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THE STUDY OF DIRECT ELECTRIC CURRENT ON BIOREMEDIATION OF SOIL CO-CONTAMINATED WITH SYNTHETIC PHENOL AND LEAD

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ABSTRACT

Electrokinetic bioremediation is an emerging technology for remediating organic-inorganic contaminated soil. The objective of this study was to evaluate the potential and feasibility of direct electric current in the biodegradation of phenol and uptake of lead from phenol-lead-impacted soil. A bench-scale uniform electrokinetic reactor was developed and the effect of varied electric voltages (6 – 30 V/cm) on bioremediation of 1 kg sandy loamy soil spiked with synthetic waste water containing 204.84 mg of phenol and 64.94 mg of lead was studied. On the application of 6, 12, 18 24, and 30 V/cm electric voltage, an average corresponding removal of (79.85 %, 81.95%, 83.76 %, *84.05%, 93.01%) and (56.43 %, 58.09%,* 63.75 %, *67.55%, 68.3%) were attained for phenol and lead respectively within 84 days. Also, the rate of phenol biodegradation and lead uptake from the contaminated soil was observed to increase with increased voltage application. The results of the experiment showed that the application of direct current (voltage) was an effective strategy to accelerate the movement and biodegradation of phenol and lead uptake in the soil. Therefore, method of electrokinetic bioremediation can be employed to remediate soil contaminated with phenol and lead contaminants.*

Keywords: *Electrokinetic, Bioremediation, Phenol, Lead, Electric current, Contaminants.*

1. INTRODUCTION

Soil contamination with mixed contaminants are major environmental problem worldwide not only for their negatives effects on living organisms but also for the complexity of their remediation (Reshma *et al*., 2014). Many of the industrial contaminated sites contain both organic and inorganic (e.g. heavy metals) contaminants and their remediation is even more complex due to the very different physico-chemical properties of both kinds of contaminants. There are very few methods that can remediate both heavy metals and organic contaminants in soils. Most of these methods, however, are energy intensive, time consuming and expensive, and the results of remediation depend largely on site characteristics. Therefore, electrobioremediation is proposed as a promising technique for remediation of sites with mixed contaminants.

In recent years, there has been increasing interest in the use of electrobioremediation, a hybrid technology of bioremediation and electrokinetics for the treatment of contaminated soils (Lei *et al*., 2007). Electroremediation is a technology that uses the conductive properties of the soil, which aims to separate and remove organic and inorganic (metals) contaminants of saturated and unsaturated soils, sludges and sediments, by applying an electric field that allows removal of charged species (ions). This technology involves the application of a direct current of low intensity between a positive and a negative electrode (Pellini, 2006; Yeung *et al*., 2011). The introduced electric current creates an electric field in the soil that leads to the mobilization and migration of contaminants via electroosmosis, electromigration, and electrophoresis (Rada and Istrate 2012; Gill *et al*., 2014). These processes occur as a consequence of the resulting pH gradient that follows the production of hydrogen ions at the anode (acid front) and hydroxyl ions at the cathode (basic front) due to the electrolysis of water (Wick *et al*., 2007). These phenomena cause changes in a number of soil properties (Acar and Alshawabkeh, 1993). Electrodes can offer a continuous and finely controlled supply of electron donors and acceptors to microorganisms in the subsurface (Thrash and Coates, 2008; Aulenta *et al*., 2009 and Zhang *et al*., 2010). Electromigration and electrophoresis result in the movement of ions, ion complexes, and charged particles, such as colloidal clay and microorganisms toward the electrode of the opposite charge. Whereas electroosmosis arises from the migration of water towards the cathode, producing an electroosmotic flow which in turn facilitates the movement of cations, hydrocarbons and microorganisms in the direction of the fluid (Bayer and Sloyer, 1990). The changes induced by the application of direct current into the soil have direct effects on the microbial activity *in situ*. The outer surface of microbial or bacteria cells possesses numerous chemical groups such that the changes in soil pH generated as a result of the direct current application allows the negatively charged microorganisms or bacteria to migrate by electrophoresis towards the anode and one-dimensional flow of pore fluid from the anode to cathode (Marks *et al*., 2000; Luo *et al*., 2005). At low pH, the bacteria membrane charge is positive and the direction of movement is towards the cathode while at a pH 7 or greater, an overall negative surface potential occurs (Bayer and Sloyer, 1990). Maintenance of soil pH between 5 and 7, is therefore necessary in order to achieve the optimum degradation of contaminants by native soil microbes (Marks *et al*., 2000). Electroremediation can be performed either in-situ or ex-situ, and it is effective on fine-grained soils and soils of low hydraulic permeability which are difficult to treat by other methods. Its advantages includes: control over the direction of movement of water and dissolved contaminants, even movement across heterogeneous soils, contaminant holding in a confined area, and low energy consumption (Martinez *et al*., 2014). Similarly, combined electrokinetic biodegradation has been documented with the addition of nutrients and donor/acceptor electrons (Reinout Lageman *et al.*, 2005; Unzueta-Medina *et al*., 2007); treatment of contaminated soil with organochlorine compounds **(**Gomes *et al*., 2012), polycyclic aromatic hydrocarbons (Pazos *et al*., 2010) and heavy metals (Virkutyte *et al*., 2002), among others.

The objective of this study is to evaluate the effect of different applied voltages on the electrokinetic bioremediation of soil co-contaminated with phenol and lead. The measured parameters included the hydrogen ion concentration (pH) values and % reduction of phenol and lead.

2.0 MATERIALS AND METHODS

2.1 Collection of Sample

Soil sample was collected from an Automechanic workshop located in Orita Naira area of Ogbomoso, Oyo State, Nigeria on longitude $8^{O}08'31N$ and latitude $4^{o}15'07E$. The soil samples was air dried, homogenized, filtered through a 2 mm (pore size) sieve and stored in a polyethylene bag in the laboratory prior to use (Agarry *et al*., 2010).

2.2 Characterization of Soil Sample

The soil sample was characterized for Total Nitrogen (TN), Total Phosphorus (TP), Total Carbon (TC), Moisture Content (MC) and pH by Gravimetric method. Total Nitrogen was determined by kjedahl digestion and steam distillation method of Brenner and Mulvaney, (1982). Phosphorus was determined using the flame photometer. Micro nutrients were determined by the Diethylene-triamine penta-acetic acid (DTPA) micronutrient extraction method of Lindsay and Norvell, 1978. Total Heterotrophic Bacteria (THB) and Total Hydrogen Utilizing Bacteria (THUB) present in the soil were determined according to the methods of Odokuma and Okpokwasili, 1993; Odokuma and Ibor, 2002; Amanchukwu *et al*., 1989 and Mills *et al*., 1978. The pH was determined according to the modified method of McLean (1982), Total organic carbon was determined by the dry weight method. The result of the soil physicochemical characterization are presented in Table 1.

2.3 Preparation of Contaminated Soil

One kilogram (1 kg) soil sample was spiked with synthetic waste water containing 204.84 mg of phenol and 64.94 mg of lead.

2.4 Electrobioremediation of soil co-contaminated with phenol and lead

The electrokinetic reactor set up used for the electrobioremediation experiments is as shown in Figures 1 and 2. The electrokinetic reactor consist of a soil cell, a pair of electrode, an electric current and voltage real-time monitoring system, and a DC power supply (solar power). The soil cell was made of transparent plastic container with an inner size of length 50 cm x height (17 cm) x width (10 cm). The power supply (solar power) provide a constant DC electric voltage in a range of 0 to 30 volts for the electrokinetic study.

The moist soil sample (1 kg) contaminated with wastewater containing 204.84 mg phenol and 64.94 mg lead, was put into the soil cell and this was labelled Bed A. The soil cell was pressed down using a perspex pestle so as to minimize the amount of void space in the soil. The extruded pore fluids were removed from the surface layer using filter paper. The soil cell (Bed A) was sub-divided into five (5) compartments labelled (A_1, A_2, A_3, A_4, A_5) as shown in Figure 3. A fraction of the soil sample was withdrawn and analyzed for the actual initial content of phenol and lead, soil pH and moisture content. Two electrodes were inserted into both terminals (at opposite sides) of the soil bed with a distance of 40 cm from each other; power supply, electrode control apparatus and monitoring equipment were then connected to the electrodes as shown in Figures 1 and 2. A constant voltage gradient of 6 volt (V/cm) was then applied through the electrodes into the soil in one direction and the bioremediation process was monitored for 84 days.

The procedure was repeated for 12, 18, 24 and 30 V/cm for the cells with labelling ranging from Bed B (B_1,B_2,B_3,B_4,B_5); Bed C (C_1,C_2,C_3,C_4,C_5); Bed D (D_1,D_2,D_3,D_4,D_5) and Bed E (E_1,E_2,E_3,E_4,E_5).

At 72 hr intervals, the soil moisture in the soil reactor was maintained by adding 30 ml of distilled water after which the whole content was well agitated by means of a stirrer. A control experiment without application of direct current (voltage) was simultaneously set up and this was labelled Bed G. At 14 days intervals, at different locations within the cells [(s.p 1, s.p 2, s.p 3, s.p 4, s.p 5) Figure 3] current passing through the soil cell was measured and soil samples collected to determine the soil pH, residual phenol and lead concentrations.

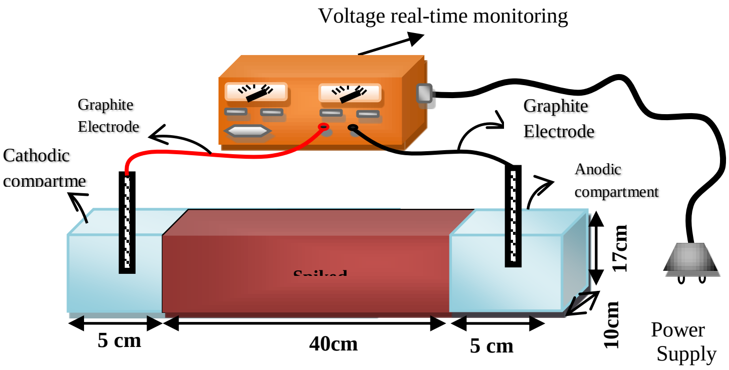


Figure 1: Schematic Diagram of Electrokinetic Reactor

Figure 2: Electrobioremediation Experimental Set up

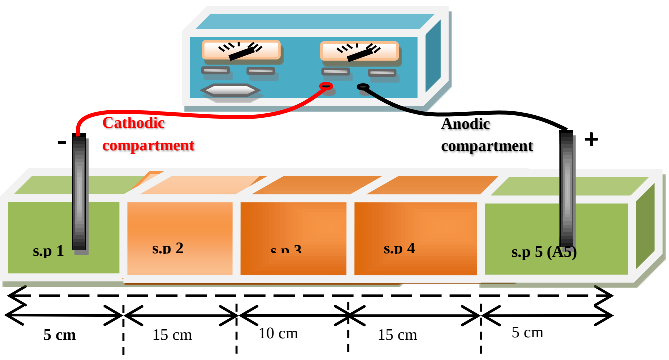


Figure 3: Soil sampling points

s.p 1 → Anode
s.p 5 → Cathode
s.p 3 → mid-point
s.p 2 → middle between s.p 1 and s.p 3
s.p 4 → middle between s.p 3 and s.p 5

3. RESULTS AND DISCUSSION

Table 1: Soil Physicochemical and Microbiological Analysis

Parameter	**Soil**
Total Nitrogen (%)	0.25±0.02
Total Phosphorus (%)	0.03±0.02
Organic Carbon (%)	0.15±0.02
Potassium (%)	0.05±0.01
pH	6.2±0.1
Residual phenol	4.84±0.01
Residual lead	14.94±0.01
Moisture Content (%)	8.5414.94±0.010.2
THB	$0.78 \times 10^5 \pm 0.2$
THUB	$16.8 \times 10^5 \pm 0.1$

*Data presented are mean of triplicate determination ± standard deviation

3.1 Effect of Applied Voltage on Percentage Phenol biodegradation and Uptake of Lead

Figures 4 (A – E) show the distribution of phenol and lead in soil at the end of the electrokinetic experiments. The amount of phenol and lead was low in all tests, but varied across the sections from anode to cathode. The results show that the amount of phenol and lead was low near the anode, which gradually increased towards the third section and decreased near the cathode. The respective percentage reduction of phenol and lead remaining in the co-contaminated soil after electrokinetic treatment at section PA1, PA2, PA3, PA4, PA5 (phenol) and LA1, LA2, LA3, LA4, LA5 (lead) (from anode to cathode) showed that application of 6 volts yielded a percentage reduction of 42.3, 50.28, 58.11, 63.65, 71.01 % (phenol) and 21.13, 28.55, 35.46, 40.82, 45.25 % (lead) after 14 days respectively. This is an indication that phenol and lead reduction increased with the level of voltage applied. This same trend was also observed in the percentage phenol and lead reduction at 84 days with percentage reduction values of 58.78, 65.02, 71.15, 76.14, 79.85 % (phenol) and 35.02, 42.85, 48.88, 52.78, 56.43 % (lead) when 6 volts was applied.

