of acidity. Silica alumina catalyst are amorphous catalyst having Lewis acid site as an electron acceptors and Bronsted acid site with an ionizable hydrogen atom. The acidity level of these catalyst is determined by the mole ratio of SiO₂/Al₂O₃. The higher the acidity, the lower the oil yield [18]. Hence a good of catalyst-temperature will be to use low acidity silica alumina catalyst and high process temperature. Other important characteristic of the catalyst are their porosity and thermal stability. A microporous catalyst with a high internal crystalline structure increases the catalyst process, produce more gases, and decrease the liquid yield [15]. While a catalyst with macro pore volume will not affect the liquid yield quantity. It is desirable to have high thermal stability for a catalyst [1].

III METHODS

3.1 Qualitative and quantitative sampling of waste in Bauchi municipality

The collection of data techniques adopted in carrying out the study includes research design, study area, population of the study sample size, sampling techniques and mode of data analysis. Characterization of municipal waste is necessary to collect actual data that will aid in determining the waste per capita generated within the municipality, determine the waste composition, and ultimately, the plastic composition of the total waste. The study sampling area is Gwallameji. Gwallameji is a suburb of Bauchi located in Bauchi state, Nigeria. The sampling of Gwallameji will be extrapolated to determine total waste per capita of the entire metropolis as the suburb represent the demography of the entire city.

3.1.1 Location

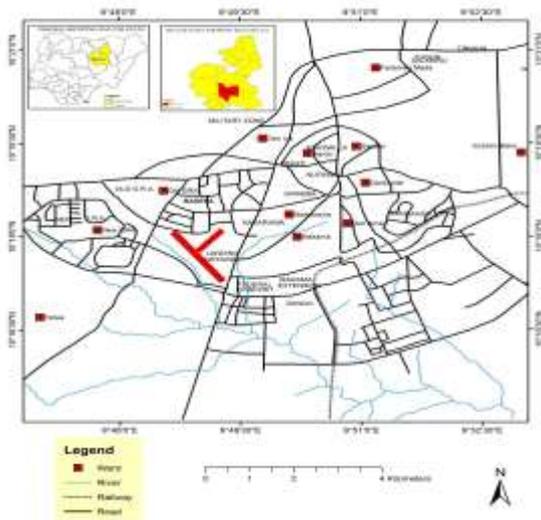
Bauchi, metropolis, capital of Bauchi State and its foremost traditional emirate, is in the North Eastern geopolitical zone of Nigeria. It is located between Latitudes 10°16' 30" – 10°21' 0" North of the Equator and Longitudes 9°48' 0" and 9° 52'30" East of the Greenwich Meridian. It is on the northern edge of the Jos plateau, at an elevation of 616m. The topography of Bauchi metropolis is relatively flat in the Centre. The town lies over 609.6 meters above sea level; it occupies a total land area of 3, 604 hectares [50]. The Bauchi Urban area according to the Bauchi State Urban Development Board has a radius of about 32km and comprises of only one local government area i.e. Bauchi. Bauchi town lies on the railroad from Maiduguri to Kafanchan (where it joins the line to Port Harcourt)

and has road connections to Jos, Kano, Maiduguri and Gombe [50].

3.1.2 Climate

According to the Koppen Climate Classification system, Bauchi has a tropical savannah climate. Two main seasons are experienced in the study area; cold dry season and hot wet season. It enjoys a rainfall total of up to 1091.4mm annually; its hottest month is usually April (with 40.56°C) while the coldest months are December and January with typically 6.11°C and 7.22°C respectively. The minimum and maximum annual temperatures in the metropolis are, 18.33°C and 32.39°C respectively (Nigeria: People, Population and Settlement, 2003).

Figure 3.1 Map of Bauchi State Metropolis



3.1.3 Population and Economic Activity

Projected from the 2006 census, using the states inter census growth rate of 3.39%, the population of Bauchi metropolis (i.e. 493,730) as at 2014 was 644,641. The sex ratio generally across the state was 105 males to 100 females. The population of Bauchi town comprises many ethnic groups, the main ones being Gerawa, Sayawa, Jarawa, Bolawa, Fulani and Hausa (United Nations High Commission on Refugee Statistical Yearbook, 2006).

3.2 Amount of Solid Waste Generated

We estimated the amount of municipal solid waste generated using the formula below.

$$n = \frac{N}{1 + N \times 0.07^2} \dots \dots (1)$$

(Slovin's Formula)

Where N is Total population in the study area n, is sample size requires, and given the finite population of Gwallameji estimated at 30000, sample size was put at approximately 203 given the average of 13 persons per household. Hence a plastic bin 15 in number were obtained for the study.

3.2.1 Sampling Stage

To determine the number of waste bin responded to in each location, Bowels (1962) proportional allocation technique was use, it is given as;

$$Nh = \frac{\pi_i}{N} \dots \dots \dots (2)$$

Where N is total house hold population, n is total sample size, h is total household population ward (13), π_i , sample size for each ward, thus, the total (13) house hold were sample in the study location with each location getting proportional amount.

3.2 Catalyst preparation protocol

The Fly ash (FA) catalyst sample used for this research was obtained from the municipal waste dump. The as-received FA was pulverized into fine particles using a mechanical grinder, and sieved via sieve < 50 µm mesh in line with established protocol. The sieved FA was transferred into a clean, dry, and airtight glass vial, and designated as sample A. SiO₂ (analytical grade) was procured from Lichro Chemical and Laboratory Supplies, South Africa. The as-received SiO₂ was pulverized into fine particles using a mechanical grinder and sieved using a < 50 µm mesh. The fine SiO₂ powder was transferred into a clean, dry, and airtight glass vial, and labelled as sample B. Part of samples A and B were thoroughly mixed in ratio 30:70 (sample A: sample B), stored in a clean, dry, and airtight glass vial, and marked as sample C. The containers of the samples were kept in a cool environment to avoid contamination and oxidation.