Natural Attenuation for Phenol (PANA) and Natural Attenuation for lead (LANA) which consists of co-contaminated soil without application of electricity gave 5.22, 6.4, 6.75, 7.14, 7.77 and 7.95 % percentage phenol and lead reduction after 14, 28, 42, 56, 70 and 84 days respectively while the control; Autoclaved soil for phenol (PAAT) and Autoclaved soil for lead (LAAT) which was co-contaminated autoclaved soil without application of electricity gave 0.83, 0.95, 1.15, 1.25, 1.36 and 1.55 % phenol and lead reductions after 14, 28, 42, 56, 70 and 84 days respectively. The variations in percentage phenol and lead reduction with time are shown in Figures 4 (A to E) which shows that percentage phenol and lead reduction increased with time. On application of 6V voltage, percentage phenol and lead reduction increased from 42.3 % (phenol), 21.13 % (lead) at 14 days to 58.78 % (phenol), 35.02 % (lead) at 84 days as shown in Figure 4A (a) and Figure 4A (b)which is the same trend followed by the other levels of treatment.

In the same manner, on the application of 12 volts, the percentage phenol and lead reduction increased with applied voltage and time as shown in Figure 4B (a) and Figure 4B (b). The percentage phenol and lead reduction increased from a low value of 50.11 % (phenol), 36.74 % (lead) at 14 days (soil microcosm PB1 and soil microcosm LB1) to a peak value of 81.95 % (phenol), 58.09 % (lead) at 84 days (soil microcosm PB5 and soil microcosm LB5). The control samples (Control PBNA and LBNA) which consists of co-contaminated soil without any applied voltage resulted in 5.22, 6.4, 6.75, 7.41, 7.77 and 7.95 % reduction (phenol) 0.83, 0.95, 1.15, 1.25, 1.36 and 1.55 % reductions (lead) after 14, 28. 42, 56, 70 and 84 days respectively.

Control PBAT and LBAT which consists of co-contaminated autoclaved soil without any applied voltage yielded 0.83, 0.95, 1.15, 1.25, 1.36 and 1.55 % percentage concentration reductions after 14, 28. 42, 56, 70 and 84 days.

Similarly for 18 volts, the percentage phenol and lead reduction increased with applied voltage and as well as with time as shown on Figure 4C (a) and Figure 4C (b). The value increased from a lowest value of 52.43 % (phenol) and 36.24 % (lead) at 14 days (soil microcosm PC1 and soil microcosm PC1) to a peak value of 83.76 % (phenol) and 63.75 % (lead) at 84 days (soil microcosm PC5 and soil microcosm LC5). Control PCNA and LCNA which consists of co-contaminated soil without any applied voltage resulted in 5.22, 6.4, 6.75, 7.41, 7.77 and 7.95 % percentage concentration reductions after 14, 28, 42, 56, 70 and 84 days respectively while control PCAT and LCAT which was co-contaminated autoclaved soil without any applied voltage gave 0.83 %, 0.95 %, 1.15, 1.25, 1.36 and 1.55 % percentage concentration reductions after 14, 28, 42, 56, 70 and 84 days respectively.

Similarly on application of 24 volts, as shown in Figure 4D (a) and Figure 4D (b), the lowest percentage phenol and lead reduction value of 53.25 % (phenol) and 41.98% (lead) was obtained at 14 days i.e. soil microcosm PD1 and soil microcosm LD1, while the highest percentage phenol and lead reduction value of 84.05 % (phenol) and 67.55 % (lead) was obtained at 84 days i.e. soil microcosm PD5 and soil microcosm LD5. Control PDNA and LDNA which consists of co-contaminated soil without applied voltage resulted in 5.22, 6.4, 6.75, 7.41, 7.77 and 7.95 % percentage concentration reductions after 14, 28, 42, 56, 70 and 84 days respectively while control PDAT and LDAT which consists of co-contaminated autoclaved soil without any applied voltage yielded 0.83, 0.95, 1.15, 1.25, 1.36 and 1.55 % percentage concentration reductions after 14, 28, 42, 56, 70 and 84 days respectively.

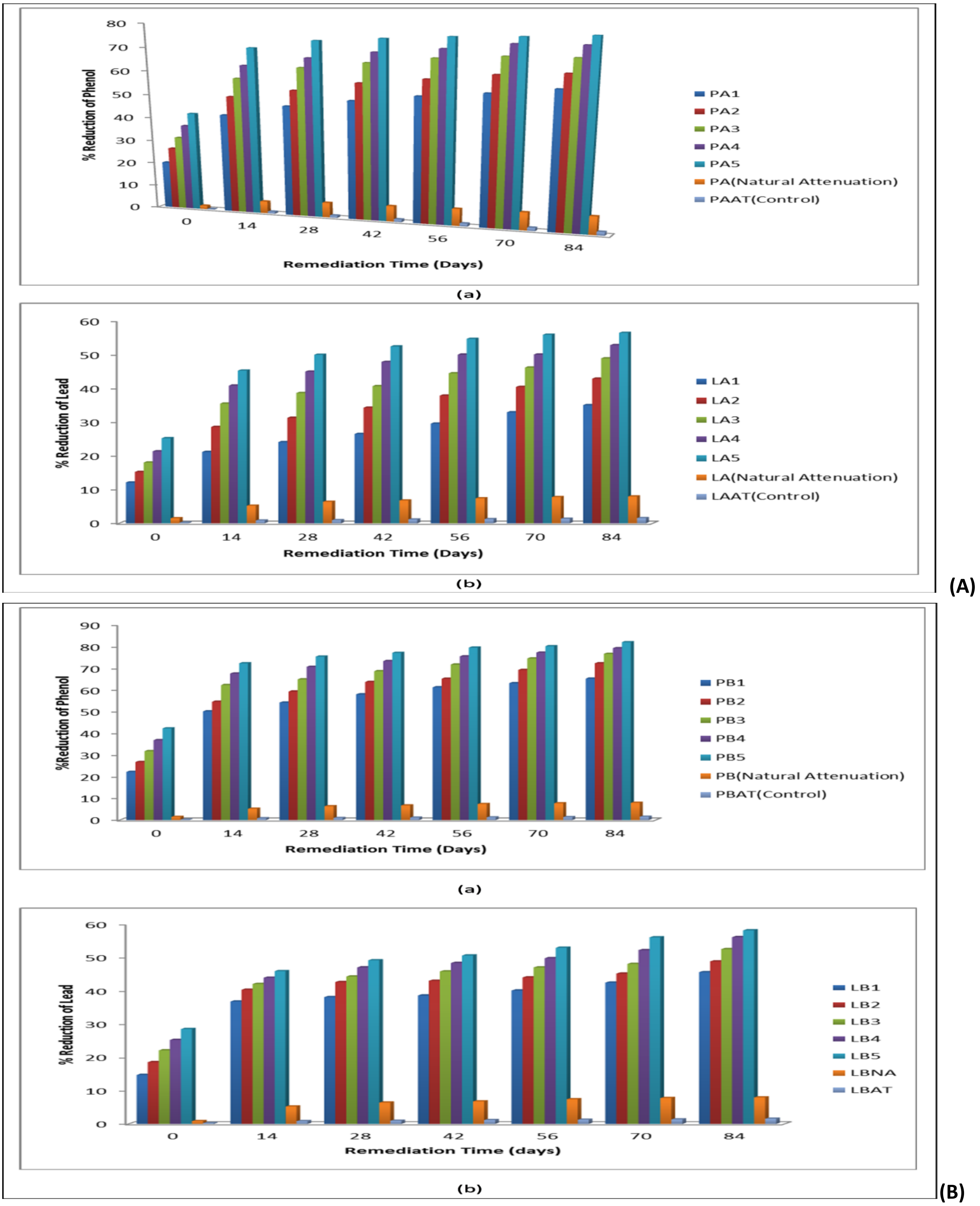
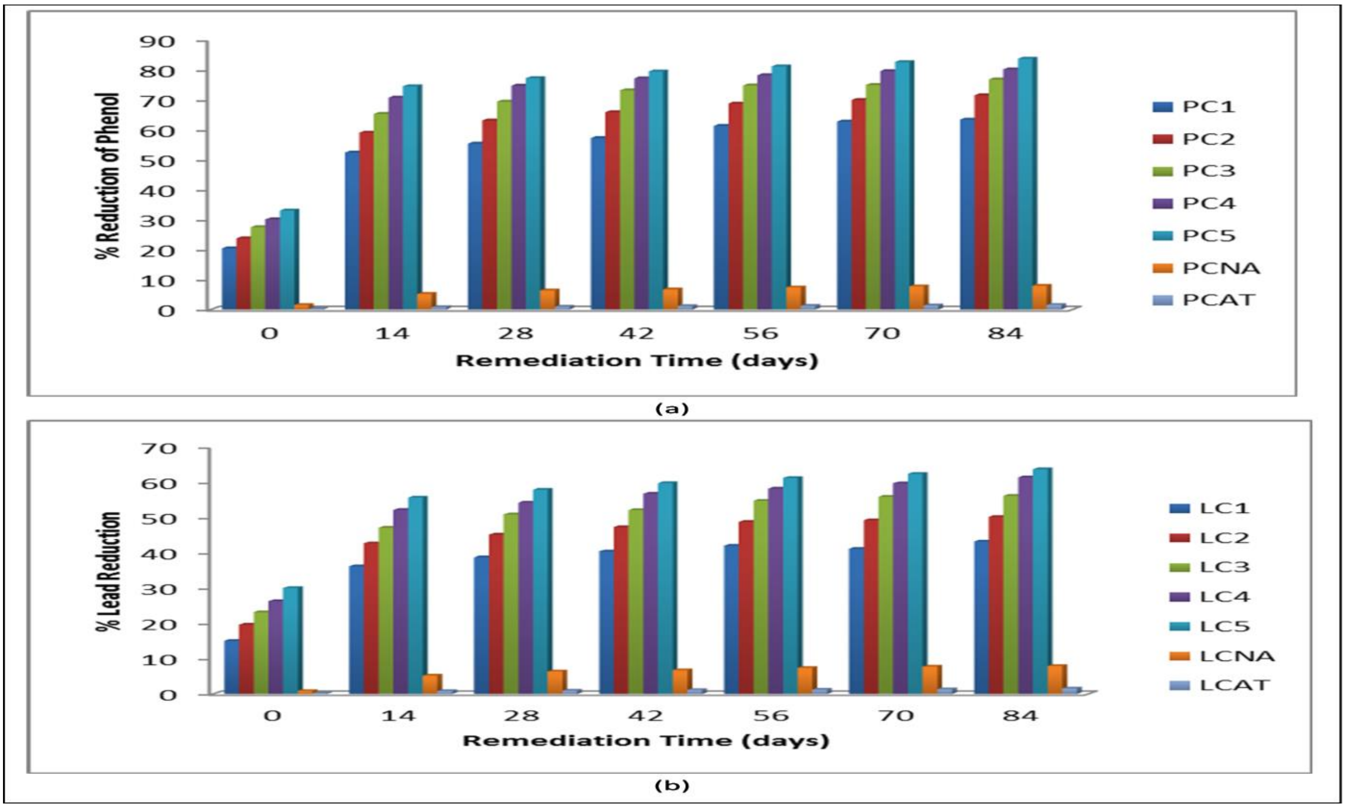
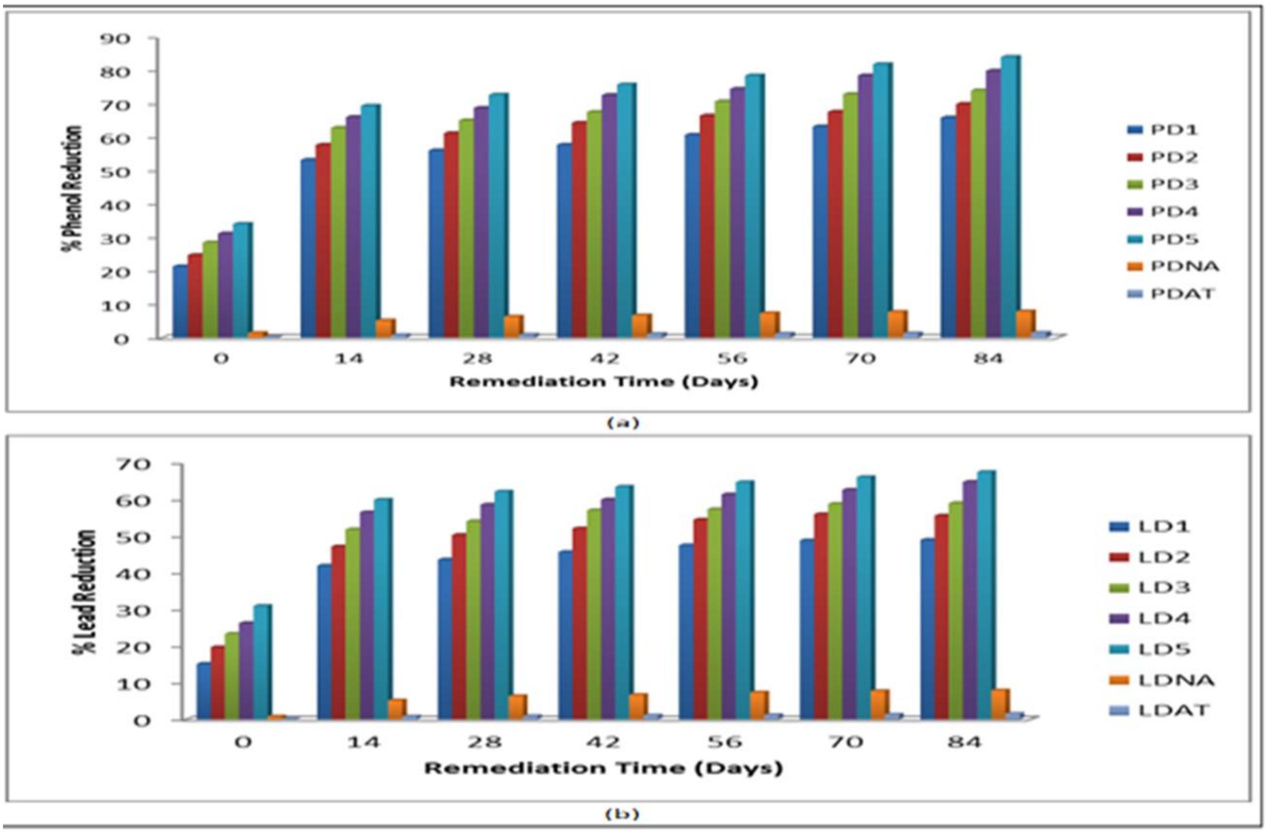