3.2.1 Sample preparation

The samples were prepared according to the flowchart illustrated in Figure 4. The three samples (A, B, and C) were characterized by various techniques including X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), thermal electron microscope (TEM), differential scanning calorimetry (DSC) and Brunauer-Emmett-Teller (BET).

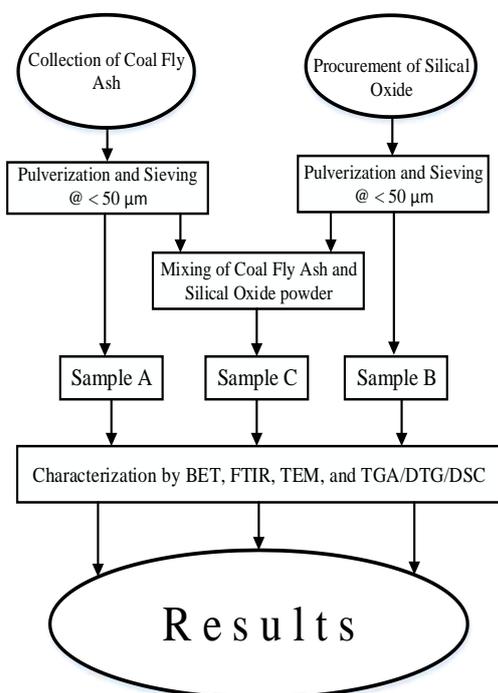


Figure 3.2: Flowchart of samples preparation

3.2.2 Methods of characterization

The three samples (A, B, and C) were characterized by various techniques including X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), thermal electron microscope (TEM), differential scanning calorimetry (DSC) and Brunauer-Emmett-Teller (BET).

3.2.3 XRD analysis

Measurements are performed using a multipurpose X-ray diffractometer D8-Advance from Bruker AXS (Germany) operated in a continuous θ - 2θ scan in locked coupled mode with Cu-K α radiation. The sample is mounted in the centre of the sample holder on a glass slide and levelled up to the correct height. The measurements run within a range in 2θ defined by the user with a typical step size of 0.034° in 2θ . A position-sensitive detector, Lyn-Eye, is used to record diffraction data at a typical speed of 0.5 sec/step which is equivalent to an effective time of 92 sec/step for a scintillation counter.

Data are background subtracted so that the phase analysis is carried out for diffraction pattern with zero background after the selection of a set of possible elements from the periodic table. Phases are identified from the match of the calculated peaks with the measured ones until all phases have been identified within the limits of the resolution of the results.

3.2.4 Thermal analysis

The thermal analysis of the three samples was analyzed by a DTG (DTG-60AH, Shimadzu) and TGA (TA-60WS, Shimadzu) thermal analyzer. About 10 mg of dry powder of each sample was weighed into an aluminum pan and scanned between the temperature range of 29°C to 1000°C , the heating rate $10^\circ\text{C}/\text{min}$, then held for 5 min at 1000°C and under nitrogen atmosphere at a flow rate of 10 ml/min in a simultaneous TGA, DTG, and DSC analyses. The data were analyzed using a TA-60 ch 1 DTG-60AH workstation.

3.2.5 Spectroscopic analysis

To obtain a recognizable absorption spectrum, the dilution and homogenization of the three dry powder samples with KBr (spectroscopic grade), were carried out with additional grinding and mixing in an agate mortar. Discs (12.7 mm ID and ≈ 1 mm thick) were prepared in a manual hydraulic press (model 15.011, Perkin Elmer Co., USA) at about 10 tonnes for a pressing time of 30 s to 60 s. The spectrum was measured and recorded from 300 cm^{-1} to 4000 cm^{-1} on a spectrometer (model system 1000 FTIR, Perkin Elmer Co., USA) with a resolution of 2.0 cm^{-1} .

3.2.6 BET Characterization

The Nitrogen sorption analyses of the samples were performed with a Micromeritics ASAP 2460 instrument. About 0.25 g of each sample was degassed at 100°C under nitrogen gas overnight. Thereafter, they were allowed to cool under a vacuum to make their surfaces and pores available for probing. The surface area of the sample (m^2/g) was computed by the Brunauer-Emmett-Teller (BET) method, while the pore size distributions like the total pore volume (cm^3/g at STP) and average pore radius (\AA) were calculated using the Barrett-Joyner-Halenda (BJH) method.

3.2.7 TEM analysis

The samples were prepared on a Quorum Q150A ES sputtering machine before transferring to the Zeiss Ultra Plus in field emission gun scanning electron microscope (FEGSEM) for morphology analysis of the powder sample. A JEOL JEM-2100 operating at an accelerating voltage of 20 kV was used for the high-resolution transmission electron microscopy (TEM) analysis.

3.4 Waste Plastic Oil Pyrolysis

In the fixed bed reactor, the catalyst is usually in palletized form and packed in a static bed. It is easy to design but the irregular particle size and shape of the plastic feedstock create challenges

during feeding process. Beside, access to catalyst reaction site are restricted. Some research has been conducted with fixed bed reactors but, with subdued interest [43, 52]. In some instances, the fixed bed reactor is used as secondary pyrolysis reactor with the primary feed coming in as liquid and gases [53-55]. However, two-step process is not cost effective, fluidized bed reactor, on the hand, solve the fixed bed challenge. Here the catalyst sits on the distributor plates where the fluidizing gas passes through it and the particles are carried in fluid state. As a result, the catalyst is well mixed with the reactant. Many researchers preferred to use fluidizing bed reactor in catalytic cracking of plastic over fixed bed reactor [56, 57]. Jung et al [58] used fluidizing bed reactor in their research because it provides almost a constant temperature with high mass and heat transfer, giving shorter residence time in the reactor and consequently more uniform range of products. The temperature ranges for plastic pyrolysis in fluidized bed is normally 290 °C – 830 °C for both thermal and catalyst process. Luo et al [59] used fluidized bed for the plastic pyrolysis in the presence of silica – alumina catalyst. A liquid yield of 87 wt% for PP feedstock and 85 wt% for HDPE feedstock were obtained at 500 °C. Fluidized bed reactor is generally considered to be the best reactor to perform catalytic pyrolysis of plastic waste. This is because the catalyst can be reused many times. In addition, its operation is more flexible than batch reactor since feedstock can be continually fed into the reactor in a continuous process format fluidized bed reactor are best suited for large scale operation for the same reasons. In his study, the fixed bed reactor was used with the catalysis being deployed in free slurries within the bed. Below is the picture of the reactor vessel used. It consists of the main vessel, the thermocouple meter and probes, the inert nitrogen feed tube and the product exit tube with three distillation flasks for product distillation and analysis.

Plate 1: Pyrolysis reactor used



3.5 ICE test bed and WPO analysis

The test engine was a single cylinder, four stroke and air cooled TD111 Techquipment direct injection diesel engine. The test rig set up is shown in figure 3.3 and technical details are

given in Table 3.1 A hydraulic dynamometer TD 115 also from Techquipment with water flow pressure head of 6-12m was used to measure the torque which is displayed on the instrument display panel TD114. TD114 also displays the engine speed, exhaust temperature, air flow and houses the test engine was a single cylinder, four stroke and air cooled TD111 Techquipment direct injection diesel engine. The test rig set up is shown in figure 3.3 and technical details are

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calibration of the torque meter is checked intermittently to confirm accuracy of the data set via an eight step process on the equipment manual (Techquipment. 2003). The exhaust gas temperature is measured with a chrome/Alumina thermocouple located in a 1/8”BSP union brazed into the exhaust port of the engine. Color coded leads from the thermocouple are connected to terminal underneath the TD114 instrument unit. The test engine is a 3.5kw rated, direct injection (DI), single cylinder diesel engine. Selected test speed was 1800, 2000, 2500, 3000 and 3600rpm. Each test cycle at selected torque consist of running the engine for 1 minute at idle speed and 9 minute at selected load in accordance with test cycle G3 of ISO 8178 – 4 (Commission 1999). The engine rated power was taken as 100% load. The test cycle was repeated for 20%, 40%, 60% and 80% load. This test cycle procedure was followed for diesel, and waste plastic oil. The SV-5Q exhaust gas analyzer was in accordance with ND112 (Non – Dispersive infra – Red) method utilize via micro computer analysis to measure the thickness of HC, CO and CO₂ in the exhaust gas and to inspect the density of NOX and O₂ via electrochemical sensor. The excess air coefficient, λ was also computed automatically by the analyzer and double checked manually to confirm accuracy. The analyzer is equipped with a microprocessor, an induction tachometer, temperature sensor, and an inner micro printer. The sampling probe is normally installed in the exhaust line where gas could be drawn through a

Table 3.2: Test rig Data

filter into the analyzer

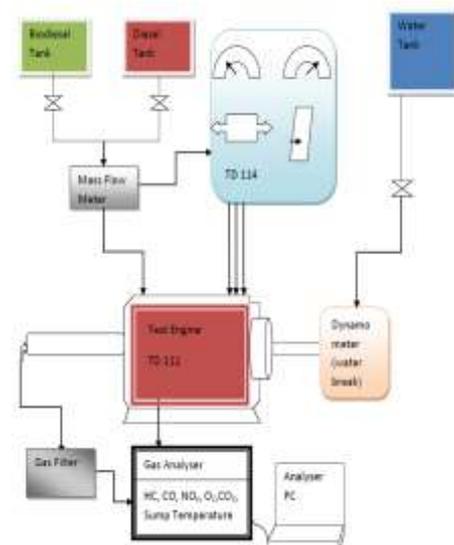


Figure 3.3: Test bed Schematics

IV RESULTS AND DISCUSSION

The results from the waste sample, catalyst analysis and preparation, pyrolysis process, Waste plastic oil test and engine test are presented and discussed below.

4.1 Waste Sample Collection

Waste accumulated in the waste bin was collected from selected site into a waste bin was weighed and sample and before taken for any laboratory test/processes. Details are given below:

Device	Description	Detail
Engine	Model	TQ:TD 111
	Maximum power(Kw)	3.5
	Type	Naturally aspirated, four strokes.
	Rated speed(rpm)	3900
	Number of cylinder	1
	Compression ratio	17.5:1
	Combustion	Direct injection
Hydraulic dynamometer	Model	TQ:TD115
	Type	Hydraulic
	Water pressure	6-12m head of water (60KPa)
	Range	0-14Nm
	Water flow rate	4lt/min
Exhaust analyzer	gas Model	SV-5Q
	HC Range	1-10000 10 ⁻⁶ (ppm) Vol.