Figure 4: Effect of voltage on % reduction of (a) Phenol (b) Lead for (A) 6 volts (B) 12 volts in soil co-contaminated with phenol and lead

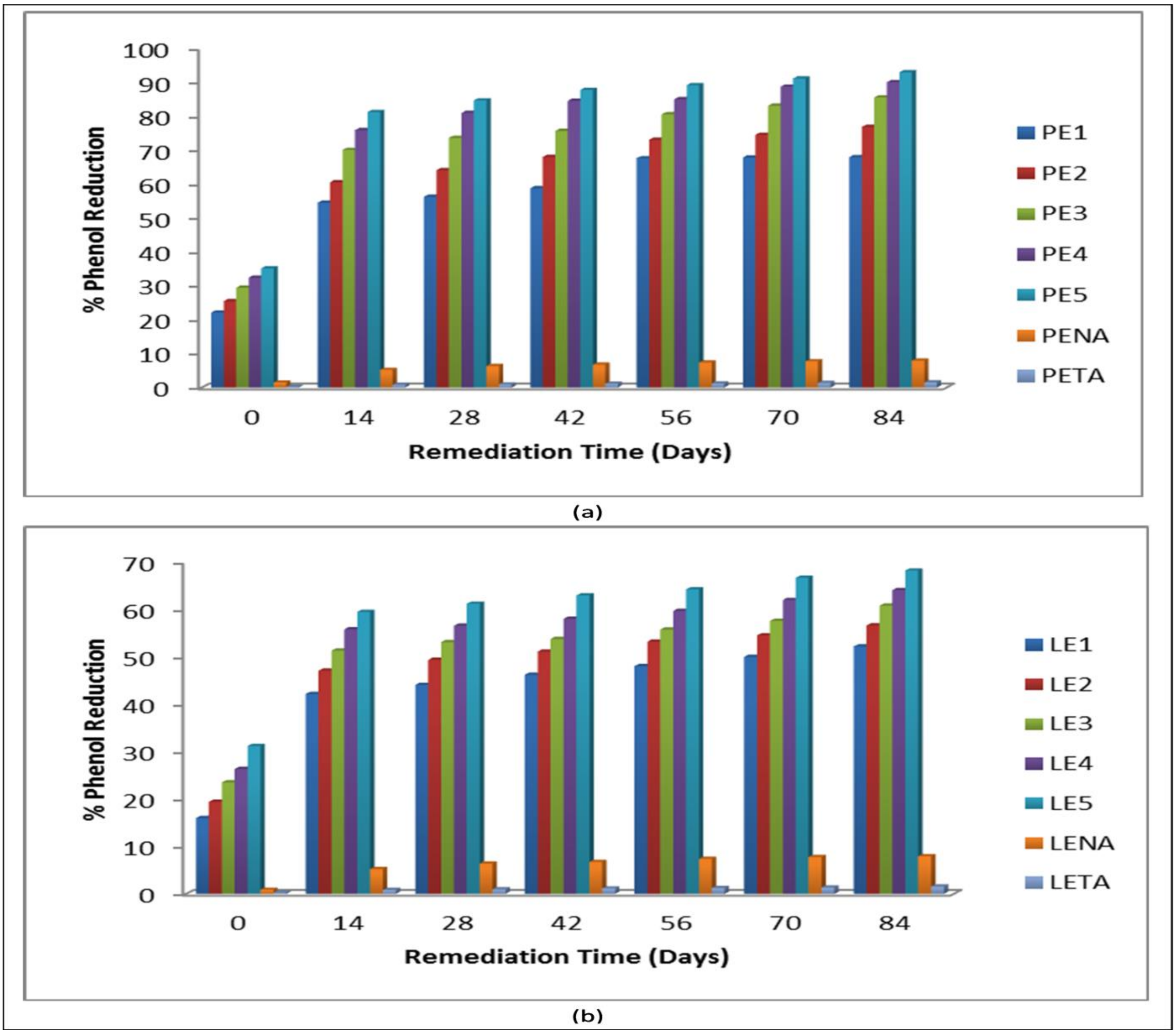


(C)



(D)

Figure 4: Effect of voltage on % reduction of (a) Phenol (b) Lead for (C) 18 volts (D) 24 volts in soil co-contaminated with phenol and lead



(E)

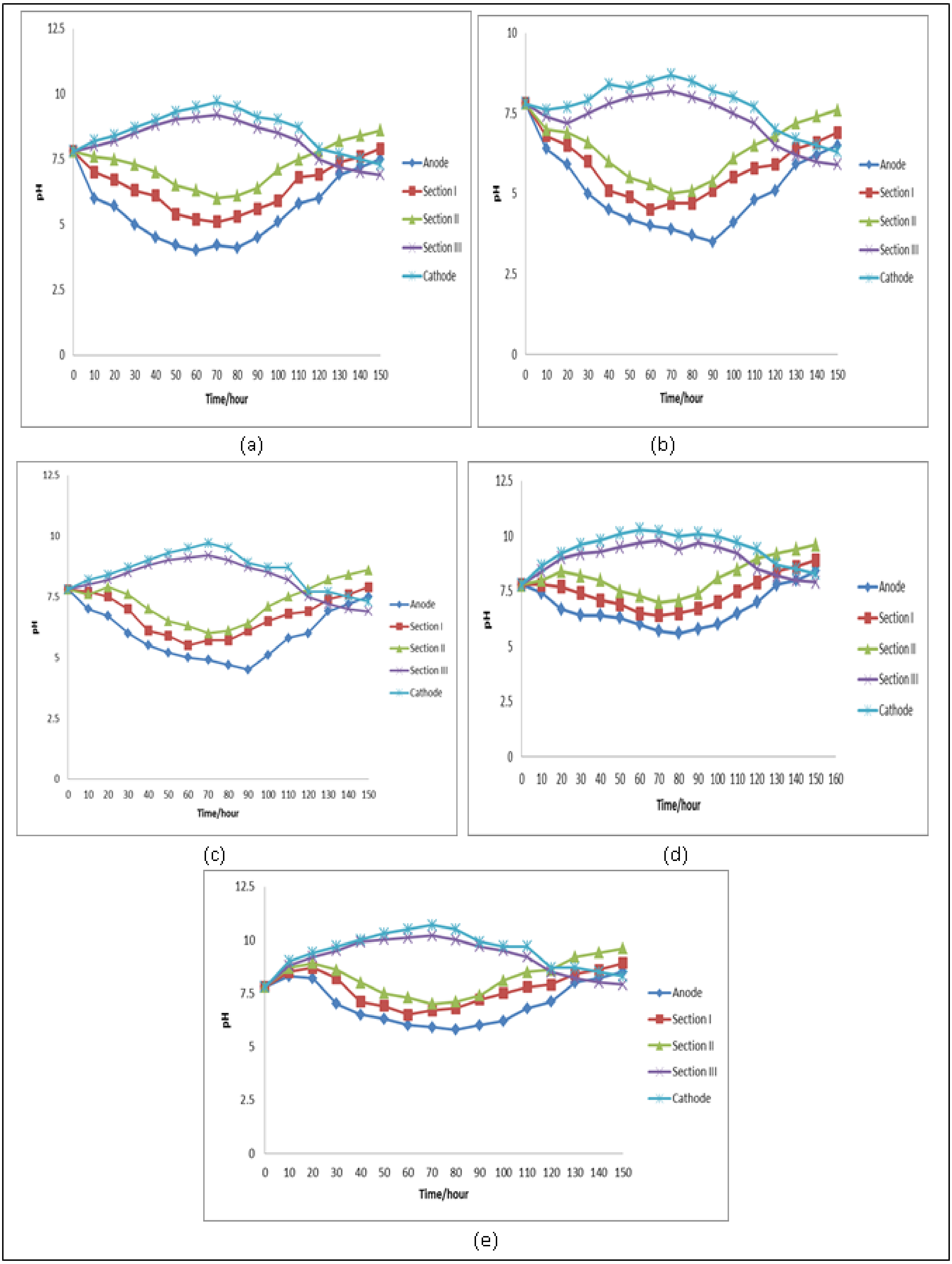
Figure 4: Effect of voltage on % reduction of (a) Phenol (b) Lead for (E) 30 volts in soil co-contaminated with phenol and lead

The application of 30 volts voltage also followed a similar trend where the % phenol and lead reduction increased with the level of voltage applied and with time as shown in Figure 4E(a) and Figure 4E(b) where the lowest percentage phenol and lead reduction value of 54.5 % and 42.22 % was obtained at 14 days (at anode compartment) i.e. soil microcosm PE1 and LE1, and the highest percentage phenol and lead reduction value of 93.01 % and 68.3 % was obtained at 84 days respectively (at the cathode compartment). Control PENA and LENA which consists of co-contaminated soil without application of electric current resulted in 5.22, 6.4, 6.75, 7.41, 7.77 and 7.95 % percentage concentration reduction after 14, 28, 42, 56, 70 and 84 days respectively. Control PETA and LETA which consists of co-contaminated autoclaved soil without application of electric current gave 0.83, 0.95, 1.15, 1.36 and 1.55 % percentage concentration reduction after 14, 28, 56, 70 and 84 days respectively.

The results of this study is similar to those reported in the works of Luo *et al.,* (2005) and Fan *et al.,* (2007) where alternating current was applied to phenol contaminated soil. The result showed that electrokinetic operation mode could affect the degradation rate of total phenol and lead in different regions in soils. The discrepancies in phenol and lead removal between the cathode and anode were possibly due to the difference in soil pH. A number of studies have described the negative effects of acidified soils on the resident microbial life, which include adverse influences on parameters such as size, activity, membrane integrity and function, bioavailability of nutrients and contaminants, and growth (Lear *et al.,* 2004). However, near the cathode, the soil pH was found to be near-neutral (around 7.8) which is suitable for bacterial growth; hence, the observed increased phenol and lead removal efficiency. The result of this study also agreed with the reports of Diannan Huang *et al.,* (2013); Khodadadi *et al.,* (2016) and Krishna *et al.,* (2003) which attributed the potential to mobilize bacteria and their substrates by electrokinetic transport processes mostly to the mechanisms of electrophoresis and in part by electroosmosis.

3.2 Variation of soil pH during electrobioremediation process

The results obtained at the end of the test across the soil samples revealed that the applied direct current electric field induced changes in soil pH during the course of electrobioremediation. The dynamics of pH change with time in different sections of the soil sample at different specific voltage is shown in Figure 5. During the electrokinetic treatment of soil co-contaminated with phenol and lead, H^+ ions and OH^- ions were produced on the anode and cathode, respectively. These ions electromigrate to the opposite sides, thereby decreasing the soil pH temporarily and spatially. In the Electro kinetic experiment with applied voltage of 6 volts, (Figure 5a), the soil pH values showed a gradual increase from anode section to cathode section, and from section I to section III with values comparable to initial pH condition of 7.8, having decreased to 7.0 at anode section after 10 hours, 7.7 at section I, and 7.6 at section II, but later increased to 8.0 in section III and 8.2 at cathode section. This result was due to the H^+ and $OH^–$ ions generated by the electrolysis of water during the EK remediation process (Probstein and Hicks, 1993). Anode produced large amount of H^+ which led to the drop in pH of the soil and the reaction zone around the anode showed acidic tendencies. On the contrary, the zone around the cathode showed alkalinity because of increased $OH^–$ (Acar and Alshawabkeh, 1993; Isosaari *et al.,* 2007). In the section nearest to the anode, pH changes to acidic values, and in the sections nearest to the cathode, pH values become alkaline. Lee and Yang (2000) reported that excess H^+ resulted in decreased electroosmosis, stopping OH^- movement to the anode from the cathode, leaving a greater concentration of H^+ ions near the anode, thereby leading to the resulting low pH at points closer to the anode. In the Electrokinetic experiment with 12 volts (Figure 5b), after 10 hours the variation in soil pH was observed to decreased to 7.42 near the anode and increased to 8.65 near the cathode. Similarly, the observed variation in soil pH with the application of 18 volts (Figure 5c), 24 volts (Figure 5d) and 30 volts (Figure 5e) followed similar trend as those of the previous applied voltage. This result is in accordance with the findings of Shen *et al.* (2007). For anode section, distribution of pH was found to be different from that of cathode section. These results therefore showed that there is an optimum pH at which effective electrokinetic remediation can occur.