	Resolution	1 ppm	
CO	Range	1-1000	10 ⁻² (%) Vol.
	Resolution	0.01%	
CO₂	Range	0-20	10 ⁻² (%) Vol.
	Resolution	0.01% Vol.	
O₂	Range	0-25	10 ⁻² (%) Vol.
	Resolution	0.01% Vol.	
NO_x	Range	0-50000	10 ⁻⁶ (ppm) Vol.
	Resolution	1 ppm	

Table 4.1 Household Population, Sample Size and Percentage

Location	Household population	Sample weight (kg)	Percentage (%)
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Business non-groceries 1	5	20	75%
Business non-groceries 2	10	12	7.52%
Business non-groceries 3	5	19.9	9%
Business groceries 1	2	70.5	23.25%
Business groceries 2	3	42.2	14.9%
Business groceries 3	6	8.09	0.51%
Lower class family 1	5	23.9	7.59%
Lower class family 2	4	13.36	4.13%
Lower class family 3	3	20.4	7.01%
Student lodge 1	3	12.5	3.79%
Student lodge 2	2	13	4.1%
Student lodge3	5	12.58	3.93%
Upper class family	3	13.5	4.12%
Upper class family	10	44	0.11%
Upper class family	4	10.4	3.75%
TOTAL	70	292.77kg	100%

Table 4.2 Household population, Sample Size and Percentage

Category	Population	Weight	Percentage
Student lodge	9 persons	38.86kg	12.2%
Lower class family	13 persons	56.88kg	18.53%
Upper class family	13 persons	31.99kg	8.36%
Business groceries	20 persons	102.5kg	22.65%
Business non-groceries	15 persons	156.7kg	38.26
TOTAL	70 persons	386.93kg	100%

Table 4.3 Total Plastic Generation

Weeks	Plastic waste in (kg)	Change in percentage
First week	11.12kg	76%
Second week	3.88kg	3%
Third week	6.96kg	5%

Fourth week	8.7kg	16%
TOTAL	30.66kg	100%

4.1.2 Total Population in Bauchi

According to 2004 census is given has 493,730

using this formula $p = p_0 e^{rt}$ to get our recent population in bauchi state where

$$p_0 = 493,730$$

$$t = 2020 - 2004 = 16 \text{ years}$$

$$r = 3.6\% = 0.036$$

$$p = 493,730 \times e^{0.036 \times 16}$$

$$p = 493,730 \times e^{0.576}$$

$$p = 835171.8726$$

total waste plastic generated in bauchi = total plastic per capita \times total population

$$\text{total waste of plastic generated} = 30.66\text{kg} \times 835171.8726$$

$$\text{total waste of plastic generatd} = 25606.3696 \text{ ton/month}$$

The annual waste plastic generation in Bauchi is therefore 307,276.32 tons/annum. While there are no local data to compare this result with, existing annual national data point to a consensus. A study published in 2019 which worked with a project population of 173 million Nigerian estimated a plastic waste generation of 19,865,593 tons [60]. This put the average generation for the 36 sub-national entity at 551,822.02 tons/annum. The scale of this waste underscore the enormity of the challenge and highlight the imperative of plastic waste valorization.

4.2 Catalyst Analysis

4.2.1 BET analysis

The data on the BET surface area, external surface area, average pore radius, pore volume, micro-pore volume, and micro-pore area are shown in Table 4.2.1. The surface area, external surface area, and pore volume of unmodified FA (sample A) have been substantially increased by the addition of SiO₂ (sample B) from 0.5928 m²/g, 0.8611 m²/g, and 0.00532 cm³/g to 35.1102 m²/g, 32.5753 m²/g, and 0.1281 cm³/g respectively. The total pore volume of 0.1281 cm³/g falls within the 0.08 cm³/g to 0.3 cm³/g recorded when FA was synthesized, modified with copper oxide, and converted to zeolites by hydrothermal activation,

atmospheric crystallization, and double-stage fusion-hydrothermal for catalytic applications. Though these increases have been accompanied by a decrease in the average pore radius of sample A from 179.68 Å to 72.98 Å in sample C. This shows that the addition of SiO₂ causes a reduction in average pore radius in the mesoporous range as a result of impurities. However, there was an increase in the micro-pore volume of sample A from -0.000121 cm³/g to 0.000582 cm³/g in sample C. The surface area and average pore radius of sample C are higher than the 17.542 m²/g and 32.59 Å reported when raw FA was impregnated by Calcium metal and calcined at a temperature of 500 °C for 4 hours as reported by Arif et al. [61] and BET surface area of 9.028 m²/g and pore volume of 0.01055 cm³/g reported for biomass fly ash by Vargas et al. [62]. The increase in pore volume lends credence to the view that new mesopores can be formed not only by the activation process but also by the addition of supports [61, 63]. The BET surface area is an important physical property that determines the catalytic activity of a solid particle. In this case, a high BET surface area of 35.1102 m²/g will aid its catalytic activity for the adsorption and desorption of molecules such as triglycerides, glycerin, and green diesel [62, 64].

Table 4.4 Textural properties of the samples

Properties	Unit	Sample A	Sample B	Sample C
BET surface area	m ² /g	0.5928	317.2404	35.1102
External surface	m ² /g	0.8611	279.1870	32.5753

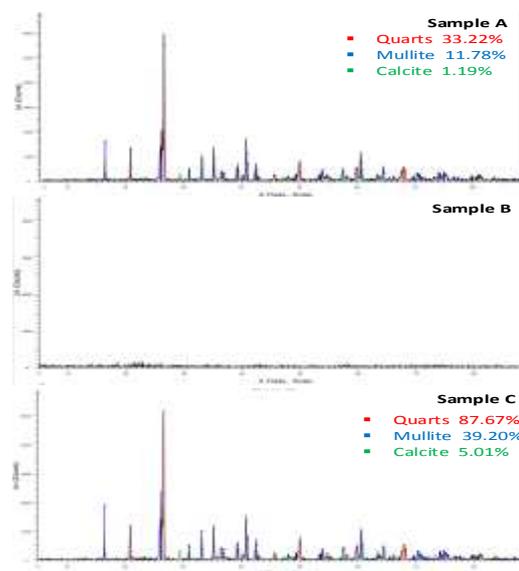
area				
Average pore radius	Å	179.68	70.72	72.98
Pore volume	cm ³ /g	0.005326	1.1218	0.1281
Micropore volume	cm ³ /g	-	0.014827	0.000852
Micropore area	m ² /g	*NR	38.0533	2.5349

*NR=Not responding

4.2.2 XRD analysis

The XRD spectrometry plot for the samples is depicted in Figure 6 while Table 4.2.2 shows the description of the major constituents of the samples. The semi-quantitative mass composition shows that the percentage of quartz increased from 33.22 % in sample A to 87.67 % in sample C while the mullite increased from 11.78 % in sample A to 39.2 % in sample C. This is due to the addition of SiO₂ to sample A. The pattern shows that raw CFA is composed mainly of quartz (SiO₂) and mullite (Al_{4.4}Si_{1.209.6}) minerals. The quartz diffraction pattern is shown predominantly at around 2θ = 21°, 26°, 50°, and 68° while mullite diffraction peak at 2θ = 16.5°, 24°, 41°, and 61°. Though the XRD diffraction of sample B did not display any pick, it can be seen that the addition of sample B to sample A significantly altered the composition of sample C. As shown in figure 7, sample C was composed mainly of quartz (SiO₂), mullite (Al_{4.4}Si_{1.209.6}), and a small percentage of calcite (CaCO₃) minerals. The quartz peaks were detected at 2θ = 20.8°, 26.5°, 36.4°, 50°, 60°, and 68° and mullite peaks were detected at around 2θ = 16.5°, 26.2°, 31°, 33°, 35.3°, 40.8°, and 60.7°. The only noticeable calcite peak was noticed at around 2θ = 29.3°. Similar results were also reported by Sharma et al.[65], Ho et al. [66], Bhandari et al.[67], and Maneerung et al. [68]. These results show a high possibility of using sample C as a potential catalyst for the conversion of waste plastic oil to diesel [61, 62, 69].

Plate 2a, b and c: Catalyst Micro-Electronic Analysis



4.2.3 Thermal analyses

The outcome of the thermal analyses comprised of the samples is reported under TGA and DSC. The TGA of the samples is shown in Figure 7 which has been plotted with the temperature range of 30 °C to 1000 °C to ascertain the percentage weight loss concerning temperature using nitrogen as the heating medium. Sample A losses of about 2 % of its weight between 30 °C and 220 °C with no further thermal degradation. On the other hand, sample B witnessed 13 % weight loss between 30 °C and 140 °C and the weight loss becomes slower until 950 °C. From 30 °C to 250 °C, sample C witnessed about 15 % weight loss and another 5 % weight loss between 250 °C and 650 °C. Sample C effectively achieved thermal equilibrium with no further weight loss at 700 °C. This shows the high thermal stability of samples C, a property believed it inherited from CFA (sample A). This conforms with the pattern reported by Kumar et al. [34].

The DSC curve of the samples is shown in Figure 9 which reveals the distinction in the heat content of the samples concerning temperature.

This provided information on phase transition parameters like crystallization point, melting point, the heat of reaction, and thermal stability of samples [71]. From the curves, sample A witnessed rapid heat input between 820 °C and 930 °C. However, the addition of SiO₂ to CFA motivated sample C to behave differently and show a more uniform differential heat addition higher than sample B.

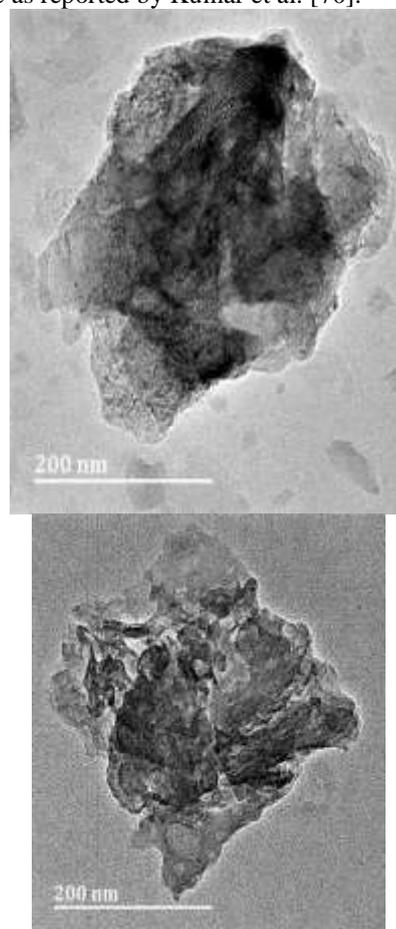
4.2.4 Spectroscopic analysis

The FTIR spectra of the samples are shown in Figure 8. It shows that the samples have major absorption bands at the same wavelength. This is due to the effect of the addition of the SiO₂ to sample A to form sample C. For the CFA, it can be seen that the absorption at a wavelength of 3754 cm⁻¹ is characteristic of stretching OH rhombohedral. The major absorption band at 1054 cm⁻¹ noticed in sample B is similar to those observed by Maneerung et al.[68] and Sharma et al.[65] which they ascribed to the presence of SiO₂ which is not prominent in samples C. The existence of the absorption sharp band at 3745 cm⁻¹ which is ascribed to -OH band, was detected in the CFA catalyst, this band agrees with the presence of CaCO₃ in sample A but unnoticeable in sample C, as determined by XRD (Table 2) is a proof of the effect of the addition of SiO₂ support. This matches with the result described by Boey et al. [72]. The presence of a major absorption band at wavelength 1054 cm⁻¹ is attributed to the asymmetric O-Si-O while the wavelength at 451 cm⁻¹ in sample B has moved to 429 cm⁻¹ in sample C. The peak shown by sample C at ~430 cm⁻¹ characterizes the Al-O-Si and Si-O-Si bending vibrations. The distinctive peaks at 705 cm⁻¹ and 831 cm⁻¹ are due to the (Si, Al)-O- (Si, Al) symmetric stretching [73]. Also, the wide peak at 1011 cm⁻¹ can be ascribed to the (Si, Al)-O- (Si, Al) asymmetric transmission stretch. The absorption recorded by sample C falls within that reported by Arif et al. [61] who compared raw CFA with modified CFA