(a)

(b)

(c)

(d)

(e)

Figure 5:Variation of soil pH with time during electrokinetic remediation process

4 CONCLUSION

The effect of application of direct electric current on bioremediation of soil co-contaminated with synthetic phenol and lead have been assessed for an ex-situ bioremediation system. On the application of 6, 12, 18 24, and 30 V/cm voltage, the technique correspondingly and averagely removed (79.85 %, 81.95%, 83.76 %, 84.05%, 93.01%) phenol and (56.43 %, 58.09%, 63.75 %, 67.55%, 68.3%) lead from co-contaminated soil within 84 days of experimentation. Therefore, bioremediation of soil co-contaminated with phenol and lead can be enhanced by electrokinetics, and the rate of biodegradation of phenol and uptake of lead from the soil increased relatively with increased voltage application. Hence, the electrokinetic bioremediation of soil can be used to remediate soil contaminated with phenol and lead contaminants.

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CHARACTERIZATION OF KAOLIN FROM NARAGUTA CLAY DEPOSIT IN JOS NORTH LOCAL GOVERNMENT AREA OF PLATEAU STATE FOR THE PRODUCTION OF CERAMIC MATERIAL

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ABSTRACT

Clay Samples from Naraguta deposit in Jos North Local Government Area of Plateau State, Nigeria have been studied for its application as raw material for ceramic material production. The effects of firing temperature on the physical properties were also studied. Naraguta clay, samples were obtained randomly from different points within each deposit from underground local mines pit at a depth of 10, 20 and 30 cm and labelled samples 1, 2 and 3 respectively. The samples were air-dried for several days and crushed using a crusher. Each crushed sample was thoroughly mixed, coned and quartered. The samples were subsequently balled milled to form a powder. The powder was pressed to form pellets which were dried at 105 ^oC until a constant weight was achieved. The samples were then heated to temperature 750, 800, 850, 900, and 950 ^oC in a furnace, respectively at a rate of 5 ^oC/min with soaking time of 1h at each maximum temperature. The elemental analysis was carried out using X-ray fluorescence (XRF) while the structural analysis was done using X-ray diffraction (XRD).The property tests such as bulk density, apparent porosity, compressive strength and shear stress were carried out using standard techniques such as American Society for Testing and Materials. The results of the elemental analysis revealed that the clays were composed majorly of silica (SiO_2), 49 – 51%; alumina (Al_2O_3), 31.49 – 33.30% with the presences of some other oxides. The XRD spectra of the clay showed that the components of the clay samples were predominantly kaolinite constituting about 80% of the particles with some traces of mica and quartz. The physical properties (bulk density, compressive strength and shear strength) of the clay sample initially increased with increased firing temperature from 750 ^oC to 800 ^oC, and then the properties decreased with further increase in firing temperature until it reached 950 ^oC because of the transformation of the clay due to dehydroxylation of kaolin to meta-kaolin. The results of both the physical and chemical analysis fall within the acceptable standards for materials for ceramic material production.

Key Words: *Kaolin, Ceramic Material, Chemical and Physical Analysis, X-Ray fluorescence, X-Ray Diffraction*

1. INTRODUCTION

Ceramics are inorganic and nonmetallic solids with a range of useful properties, including very high hardness and strength, extremely high melting points, and excellent electrical and thermal insulation. The best-known ceramics are pottery, glass, brick, porcelain, and cement (Emmanuel 2015). Clay remains the major raw material in the ceramic industry. It has also found wide applications in the paint and paper industries. This versatility depends principally on the composition and physical properties. The properties of a particular ceramic depend not just on the materials from which it is made but also on the crystalline structure**.** The clay used for the production of ceramics should have the following specifications; plastic enough for shaping, dry without excessive cracking and warping, have low and wide vitrification range, low carbonate content, and a good spread in particle size. (Angelica *et al*., 2008). Low and wide vitrification range is desirable for favourable unit firing cost and for ease of firing. Because the fluxing action of carbonates tends to shorten the firing range and trigger localized flux spots, the low carbonate content is desirable, and CaO and MgO resulting from the firing of typical carbonate-bearing clay can hydrate relatively easily with no damage to the fired material.

In the fabrication of ceramic products, raw materials selection plays a vital role in the final product. The properties of the components present in the clay and the firing temperature affect the physicochemical properties of the resulting ceramics (Jordan et al., 1999) critically.

The sintering process has been widely used in producing ceramic components. Sintering processes can be divided into two types: solid-state sintering and liquid phase sintering. Solid-State Sintering (SSS) happens when the powder compact is fully densified in a solid-state at sintering time, whereas fluid phase sintering occurs when the powder compact is still in a liquid phase during sintering (Kang, 2005).

Sintering of ceramic mass is therefore critical in adjusting desired properties and occurs in general during liquid-phase formation. The presence of components such as low-melting clays is significant in the process. Fluxes (alkaline oxides, mainly K_2O and Na_2O), in reaction with silica and alumina, promote liquid phase formations and therefore assist the densification process (Hamisi *et al*., 2014). Evaluating the phase transformations which take place during the firing process is, therefore, crucial in determining the quality of the clay used in the formulation of ceramic materials (Sousa and Holanda, 2005).

According to Emmanuel (2015), Nigeria is immensely endowed with ceramic raw materials like alumina, coal, clay, feldspar, kaolin, quartz, silicon, and zirconium, located throughout the country's geographical zones. Local demands for ceramic products are very high, considering the population of Nigeria which is presently about 180 million, yet the supply is met mostly through importation. Despite the fact that both raw materials and human capacity are available for research, production and development of high-quality ceramic products of international standard, the country imports more than 50 containers a day (Emmanuel, 2015). The author also reported that the housing deficit in *Nigeria* is about 17 million units with an annual growth *of* 2 million units. With massive developments in *real estate sector* in the country to meet the increasing *demands* for decent housing, *the demand for ceramic tiles which are used for floor, walls, ceiling and even roof* is *high* in the country.

Next is the power sector with its high demand for electrical porcelain insulators. Another area worth considering is ceramics for home use. This includes dinner wares, pottery wares and decorative wares. Other products such as spark plug ceramics, beryllium oxide ceramics, chemical or refractory porcelain, engine and turbine combustion chambers can be categorized for industrial applications (Emmanuel, 2015).

It makes economic sense to invest in the production of ceramics in Nigeria at this time with all these demands in the different sectors, even as the raw materials are readily available in commercial quantities. This will not only help meet the growing demand for these products but will also help create jobs and help the state economy to grow. Clay bodies are widely distributed on the Precambrian basement complex of Nigeria. Clay occurs in deposits of greatly varying nature. No two deposits have the same clay, and frequently different samples of clay from the same deposit differ. Due to its small size, complex structural structure and relative slow kinetics of forming and transition, clay can be challenging to define.

Naraguta clay deposit is located in Jos North Local Government Area of Plateau State, North Central Nigeria. Clay samples were collected from three different locations in the upper part of the area. The study areas are bounded between latitudes 8˚30E and 9˚00E and longitudes 9˚30N and 10˚00N. Fresh samples in lump form were obtained randomly from different points within each deposit.

This work is therefore to evaluate the properties of kaolin from Naraguta clay deposit in Jos North Local Government Area of Plateau State, Nigeria to determine its suitability for ceramic materials production.

EXPERIMENTAL PROCEDURE

Sample Preparation

The material preparation was carried out using the procedure adopted by Ituma *et al*. (2018) and Lydia *et al*. (2018). In this experiment, 5 kg of fresh samples in lump form were obtained randomly from different points within each deposit from underground local mines pit at a depth of 10, 20 and 30 cm and labelled samples 1, 2 and 3 respectively. The samples were air-dried for several days and crushed using a set of Denver crushers by Denver Equipment Co. England. Each crushed sample was thoroughly mixed, coned and quartered. These were packaged in small polythene bags as representatives of the samples for the required test. The clay sample was subsequently ball milled to form a powder. The powder was pressed to form pellets which were dried at 105 ^{o}C until a constant weight was achieved. The samples were then heated to 750, 800, 850, 900, and 950 ^{o}C, respectively at a rate of 5 ^{o}C /min with soaking time of 1h at each maximum temperature.

Sample Characterization

The elemental compositions of the clay samples were determined using X-ray fluorescence (XRF). The clay samples were mixed inside a cleansed crucible and heated to 500 °C for 8 min and allowed to cool at room temperature until the sample fused and later used for the analysis. The chemical composition of the sample is presented in Table 1.

The X-Ray Diffraction (XRD) patterns and phase identifications of the samples were carried out using X-ray diffractometer (XRD); PW 1800 diffractometer, Philips, the Netherlands with graphite monochromatized copper Kα-radiation.

Apparent porosity

Apparent porosity of the clay material was carried out by preparing a clay brick measuring 5x5x4 cm. The brick was then dried in an oven at 100 °C, fired in a furnace at a temperature of 900 °C. The fired specimen was cooled and then transferred into a desiccator, and the dry weight noted and recorded as x. The specimen was then immersed in a water-filled beaker, allowed to soak in boiled water for 30 min while being agitated to free trapped air bubble. The specimen was then allowed to cool in a desiccator and then soaked weight recorded as y. The specimen was weighed suspended in water using beaker placed on a balance, and the suspended weight noted and recorded as z. The apparent porosity was calculated using Equation (1) (Abubakar *et al*., 2014)

$$\text{Apparent porosity} = \frac{y-x}{y-z} \times 100\% \qquad (1)$$

Bulk density

The samples were dried for 24 h, the test pieces were put in an oven and dried at a temperature of 110 °C for 6 h. They were allowed to cool and weighed by means of weighing balance and their dried weights (D) recorded in turn. They were transferred to a beaker and heated for 40 min and then cooled, the soaked weight (W) was recorded. Water was put in another beaker and each of the test pieces suspended in the water so that their suspended weight (S) were recorded. The bulk density was calculated using 2 (Ovat and Bisong 2017).

$$\text{Bulk density} = \frac{D\rho W}{w-s} \qquad (2)$$

Where D = Dried weight
W = Soaked weight
S = Suspended weight
ρW =Density of water

Loss on ignition

The loss on ignition was calculated by measuring 50 g of the sample, dried in an oven at 110 °C and cooled in a desiccator. A porcelain crucible was cleaned, dried and weighed (A). The dried sample was introduced into the crucible and weighed (B). The crucible containing the sample was placed in a muffle furnace and heated to a temperature of 900 °C for 3 h, cooled in a desiccator and then weighed (C). The loss on ignition was calculated from Equation (3) (Abubakar *et al.*, 2014)

$$\text{LOI} = \frac{B-A}{B-C} \qquad (3)$$

Compressive and Shear Strength of the Kaolin Sample

The compressive strength was determined according to the ASTM Standard Test Method (D2166-13). Clay samples were ball milled to form a powder. The powders were pressed to form pellets which were dried at 105°C until a constant weight was achieved. The samples were then transferred into a furnace and heated to a temperature of 750, 800, 850, 900, and 950°C, respectively, at a rate of 5°C/min. The samples were cooled to room temperature. The samples were placed on a compressive tester and load was applied by turning the handwheel of the tester at a uniform rate of 10 N/m^2 until failure occurred. The manometer readings were recorded, and the compressive strength (CS) and Shear strength were calculated using Equation (4) (Abubakar *et al*., 2014).

$$CS = \frac{maximum\ laod\ (N)}{cross\ sectional\ area\ (m^2)} \qquad (4)$$

RESULTS AND DISCUSSION

The chemical composition of kaolin is essential because of its influence on the behaviour of ceramic masses during thermal treatment. Table 1 shows the oxide compositions of the clay samples.

Table 1: Chemical Composition of the Kaolin Sample

Oxide	Kaolin Sample 1 (%ppm)	Kaolin Sample 2 (%ppm)	Kaolin Sample 3 (%ppm)
CuO	0	0	0
NiO	0	0	0
Fe_2O_3	0.483	0.387	0.694
MnO	0	0	0

Oxide	Kaolin Sample 1 (%ppm)	Kaolin Sample 2 (%ppm)	Kaolin Sample 3 (%ppm)
Cr_2O_3	0.011	0.009	0.017
TiO_2	1.112	0.801	1.483
CaO	0.083	0.106	0.093
Al_2O_3	31.494	32.878	33.301
MgO	0.328	0.317	0
ZnO	0.004	0.004	0.006
SiO_2	49.038	51.102	50.673
Total	82.553	85.604	86.267
LOI	17.447	14.396	13.733

From Table 1, it could be deduced that the silica contents of the samples are 49.04, 51.10 and 50.67% of clay sample 1, 2 and 3, respectively. This showed that all the clay samples met the requirements for the manufacture of ceramics, as reported by Abubakar *et al*. (2014). In their work, they reported that a clay material having silica contents of between 40 – 65 % satisfies the requirements for the manufacture of refractory bricks and ceramics. This may be due to the presence of higher bond impacted into the matrix of the clay by the silica content.

An Al_2O_3 content higher than 30 % is necessary for increasing the refractory and mechanical resistance (Benea and Gorea, 2004). From Table 1, it could be deduced that the alumina contents of the clay samples were found to be between 31 – 33%, an indication that the samples fell within the range of standards for the manufacturing of ceramics (above 30%) and refractory bricks (25 – 44%). From Table 1 also, the Fe_2O_3 contents of the clay samples are 0.483, 0.387 and 0.694 % for sample 1, 2 and 3, respectively. These values of the Fe_2O_3contents also fell within the range of standards (0.4 – 2.4 %) for the manufacture of refractory bricks. Such level of Fe_2O_3 usually alters the colour of the clay to reddish-brown, thereby making it attractive as a ceramic material as reported by Marcel and Bernea (2004). Marcel and Bernea (2004) reported that the Fe_2O_3 content of clay influenced the high-temperature characteristics of the clay such as the fired strength.