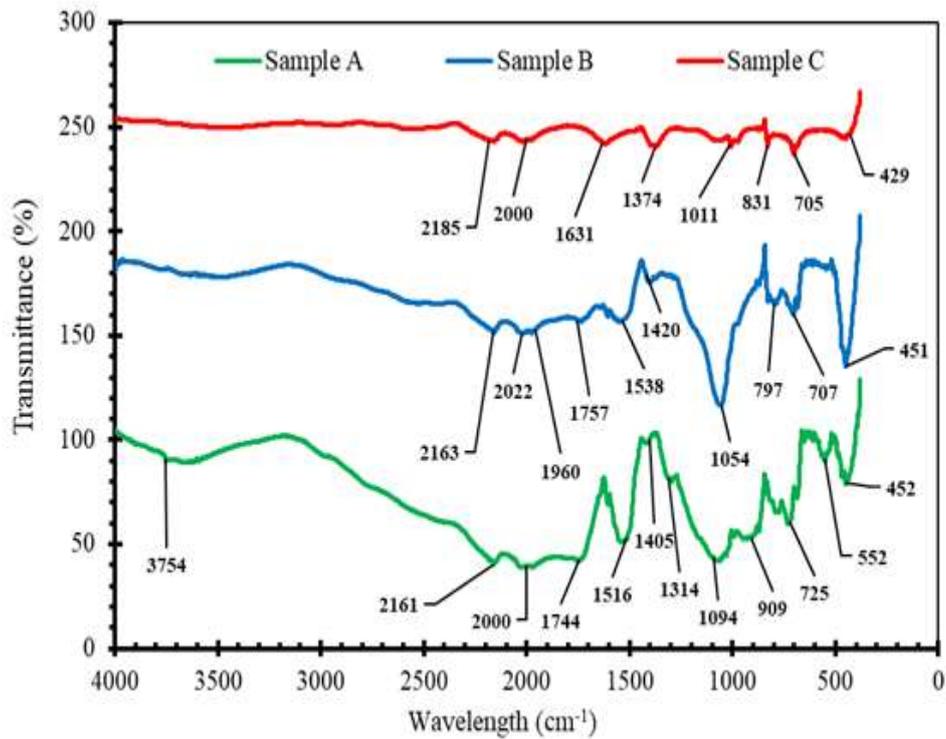
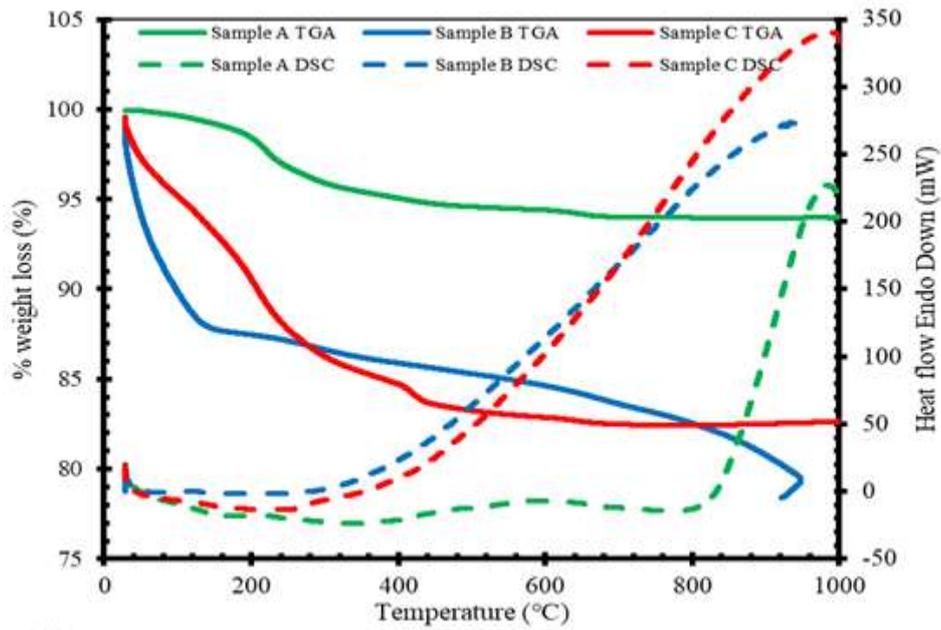
4.2.5 TEM analysis

The TEM micrographs showing the structural information of the samples are shown in Figure 9. The mesostructure is detectable in the

TEM pictures of the samples confirming that active metals are homogeneously filled and dispersed on the mesoporous structure [74]. The nano size, structural dimension, and active components of the FA and its support provided effective surfaces capable of enhancing its catalytic efficacy during the hydrogenation of triglyceride, irrespective of the FFAs present in the oil. Sample C has more pores, a regular surface structure, and hexagonal-shaped particles which reflects the presence of a high percentage of SiO₂ when compared with samples A and B. The TEM micrographs confirm the result of the XRD analysis that sample C has the capacity to effectively crack plastic waste to WPO. This agrees with the outcomes of a similar sample as reported by Kumar et al. [70].