The Loss on Ignition (LOI) values of the clay samples was within 13.73 – 17.45%. The values, which fell within the range of 8 – 18 % for ceramics and refractory bricks products as reported by Omowumi (2000). Omowumi (2000) reported that the LOI characteristics of the clay materials should be low in other not to impact adverse effects on the porosity of the materials especially those used for refractory bricks.

The bulk density, compressive strength and shear stress of the fired clay are presented in Table 2, 3 and 4, respectively.

Table 2: Compressive Strength of the Kaolin Sample

Temperature (^oC)	Compressive Strength (N/m^2)
750	7.86
800	7.88
850	7.32
900	7.43
950	8.21

Table 3: Shear Strength of the Kaolin Sample

Temperature (^oC)	Shear Strength (N/m^2)
750	1.76
800	2.27
850	1.24
900	1.23
950	2.86

Table 4: Bulk Density of the Kaolin Sample

Temperature (^oC)	Bulk Density (g/cm^3)
750	1.55
800	1.63
850	1.59
900	1.60
950	1.56

From Tables 2 - 4, it could be observed that the properties (bulk density, compressive strength and shear strength) of the fired bricks produced from the kaolin sample initially increased with increased firing temperature from 750^{o}C to 800 ^{o}C, and then the properties decreased with further increase in firing temperature until it reached the minimum at 950 ^{o}C for the considered firing temperatures. The observed trend could be as a result of the transformation of the clay sample used for producing ceramic from one phase to another. As the dehydration of kaolinite completes by ~150 ^{o}C, followed by dehydroxylation at ~500-600 ^{o}C and its structural breakdown occurs in the temperature range ~800-900 ^{o}C, depending upon the particle size and amount and type of the impurities present (Francisca, 2014). Also, the bulk density of 1.56 g/cm^{3} obtained at a fired temperature of 950 ^{o}C showed that the sample is suitable for producing ceramic materials. The apparent porosity of the clay samples is presented in Table 5.

Table 5: Apparent porosity of the clay sample

Clay samples	**1**	**2**	**3**
Apparent porosity	4.1	5.8	8.2

The apparent porosity of the clay samples as revealed in Table 5 were found to be 4.1, 5.8 and 8.2 for samples 1, 2 and 3, respectively. These low porosities exhibited by these clay materials fell within the standard for the production of fired clay and refractories as reported by Tiffo *et al.* (2015). Tiffo *et al.* (2015) reported that low porosity found in a clay sample leads to an increase in their mechanical strength. Therefore, these samples are found suitable for the manufacture of refractories, ceramic materials and siliceous fired clays.

The phases present in the clay samples and their crystallinity were identified using XRD, as shown in Figure 2.

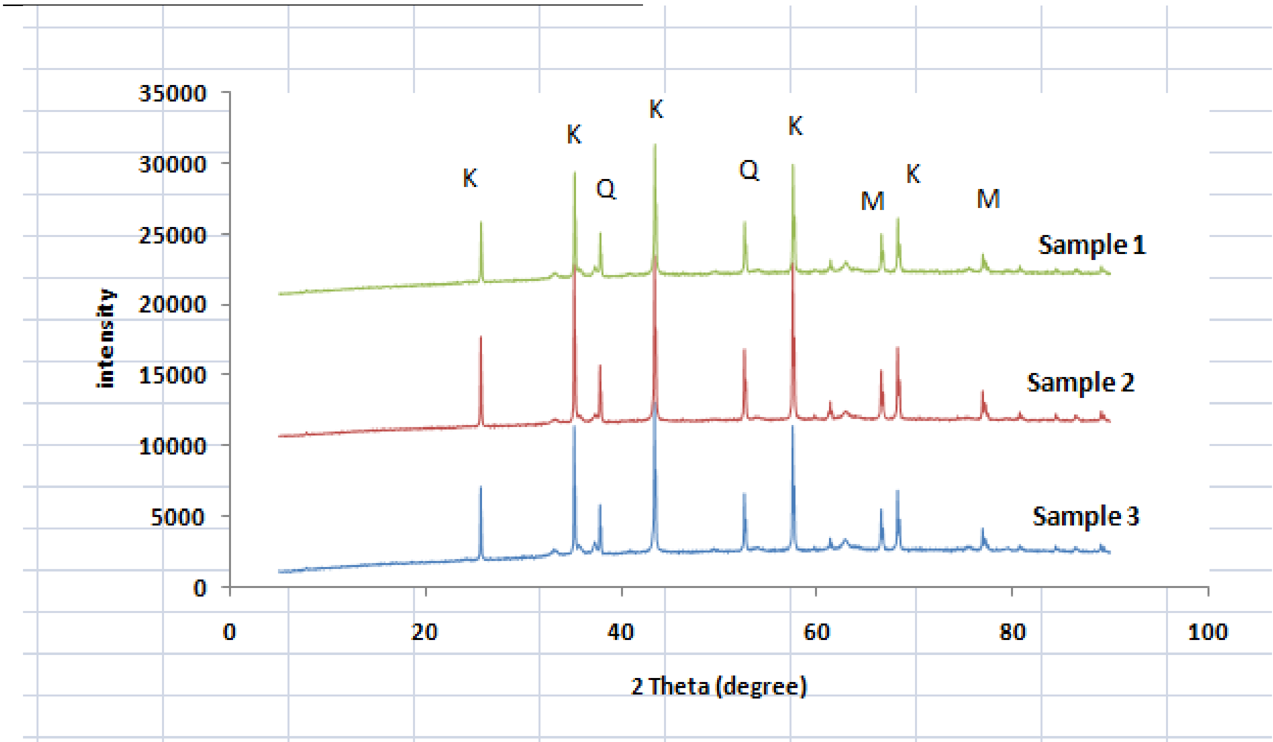

Figure 2: XRD spectra of Jos clay samples

The results, as presented in Figure, showed nine major peaks at diffraction 2θ angles, of 24.9, 33.1, 38.3, 43.8, 52.2, 57.9, 67.1, 68.9 and 78^{o}. The presence of mica and quartz was as a result of silicate minerals present in the kaolin sample. The XRD study confirmed that the major component present in the clay samples were predominantly kaolinite constituting about 80 % of the particles. Other components include mica and quartz. The average lattice parameters from indexing of the peaks in the XRD were calculated to be 0.999 nm. The particle diameter of the kaolin sample was calculated using the Debye-Sherrer, Equation (5)

$$D = \frac{0.9\lambda}{\beta\cos\theta} \qquad (5)$$

Where λ is the wavelength of the x-ray (0.1541 nm) β is the full width at half maximum (FWHM), θ is the diffraction angle in radian, and D is the particle diameter size. The interspacing between the atoms (d) was calculated using Bragg's law,Equation (6).

$$d = \frac{\lambda}{2\sin\theta} \tag{6}$$

The average interspacing between the atoms, average crystal size and average lattice parameters of the study clay samples calculated are 0.3764 nm, 17.480 nm and 1.003 nm, respectively. These indicated that the clay samples used showed had fewer spaces between the particles. This wider angle between the unit cells of the kaolin crystal of 1.003nm is more than general well-crystallized kaolinites having a graphitic line of 001 d-spacing of 7.1 to 7.2 as reported by Aroke *et al.* (2013). The difference could be connected with a small amount of interlayer water within the kaolin crystals. However, there were some incompleteness and imperfections in some patterns in Figure 2, indicating the overshadowing amounts of other minerals of clay size with the kaolin. Some peaks related to crystallized phase were also detected, which is attributed to quartz, and mica initially present in the kaolin. This observation was similar to the findings of Francisca (2014).

CONCLUSION

Clay Samples from Naraguta deposit in Jos North Local Government Area of Plateau State were prepared and characterized using physical and chemical analysis. The results of the chemical analysis showed that kaolinite was the major components of the clay with the composition of silica (SiO_2), 49 – 51%; alumina (Al_2O_3), 31.494 – 33.301%; and other oxides. The bulk density, compressive strength and shear strength of the clay was stable at a temperature of 950 ^oC due to dehydroxylation of kaolin. It was found that the physical properties and chemical compositions of the clays are within the acceptable standard ranges for the manufacture of ceramics.

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STUDIES ON THE RHEOLOGICAL PROPERTIES OF WATER BASED DRILLING FLUID FORMULATED FROM BLEND OF LOCALLY SOURCED SABON GARIN NGALDA BENTONITE AND CONVENTIONAL BENTONITE

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ABSTRACT

This research focused on studying the rheological properties of water-based drilling fluid formulated from blend of locally sourced Sabon Garin Ngalda bentonite (SGN) and conventional bentonite (American Petroleum Institute (API) standard). The bentonite samples were characterized using X-ray diffraction (XRD), X-ray Fluorescence (XRF) and Scanning Electron Microscope (SEM) characterization techniques. Five different formulations were considered by blending SGN and conventional bentonite with ratios of A (60:40), B (65:35), C (70:30), D (75:25) and E (80:20) mixed each one with 350 mL of water and 1.5 g of poly anionic cellulose. The rheological properties (apparent viscosity, plastic viscosity and yield points) as well as the mud weight of the formulated drilling fluids were determined. The XRD results revealed that both the local and the conventional bentonites are rich in montmorillonite content with free silica and accessory minerals as impurities as confirmed by the XRF results (SiO_2 57.81% for SNG bentonite and 43.51% for conventional bentonite). The SEM images depict the presence of clear voids or cavities observed in both images. The formulation results revealed that the best formulation is formulation "A" having mud weight of 8.167 lb/gal and apparent viscosity, plastic viscosity and yield point of 20 cP, 13 cP and 14 lb/100ft^2 respectively. The results are relatively close to API standard formulation having mud weight of 8.60 lb/gal, apparent viscosity17 cP), plastic viscosity (9 cP) and yield point (22 lb/ft^2). Therefore, it can be concluded that the formulated drilling fluid has a very good capacity for drilling application, but still requires more enhancement by free silica reduction through wet beneficiation.

Key words: *Rheological Properties, Bentonite, plastic viscosity, yield point*

INTRODUCTION

Nigeria has the second largest oil reserves in Africa after Libya and is the continent's primary oil producer. Nigeria's 37.2 billion barrels of oil reserves also places it among the top 10 countries in terms of reserves on a global basis (KPMG, 2013). Drilling techniques are required to access oil and gas reserves at the extremities of existing production zones (Doug and Daryl, 2007). There was no single oil well drilled without using drilling fluid having Bentonite as a major constituent (Arabi *et al.*, 2011).

Drilling is the process of creating a passage for the discovered hydrocarbon to be produced at the surface. It involves the penetration of the earth's crust to several thousand feet where the hydrocarbons are accumulated in the reservoir using rotary drilling process. So far, from the era of cable tool rig to the use of rotary drilling rigs, a lot of technological advancements have been put forth on how best drilling operations can be carried out in the best economic and environmental possible way (Francis and Anietie, 2012).

Drilling fluids are heterogeneous mixture of chemical, water or oil and clay materials that aid drilling operations. They are vital in successful well drilling as they have common properties that facilitate safe and satisfactory completion of the well such as bottom hole cleaning, controlling high pressure zones and removal of cuttings to the surface. The importance of drilling fluid, otherwise known as 'drilling mud' cannot be over emphasized as the knowledge of drilling fluid is a requisite in the rotary drilling operation in the petroleum industry (Francis and Anietie, 2012). The drilling companies operating on the shores of the Niger Delta import bulk drilling fluid materials to carry out their respective operations. This has been a great burden and major concern to the industry since some of these drilling fluid materials cannot be recycled. Secondly, the foreign exchange involved and the high cost of drilling fluid materials also constitute a problem for the petroleum industry (Odumugbo (2005); Francis and Anietie, 2012).

The effectiveness of the drilling fluid to perform its primary functions is based on its properties, which are formulated continuously to meet the formation conditions encountered during drilling operations. Failure of the drilling fluid to meet its designed function can prove extremely costly in terms of materials and time, may jeopardize the successful completion of the well and even result in major problems such as stuck pipe, kicks or blowouts (Rabia, 2000).

The establishment of Nigerian Local Content Initiative in the Oil and Gas Sector by the Federal Government of Nigeria has necessitated the need for local substitutes to foreign drilling fluid materials. Thus, it is imperative to source for locally available drilling fluid materials and evaluate their various characteristics, then formulate fluids that can be used in drilling process (Francis and Anietie, 2012).

The search for better products for well bore drilling that will achieve a good level of performance particularly with local materials is being intensified. Although, substantial strides have been made in the development of environmentally friendly, sound performance chemistry for corrosion inhibition, etc, much has not been done in the development of such mud systems with local materials. Drilling operations rely heavily on the use of water based drilling muds. These are mixtures of solids, liquids and chemicals. Water is the continuous phase. Active solids like bentonite are added to the water (Ekeigwe *et. al.,* 2013).

Bentonite is the commercial name of a whole range of natural clays with a high water absorption capacity causing it to expand and swell. Bentonite predominantly consists of montmorillonite: a clay mineral belonging to a class of phyllosilicates called smectites. Bentonites may contain a variety of accessory minerals in addition to montmorillonite. These may include lesser amounts of other clay minerals such as kaolin, mica, illite, as well as non-clay minerals like quartz, feldspar, calcite, and gypsum. Bentonite quality, and, consequently, its applications, depend on whether it contains any of these other minerals. (Mike and Kelvin, 1998).

Bentonite acts mainly as the dispersed phase providing the main gel structure. Chemical additives are added in various proportions to control the fluid properties. The chemical additives are commonly used for the control of pH, viscosity, weight, fluid loss. The major success of every drilling operation depends solely on the performance of its drilling fluids (Ekeigwe *et. al.,* 2013).

Many researchers have studied the improvement of rheological properties of drilling fluid using different approaches and additives. Some of them includes; Ibrahim *et al.,* (2019) studied the improvement of rheological properties of drilling fluid using Guar-Tamarind Gum and Xanthan -Tamarind Gum Blends. Bala *et al.,* (2019) modelled the rheology and determined the fluid loss of drilling mud formulated from organophyllic clay developed from locally sourced Nigerian bentonitic clay. This research work is aimed at studying the rheological properties of water-based drilling fluid formulated from a blend of locally sourced Sabon Garin Ngalda bentonite and conventional bentonite for oil and gas drilling application.

MATERIALS AND METHODS

The materials used for the research are Sabon garin Ngalda (SGN) bentonite, conventional/standard bentonite, viscosifier (poly anionic cellulose) and distilled water.

Determination of the Mineral Composition of the Bentonitic Clays using X-ray Diffraction

A standard X-ray Diffraction (XRD) machine known as Empyrean diffractometer with a cupper anode material manufactured by panalytical was used for the analysis. It is made up of other components like the water chiller which cools the x-ray tube and maintains a uniform temperature. It has provision for the compressed air that helps in opening and closing of the cabinet door. Reynold (1989) procedure was used in carrying out this analysis.

Determination of Elemental Composition Using X-ray Fluorescence Spectrometer

The elemental composition of the sampled bentonitic clays were also analyzed using a standard -Supreme 8000 energy dispersive x-ray fluorescence spectrometer. Chapman (1965) procedure of sample preparation for the X-ray fluorescence (XRF) analysis was adopted.

Scanning Electron Microscope Analysis.

A Phenom ProX desktop scanning electron microscope (SEM) was used to analyze the morphological features of the raw Sabon Garin Ngalda and conventional bentonites. Scanning Electron Microscopy (SEM) is an electron that describes the sample by scanning a beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample surface topography, composition and properties. Scanning Electron Microscopy (SEM) aims to look at the structure and shape of the surface of bentonite (Muhammad *et al.,* 2013).

Drilling Fluid Formulation

The local bentonite obtained from Sabon Garin Ngalda of Yobe State and the conventional/standard bentonite obtained from Centre for Energy and Training (CERT), were blended together into five different formulations as A, B, C, C, D and E with each formulation containing 24.5 g of bentonite in the ratio of A (60:40), B (65:35), C (70:30), D (75:25) and E (80:20) for SGN and conventional/standard bentonite respectively. Table 1 depicts the blending ratio in grams used for the various formulation.

Table 1: The blending ratio SGN and Conventional Bentonite in grams

Sample Type	A (g)	B (g)	C (g)	D (g)	E (g)
SGN bentonite	14.800	16.075	17.350	18.625	19.900
Conventional bentonite	9.700	8.425	7.150	5.875	4.600
Total	24.500	24.500	24.500	24.500	24.500

Each blended sample was mixed with 1.5g of poly anionic cellulose and 350 ml of distilled water in a plastic container continuously stirred with an electric agitator for 30 minutes to have a homogenous mixture. After achieving homogeneity, the samples were allowed to age for 24 hours before taking the rheological properties as well as the respective mud densities of the formulated drilling fluid. The viscosity readings were recorded at 40 ^{o}C using Fann viscometer 35S at 3, 6, 100, 200, 300 and 600 revolutions per minutes (rpm).

Viscosity Measurement

The first formulation ‘A’ was poured into the cup of the Fann viscometer and placed on the viscometer stand. The stand was adjusted and held in position as the rotor sleeve was immersed in the cup containing mud at exactly the fill line and then the lock knot on the platform was tightened. The speed selector knob was selected to rotate at 600 rpm and the power was switched on. The 600 rpm dial reading was recorded when a steady dial reading was established. The speed selector knob was then set to proper position of the viscometer switch and gear knob as shown in Table 2, and then the respective dial reading values for 300 , 200, 100 , 6 and 3 rpm were recorded after establishing steady dial readings. The above procedure was repeated for the formulation B, C, D and E respectively. Consequently, the yield point, plastic and apparent viscosity were calculated as explained by Arabi *et al.,* (2018).

Table 2: Speed combination of fann viscomete.

Speed RPM	Viscometer Switch	Gear knob
600	High	Down
300	Low	Down
200	High	Up
100	Low	Up
6	High	Center
3	Low	Center

RESULTS AND DISCUSSION

X-Ray Diffraction (XRD)

The X-ray diffraction (XRD) was carried out on all the bentonite samples with the aim of identifying the mineral composition of each sample. The results are presented in Figures 1 and 2 as Sabon Garin Ngalda and Conventional bentonite (API grade) bentonite respectively.

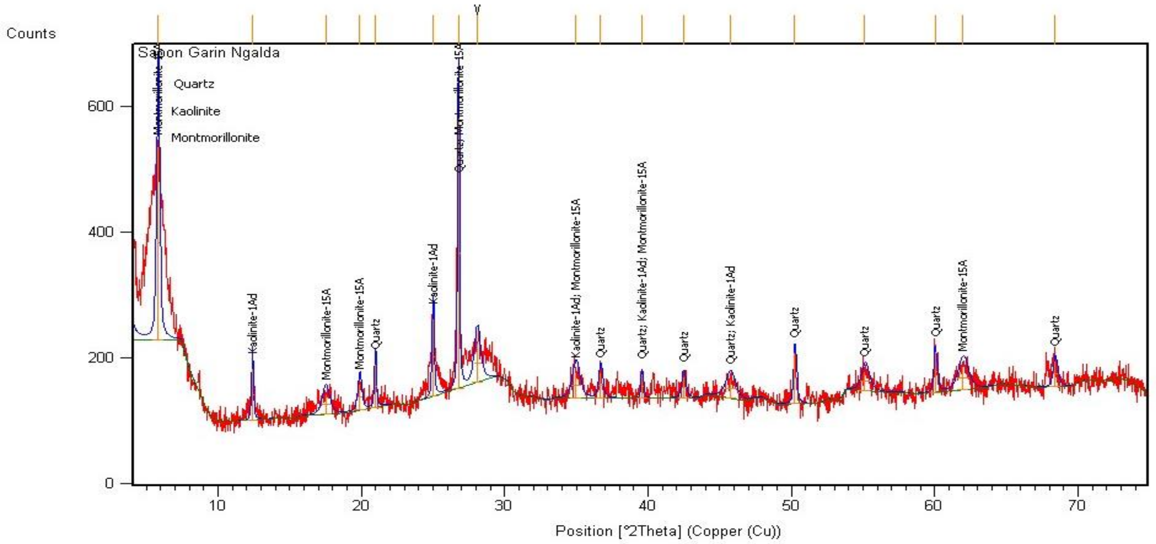


Figure 1: XRD Pattern for Raw Sabon Garin Ngalda Bentonite

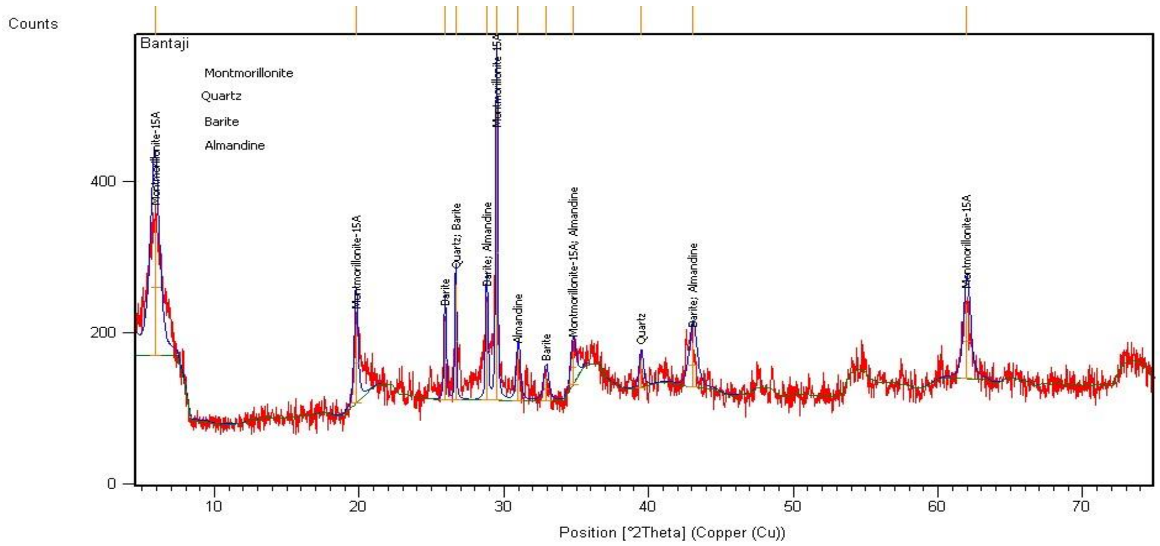


Figure 2: XRD Pattern for conventional (API Grade) Bentonite

The XRD pattern for the API grade (Figure 2) has shown that the major minerals present in the sample are predominantly montmorillonite with quartz as impurities, barite and Almandine as accessory minerals while, Sabon Garin Ngalda bentonite (Figure 1) contains montmorillonite with Kaolinite and quartz as impurities.

Montmorillonite mineral is a clay mineral of smectite group associated with bentonite. It is viscous when mixed with water and has high swelling capacity that results to good rheological properties, that is why it is used for drilling fluid formulation, increase in montmorillonite in a clay sample indicates good performance and vice versa. The clay minerals that affect the viscosity as well as the rheological properties of the clay include: quartz, kaolinite and dolomite which are present in the characterized samples. Numerous researches have been done on enhancing the quality of local bentonites through beneficiation by various researchers (Bilal, 2016), hence there is need to blend the raw bentonite with the conventional bentonite so as to study the rheological properties of the blended formulation.

X-ray Fluorescence (XRF) Result

The chemical compositions of both the raw Garin Hamza Bentonite and conventional bentonites were determined using X-ray Fluorescence technique and the results are presented in oxide form in Table 1. Presence of Na_2O in all the samples indicates that the sediments were deposited in an alkaline environment and its availability in clay materials enhances the viscosity and the swelling power of the clay as discovered by many researchers (Dewu *et al.*, 2011; Arabi *et al.*, 2011). The percentage of Na_2O in the raw Sabon Garin Ngalda bentonite sample is slightly close to what is obtainable in the conventional bentonite (2.56%).

Table 1: XRF Results of Raw Sabon garin Ngalda and Conventional Bentonites.

Element (Wt%)	Raw S/Garin Ngalda Bentonite	Conventional Bentonite
Na_2O	2.51	2.56
MgO	5.62	2.52
Al_2O_3	14.32	16.56
SiO_2	57.81	43.51
P_2O_5	1.09	0.96
K_2O	1.70	0.79
CaO	1.88	5.64
TiO_2	0.83	1.11
Fe_2O_3	5.15	5.71
Others	9.09	18.08
Al/Si	0.25	0.38

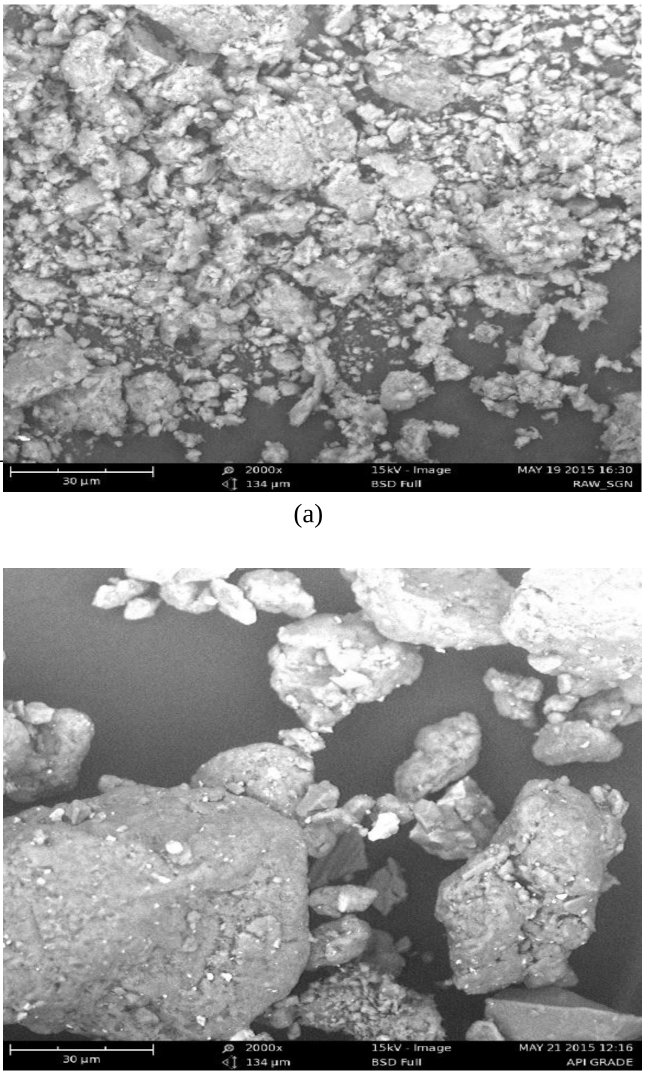
The magnesium content (MgO) in the raw bentonite (2.62%) is slightly higher than the standard 2.52%. Presence of excess MgO beyond the standard value may affect the rheological properties of the formulated drilling fluid.