Compound name	Chemical formula	Lattice	Molecular weight	Volume	Sample Composition (%)		
					A	B	C
Quartz	SiO ₂	Hexagonal	60.08	113.59	33.22	N/A	87.67
Mullite	Al ₄ Si	Hexagonal	132.02	49.71	11.78	N/A	39.2
Calcite	CaCO ₃	Rhombohedral	100.09	367.78	1.19	N/A	5.01



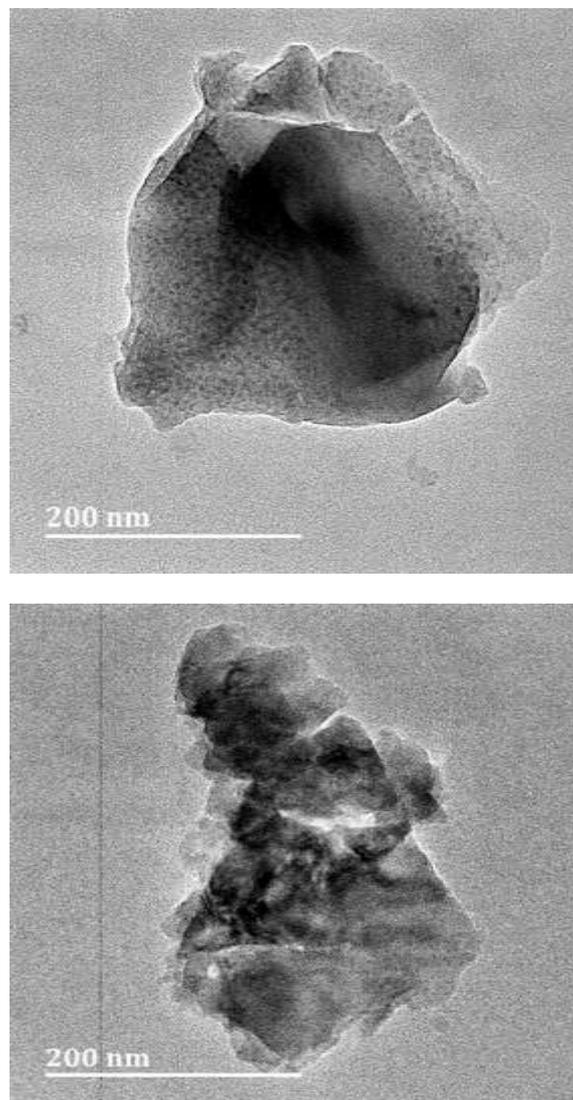


Plate 3:Sample A, B, C, C1 in descending order

4.3 Waste Plastic Oil Pyrolysis

From table 4.6 shown below, the pyrolysis yield from the different catalyst can be seen to favour a more synthetic mix of the fly ash and silicate although, it appears to produce more chars which rapidly damage the catalyst pore opening and makes regeneration difficult, its gas yield is minimal compared to the other catalyst. Its wax production is also negligible. From the data, cracking tend to be more severe in the SiO₂ catalyst. This is understandable as its BET data and SEM profile indicates a disposition to behave is

such manner. What is difficult to explain is a combination of high wax production occurring simultaneously with severe cracking. Often, these are diametrically opposed to each other as suggested in several literatures [74]. The high point of the pyrolysis data is the encouraging result obtained from the Fly Ash catalyst result. At 61.5% oil yield, it competes quite well with the commercially available alternative and since it is obtained from the same waste dump, it enhances the valorization scheme of the municipal waste value chain at no additional cost.

Table 4.6: Pyrolysis Results

Catalyst	Yield (%)			
	Liquid Oil	Char	Gases	Wax
Fly Ash (A)	61.5	13.2	22.5	2.8
SiO ₂ (B)	55.2	10.4	31.4	3.0
Fly Ash + SiO ₂ (C)	63.4	14.2	22.0	0.4

4.4 Engine Performance and Emissions

The oil obtained from the pyrolysis were analyzed and result obtained are shown in table 4.4 below. The oil was then blended with Diesel in the ratio of 20% WPF-80% diesel, 30% WPF-70%

diesel and 100% diesel for the purpose of performing engine test and emission analysis on an engine test rig whose configuration has been given earlier.

S/N	Properties	WPF	Diesel	ASTM D6751	Methods
1	Kinematic Viscosity at 40 ^o C	2.149	3.05	6(max)	EN ISO 3104
2	Density (Kg/m ³)	796	843	875-900	EN ISO 3675 EN ISO 12185
3	Calorific Value(kJ/kg)	41,800	43,000		
4	Refractive Index	1.32	1.44	1.245-1.675	Abbe refractometer (prolabo)
5	Flash point (°C)	72	91	90.00-130	D93
6	Ash Content (%)	<1.01%wt	<0.045wt		
7	Colour	Pale	Light green		
8	Sulphur Content %	<0.002	<0.035		D5453
9	Pour Point (°C)	-4	3-9	-15- 10	Van Garpen et al (2004)
10	Cetane Number	51	55		EN ISO 5165

The engine test results are hereby presented in Figure 4.1 to 4.4. They include the engine efficiency, brake specific fuel consumption (BSFC), brake specific carbon monoxide (BSCO) emission and brake specific nitrogen oxides (BSNOx) emission, all plotted against the engine speed. The plots are a comparative evaluation of the waste plastic fuel (WPF) versus the conventional diesel. The first two plots give an indication of engine performance whilst the last two, an indication of the emission when WPF is used compared to the diesel.

In figure 4.1 generally the engine efficiency at low speed for both WPF and diesel were low at low engine speed but the pattern trend higher as the speed increases. This is a common trend for compression ignition (CI) engines [ref]. This is because combustion efficiency at low speed is low due to engine inertia and low temperature. At low speed WPF efficiency was better than diesel

by about 6.7% because of a lower viscosity of the WPF which allows for good fuel flow and vapour dynamics but as the speed increases, diesel efficiency began the increase due to higher calorific value and better combustion efficiency. This trend is supported by similar work in literature [75]. The brake specific fuel combustion (BSFC) data is shown in figure 4.2. At initially low engine speed, the values for both WPF and diesel were high, they both trended lower at medium level mid-engine speed because of improved combustion efficiency and began to increase with increasing power demands, giving a bath-tube shape curve. This is common for CI engine [76]. The BSFC data generally showed a mix outcome for WPF and diesel, indicating a statistically equal performance throughout the entire load spectrum. This is a slightly different outcome from observation in literatures of similar works. This trend, it is

believed, arise as a result of non-homogeneity of fuel mix for the WPF.

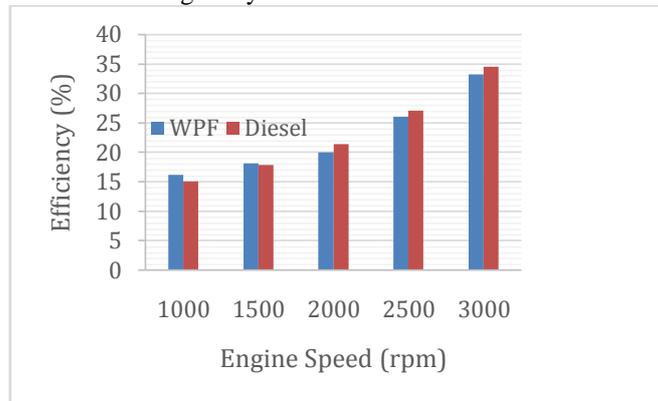


Figure 4.1: Engine Efficiency

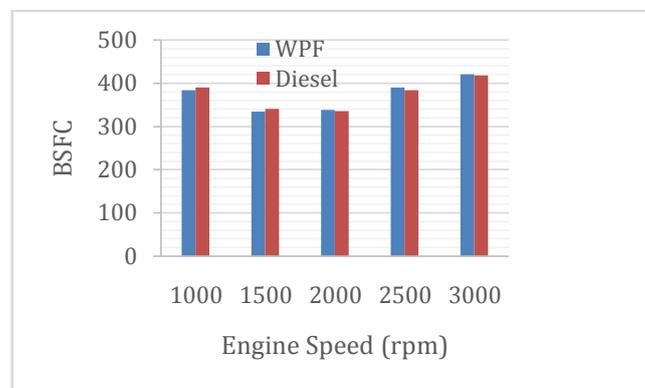


Figure 4.2: Engine BSFC

Figure 4.3 and 4.4 shows the BSCO and BSNO_x emission for the two types of fuel. The former decreases with increasing engine speed whilst the later increases with increasing speed. The obvious reason for both trends being the engine temperature. Increasing engine temperature improves combustion efficiency thus lowering CO production whilst the same phenomenon increases

NO_x emission due to Zeldovich mechanism for NO_x emission. A wide array of literature agrees with this result [77].

The important highlight is that WPF compared to diesel, is quite competitive in performance and emission and, if all technical as well as economic factors are considered, WPF is a viable alternative to conventional diesel.

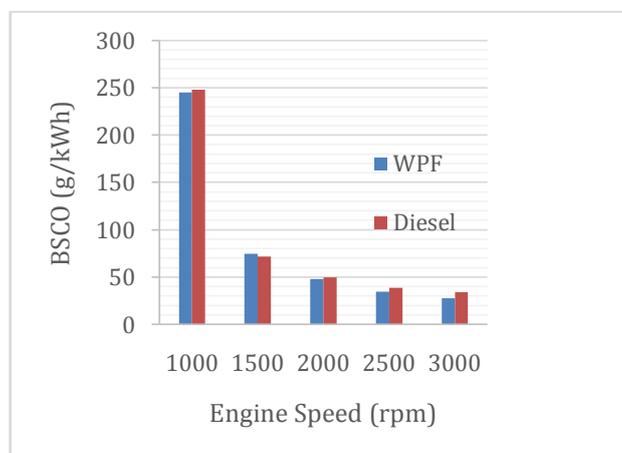


Figure 4.3: Engine BSCO

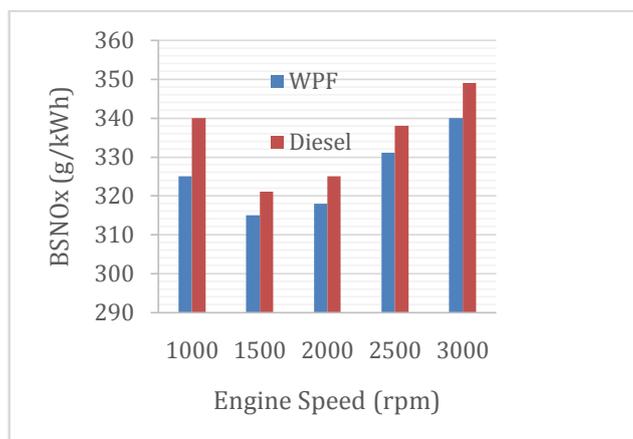


Figure 4.4: Engine BSNOx

V

CONCLUSION

The result has established the challenge associated with municipal plastic waste (MPW) disposal in Bauchi metropolis, determine the viability of waste fly ash as a potential catalyst for MPW pyrolysis, proven the physico-chemical suitability of WPF for use in CI engine and determined the emission from WPF falls within current level of diesel emissions.

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