Presence of K_2O is an indication that the Bentonitic clay contains K-Feldspar which can also be associated with Kaolinite mineral, as clearly shown in the XRD results of the raw Bentonites. The API grade sample contains only 0.79 % K_2O, while in the local Bentonitic clay it is 1.70%. Presence of much potassium may have effect on the viscosity as well as the rheological properties of the drilling fluid.

CaO originated from $CaCO_3$. Its presence in the Bentonitic clay affects the viscosity, swollen power as well as the rheological property of the drilling fluid. It has been observed that Nigerian Bentonitic clays are mostly calcium based which can be converted to sodium based by sodium activation (Bilal, 2016). The percentage of CaO in the conventional bentonite is 5.64%, while in Sabon Garin Ngalda bentonite it is 1.88% which is within the standard limit. The percentage of Fe_2O_3 in the locally sourced Bentonitic clay is within the normal range when compared with the standard.

Scanning Electron Microscope (SEM)

A scanning electron microscope (SEM) is used to generate surface images of a sample at a microscopic level. The scanning was carried out at 2000x magnification to be able to clearly identify all the morphological features, clay structures and larger interactions of the samples in SEM at higher resolution as depicted in Figures 3 (a) and (b) for raw SNG and conventional bentonites respectively.



(a)

(b)

Figure 3 (a) Raw Sabon garin Ngalda Bentonite (b) Conventional Bentonite

The SEM images depict the presence of clear voids or cavities observed in all of the images. moreover, the particles are well aggregated as flocs in Sabon garin Ngalda bentonites. The conventional bentonite was observed to have irregular shaped and dispersed clay minerals that could be predominantly alumina (Bilal *et al.*, 2016).

The Viscosity Consistency Curve

The viscosity consistency curves the various formulations are shown in Figure 4. The result indicates that formulation A was relatively close to the API standard, then followed by formulation B, D, E and then C, in that order.

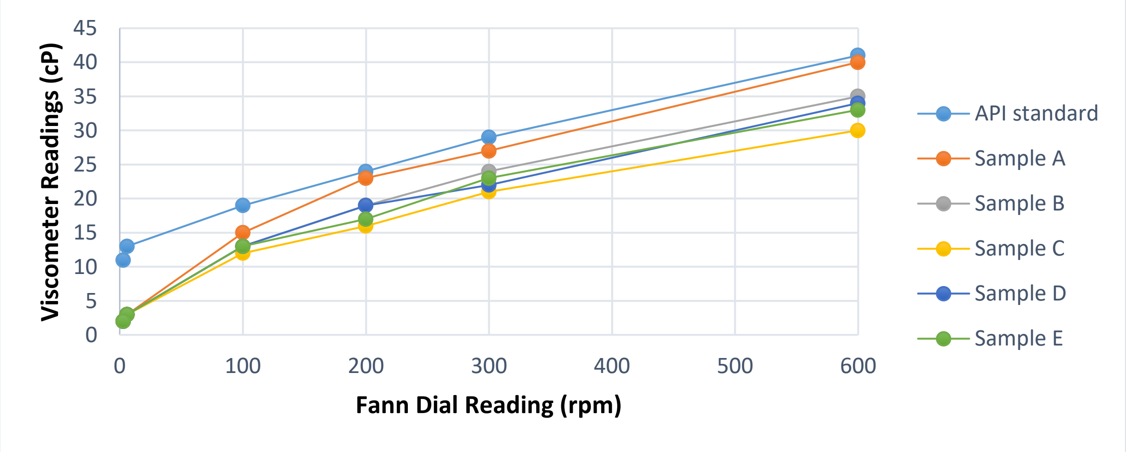


Figure 4: Viscosity consistency curve of formulated drilling fluids.

Formulation A seems to be the best with blending ratio of 60:40 which is 15.30g and 10.20g of Sabon Garin Ngalda bentonite and conventional bentonite respectively.

Mud Density

The mud densities of the formulated drilling fluids for the formulations A, B, C, D, E and conventional bentonite were 8.167, 8.58, 8.51, 8.42 and 8.42 lb/gal and respectively as depicted in Figure 5. The mud density in g/cm^3 shown in the figure can be converted to mud weight in lb/gallon as API standard unit. The conversion factor is multiplication by 8.33 as explained by Bilal (2016).

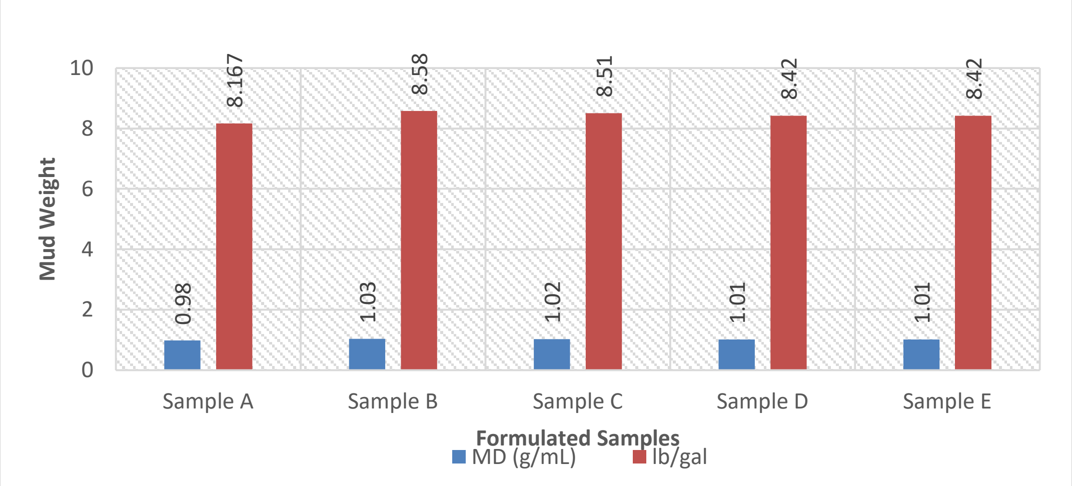


Figure 5: The mud weight/density of formulated drilling fluids.

The results indicate that the mud densities of the various formulations are slightly lower than API specifications of 8.60 lb/gal as revealed by Bilal (2016), hence there is need to add weighing agent such as barite to enhance the density of the fluid.

Rheological properties of the formulated fluid

Table 3: Table showing the rheological properties of the formulated drilling fluid

Rheological Properties	Sample A	Sample B	Sample C	Sample D	Sample E	Raw SNG Bentonite	Conventional/ Standard Bentonite
Apparent viscosity (cP)	20.0	17.5	15.0	17.0	16.5	1.6	17.0
Plastic viscosity (cP)	13.0	11.0	9.0	12.0	10.0	0.9	9.0
Yield point (lb/100ft^2)	14.0	13.0	12.0	10.0	13.0	1.3	22.0

Table 3 shows rheological properties of the formulated drilling fluids; apparent viscosity (20, 17.5, 15, 17, 16.5, 1.6 and 17.0 cP), and plastic viscosity (13, 11, 9, 12, 10, 0.9 and 9.0 cP), yield point (14, 13, 12, 10, 13, 1.3 and 22 lb/100ft^2) for sample A, B, C, D, E, raw SNG bentonite and standard/conventional bentonite respectively. Initially, the raw SNG bentonite has low rheological properties compared to the conventional/API standard. After blending the raw sample with the conventional bentonite there was significant increase in the rheological properties. The plastic viscosities of all the formulated samples revealed that the values obtained are higher than the value for the standard bentonite with the exception of sample C, which has similar value to standard as 9 cP. This means that samples A, B, D and E have better plastic viscosity than the standard/conventional bentonite. For the yield point it was observed that the standard/conventional bentonite has higher yield point compared to all the formulations. This means in practical terms, an increasing yield point means a good and stable mud which helps in removing cuttings from the hole, while a reducing yield point means a bad and unstable mud (Adeleye *et al.*, 2012).

CONCLUSION

In conclusion, the two blended clays (local SGN and conventional bentonites) were confirmed by XRD results to be rich in montmorillonite content with free silica and accessory minerals as impurities. The presence of excess free silica was confirmed by XRF results (SiO_2 57.81% for SNG bentonite and 43.51% for conventional bentonite). The SEM images depict the presence of clear voids or cavities observed in all of the images. The generated results ranging from the rheological properties (apparent viscosity, plastic viscosity, yield point) and mud weight of the formulated water-based drilling fluid from blended Sabon Garin Ngalda (SGN) bentonite and conventional bentonite samples revealed that the blended samples have almost similar properties compared to the standard conventional bentonite. The best formulation is formulation “A” having mud weight of 8.167 lb/gal and apparent viscosity, plastic viscosity and yield point of 20 cP, 13 cP and 14 lb/100ft^2 respectively. The blending ratio of “A” is 60:40 which is 15.30g and 10.20g of Sabon Garin Ngalda bentonite and conventional bentonite respectively, 1.5g of PAC and 350 mL of clean water. The information revealed that the local SGN bentonite still requires more modification for it to meet all the API specifications.

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A REVIEW ON PRODUCTION OF AVIATION FUEL FROM WASTE PLASTICS

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ABSTRACT

The need to reduce the quantity of carbon dioxide (CO_2) released into the atmosphere by the aviation industry have become the driving force towards developing an alternative aviation fuel. Plastic wastes currently constitute a major environmental problem since it is not bio-degradable. There is a possibility that plastic waste reduction can be achieved through the thermochemical conversion of waste plastics to aviation fuel range alkanes. This paper reviews different technologies that are being used for such plastics waste conversion with emphasis on pyrolysis. The use of catalytic pyrolysis for the production of aviation fuel from wastes plastic materials was highlighted due to its high products selectivity. It is observed that one of the challenges facing the commercialization of the catalytic pyrolysis process is the high cost of catalyst and its contamination by the feed stock.

1. INTRODUCTION

Plastics are materials composed of polymers which may either be thermoplastic or thermosetting (Sogancioglu *et al*., 2017). The most commonly used thermoplastics includes polyethylene (PE), polyethylene terephthalate (PET), polypropylene (PP) and polystyrene (PS). These types of plastics are recyclable and are usually used to make containers and packing materials (Bajus & Hájeková, 2010; Gutiérrez *et al*., 2012). On the other hand, thermoset plastics include phenol formaldehyde and urea formaldehyde but are not recyclable as the materials cannot be modified after solidification (Aahik, *et al*., 2016).

Plastics play major roles in different sectors such as packaging, construction, transportation, electronics and healthcare (Anene *et al*., 2018). This may be due to its versatility and low cost (Almeida & Marques, 2016). Annually, the global production of plastics is estimated to be about 300 million tons with its production continuously increasing every year (Miandad *et al*., 2016). As the production of plastics increases annually, so the quantity of wastes generated also increases. This increase in plastics wastes impacts on the environment as they make the environment dirty, block drainages, pollute the water bodies and has contributed to flooding in Nigeria and around the globe. Plastic wastes are also not bio-degradable.

Over the years, various mechanisms have been used to manage plastic wastes, such as incineration, dumping them in landfills and recycling them into useful products. These methods are not enough in creating and ensuring a circular economy for plastics. The disposals of plastic waste in landfills and by incineration are expensive, because plastic waste is bulky and incineration leads to release of toxic substances into the atmosphere, which pollutes the environment (Gandidi *et al.,* 2018). Conversely, values can be recovered from waste plastics in form of materials recycling or energy depending on the plastic type, ecology, ease separation from other waste materials and cost required for processing (Panda *et al.,* 2010). This can be achieved through thermochemical processes such as gasification, pyrolysis, hydrocracking and catalytic cracking (Lopez, *et a*l., 2011; Kumar *et al*., 2013). Although, most of these processes are expensive, require high amount of energy and might result in producing low-grade materials, pyrolysis is viable and sustainable (Xue *et al.,* 2016).

Plastic waste oil from catalytic pyrolysis is often associated with some impurities such as sulphur, chlorine, solid residue, moisture and acids. These impurities in the raw waste plastic oil make it unsuitable for use directly as transportation fuel as well as reduces its commercial value (Miandad et al.,2016). Thus, several researches have been carried out to upgrade waste plastic oil to different transportation fuels such as gasoline and aviation fuel.

Aviation fuel is a middle distillate of crude oil fractional distillation, specifically kerosene range. In the last decade, several developments in the use of alternative aviation fuel have led various demonstration flights by some major airlines. Concerns over the use of alternative sources of fuels for aviation operations, especially in terms of their compatibility have been a great set back. Various characteristics are expected if a fuel should be fit for aviation use. These characteristics are: high energy to maximize range, good atomization, rapid evaporation, low viscosity, extremely low freezing point, and good chemical stability as well as availability in large volumes to be able to compete economically with Jet A-1 fuels, (Chucks & Donnelly, 2014). The need to reduce the carbon emissions contributed by the aviation sector, also the exposure to crude price volatility are more reasons why researches are working on the possible alternative fuel to fossil-based aviation fuels.

Technically, the production of aviation fuel from plastic waste consists of: (a) waste plastic pyrolysis processes, (b) upgrading the waste oil and gas cleaning, (c) Fischer-Tropsch (FT) synthesis, and, finally, (d) hydro-processing and distillation of the liquid hydrocarbons. The synthetic aviation fuel produced via FT synthesis is environmentally friendly because of the lower concentrations of nitrogen, sulfur, and aromatics. The aim of this paper is to review the potential of plastic waste beneficiation in terms of waste to wealth, technological options and opportunities available in the production of aviation fuels from plastic waste, which have been one of the major environmental challenges. The first step is to quantify the waste plastics availability; some of the available data in this regard for Nigeria is presented in Section 2. Pyrolysis is discussed in Section 3 and some of the existing methods for producing transport fuels from waste plastic oil are presented in Section 4.

2. TYPICAL PLASTIC WASTE AVAILABILITY IN NIGERIA

Ikebude (2017), investigated the components of wastes generated in Port Harcourt and grouped these components as garbage, paper, plastics, scrap metal and glass, construction waste, sludge and others. The data was collected through questionnaires, literature examination, oral interview, field survey and physical observation. Three major sampling sites were used – Borokiri, main town and GRA areas of Port Harcourt. The data obtained show that 35% of solid waste generated in Port Harcourt Metropolis is composed of paper and plastic (Fig. 1). This indicates that there is a large amount of plastic wastes produced in Port Harcourt.

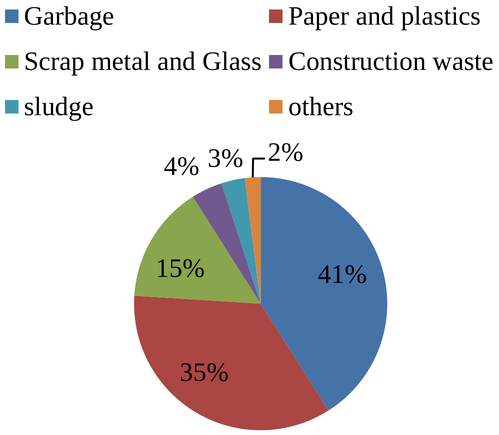

Fig 1: Physical composition of solid waste generated in Port Harcourt metropolis (Ikebude, 2017)

Oghenefejiri *et al.*, (2016) assessed the various components of municipal wastes in Nigeria. Group discussions involving professional environmentalists and solid waste managers were used for data collection. His studies areas were the six geopolitical zones in Nigeria. The results obtained are presented in Table 1. Table 1 shows that the cities with large dumps of waste plastics are Abuja, Kano, Ota, Cross river, Delta, Lagos, Niger while States like Rivers possessed less amount of plastic wastes compared to other cities in Nigeria. Based on these results, Oghenefejiri *et al.*, (2016) concluded that there are sufficiently large quantities of plastic wastes in Nigeria.

Table 1: Components of municipal solid waste in the six geo-political zones in Nigeria (Oghenefejiri *et al.*, 2016).

Zone	States	Organics	Plastics	Paper	Glass	metal	Textile/leather	Unclassified debris
North East	Borno (Maiduguri)	28.8	18.1	7.5	4.3	9.1	3.9	31.3
North Central	Niger	31	16	13	9	11	6	14
	Nasarawa	31.5	7.25	3.5	18	6.5	1.5	31.75
	Abuja	43.57	20.97	23.11	3.23	3.79	2.77	2.56
North West	Kano (Sabon-gari)	57.5	17.5	6.7	5.7	3.9	4.5	4.2
South West	Oyo (Ibadan)	47	12.6	21.9	0.9	6	8.8	2.8
	Lagos	53	15	10	5	5	4	8
	Ogun (Ota)	42.07	21.01	8.29	9.59	1.06	7.44	10.54
South South	Rivers	63	3.5	9.9	1.9	3.4	14	4.3
	Delta	37	21	18	6	10	5	3
	Cross River (Calabar)	23.33	14.67	16	12	15.33	0	18.67
South East	Enugu	30.7	9.2	23.1	9.2	6.2	6.2	15.4

3. PYROLYSIS OF PLASTIC WASTE

Pyrolysis can be described as the decomposition of long chain hydrocarbon polymer molecules into smaller sizes monomer at a temperature range of 450 – 800 ^{0}C within a short period of time in an environment devoid of oxygen (Thahir *et al.*, 2019). The pyrolysis products are in the form of carbon as residues and volatile hydrocarbons which can be condensed as liquid and non-condensable gaseous. As the temperature is increasing the weak bonds binding the polymer gets damaged, this is followed up by the formation of free radicals, these free radicals get separated again forming stable compounds of paraffins, iso-paraffins, olefins, naphthenes and aromatics (Thahir *et al.*, 2019). These compounds are the major components of petroleum.

The relative amount of solid, liquid and gases produced in a typical process depends on the operating conditions. The range of the main operating parameters for pyrolysis processes are shown in Table 2.

Slow pyrolysis is an ancient method used for producing charcoal (Patni *et al.*, 2013). In fast pyrolysis (also called thermal pyrolysis) the material is rapidly heated to high temperatures in the absence of oxygen.

Table 2: Operation conditions for pyrolysis processes (Patni *et al.*, 2013).

Parameter	Conventional	Fast	Flash
Pyrolysis temp. (K)	500-900	850-1250	1050-1300
Heating rate (K/s)	0.1-1	10-200	>1000
Particle size (mm)	5-50	<1	<0.2
Solid residence (s)	300-3600	0.5-10	<0.5

The liquid oil from thermal pyrolysis may contain impurities and residues. To overcome these problems catalysts are used to improve the pyrolysis process of plastic waste and to enhance process efficiency (Miandad *et al.,* 2019). When catalysts are used it is called catalytic pyrolysis. Thermal and catalytic pyrolysis of waste plastics are discussed further in Sections 3.1 and 3.2.

3.1 Thermal pyrolysis

Thermal pyrolysis of plastic wastes leads to the formation of a wide range of hydrocarbons (Almeida and Marques, 2016). The reaction mechanism of thermal pyrolysis of waste plastics is complex, and this contributes to the limited commercial value of it being used as fuels. The products obtained by the thermal pyrolysis of plastic wastes are grouped into non-condensable gas fraction, liquid fraction (paraffin, olefins, naphthenes and aromatics) and the solid residue (Almeida and Marques, 2016). The liquid fraction obtained from the thermal pyrolysis are gasoline range (C_4-C_{12}), diesel range (C_{12}-C_{20}), kerosene range (C_{10}-C_{18}) and motor oil range (C_{23}-C_{45})

3.2 Catalytic pyrolysis

Catalysts are used to reduce the activation energy and to improve the thermal efficiency in pyrolysis process. The presence of catalyst helps secondary cracking to the solids and liquids, which results in higher pyrolytic products and also high selectivity the desired product. Muhammad *et al.,* (2015a) carried out the catalytic pyrolysis by using Y-zeolite and ZSM-5 as catalyst to convert electric and electronic plastic waste into oil, the oil produced contained mainly styrene. The ratio of Si:Al in the Zeolite determined the extent of influence of the catalyst. With lower Si:Al ratio in the zeolite, a higher conversion of styrene to other aromatic products particularly benzene and toluene was observed. When Y Zeolite catalyst was compared to ZSM-5 catalyst, a higher conversion of styrene to other aromatic products was observed with Y zeolite, this can be attributed to the larger catalyst active sites and also larger pore sizes when compared to ZMS-5 catalyst. Aida *et al.,* (2015) used fluidized catalytic cracking (FCC) catalyst to convert plastic waste to liquid using a pyrolysis temperature of 400°C and reaction time of 2 hours, the mixed plastic waste used (polyethylene, polypropylene and polystyrene) were combined in the ratio5:3:2 and a catalyst to waste plastic ratio of 10:90 was used. The volume of liquid product obtained was 20 mL under non-catalytic condition and 35 mL under catalytic condition. The energy required for this process may be decreased as the reaction temperature is reduced. This decrease is caused by the reduced activation energy of the pyrolysis reaction (Anene *et al.,* 2018). The catalyst used in the process may favour the yield of lighter hydrocarbons, gasoline range and gases. The product obtained will depend on the type of polymer, their sources and structure, (Anene *et al.,* 2018). The products are hydrocarbons with so many applications; the pyrolysis oil can be used as an energy source and also for producing other chemicals. The pyrolysis liquids will need to be refined and upgraded before it can be used as a transportation fuel and other petrochemical products (Ghodrat *et al.,* 2019).

4. TRANSPORT FUEL PRODUCTION FROM WASTE PLASTIC OIL

In general, available methods for producing transportation fuels from waste plastic oil can be classified into two main groups namely: refining and blending (Miandad *et al.,* 2016). Some of these works are presented in this section.

Sharma (2014) used a Be-h desktop plastic oil system for the pyrolysis of plastic grocery bags (HDPE) to waste plastic oil (WPO). The WPO was then distilled into four fractions: gasoline (<190 ^{o}C), #1 diesel (190–290 °C), #2 diesel (290–340 °C) and VGO (>340 ^{o}C).

The pyrolysis yield was 9% gas, 74% WPO and 17% solid while the WPO contains 41% of #1 diesel.

Syamsiro *et al.*, (2014) reports the use of FCC catalyst as a cracking catalyst, this improved the liquid, gas yields, and a high fraction of heavy hydrocarbons was in the fuel due to more cracking residue. The low thermal conductivity and high viscosity of plastic crude oil are the main challenges for designing the cracking reactor. Syamsiro *et al*., (2014) used a pilot scale two stage reactor, operating a batch system consisting of a pyrolysis reactor and a catalytic reforming reactor. The gas generated from the pyrolysis reactor was reformed in the reforming reactor, the resulting liquid was condensed and the product collected. From the experiment carried out, it was reported that feed type and catalyst type have an effect on the products. When no catalyst was used, the product yield was 58% liquid waste plastic oil (WPO), 28% gas and 14% solid (char). With natural zeolite as catalyst, the yield was 52% WPO, 36% gas and 12% char. The yield values were 50% WPO, 39% gas and 11% char when Y-zeolite catalyst was used. This shows that the presence of catalyst promoted the formation of gaseous products, unlike the non-catalyzed pyrolysis that had more yield of the liquid product. Their results also indicated that the diesel fraction in WPO was almost the same with or without catalyst.

Chen *et al.* (2014) carried out an experiment on pyrolysis using hydrolysis reactors having steam as carrier gas and Fe based catalyst, followed by the catalytic cracking reactor having zeolite as a catalyst. This could be a positive move towards pyrolysis fuel upgrade. Using a fluidized bed reactor operating at a temperature of about 500°C, the gases can be extracted before the secondary cracking takes place. This will result to a higher yield of the liquid product.

Muhammad *et al.* (2015b) used a two-stage pyrolysis fixed bed reactor in his experiment to determine the product yield, composition and hydrocarbon distribution of a catalyzed pyrolysis process to convert virgin polyethylene, polypropylene, polystyrene and PET using a zeolite HZSM -5 catalyst. It was observed that the yield of the liquid product dropped in the samples where catalyst was used from 45 wt.% and 55wt% when it was compared to the 81 wt.% - 97 wt.% obtained from uncatalyzed pyrolysis. The catalyzed pyrolysis oil was rich in aromatic hydrocarbon content. The composition of the catalyzed pyrolysis oil moved from high molecular weight hydrocarbons (C_{16}) to full range hydrocarbons (C_5-C_{15}).

Zhang *et al.*, (2019) investigated seven types of commercial and home – made activated carbon on the pyrolysis of waste plastics in a facile tube reactor, the liquid obtained had components of Jet-range hydrocarbons accounting for 28.8% aromatics and 71.8% alkanes. It was observed that activated carbon catalyst transformed low density polyethylene into Jet fuel and hydrogen gases excellently. In addition, it is important to note that these activated carbon catalysts could be sourced and prepared locally from biomass residues or agricultural wastes from available crops such as walnut shells, palm shells, coconut shells, beans husks, banana peels, tobacco stems and so on (Tadda *et al.*, 2016). Zhang *et al.*, (2019) suggested a possible route to obtaining Jet-fuel range hydrocarbons from low density polyethylene waste plastics, ground to a particle size of 3 mm (Fig 2). Unit (1) is a cylinder filled with the Nitrogen gas which was used as the carrier gas, (2) is a control valve for the Nitrogen gas coming from the cylinder, (3) is a tube which carried the waste plastic (7) into the reactor (8) where pyrolysis occurred alongside with catalytic cracking with activated carbon catalyst (10), (11) is a condenser which cooled the outlet vapor to liquids in (12) and the uncondensed gases were collected in (13).

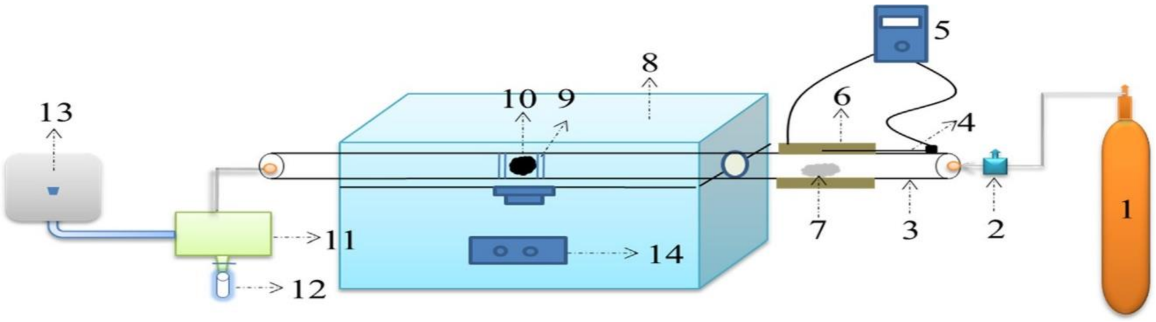

Fig 2: The catalytic pyrolysis system of daily waste plastics (separating feedstock and catalyst): 1-Nitrogen gas; 2-Gas flow meter; 3-Quartz tube; 4-Thermocouple for heating tape; 5-Heating tape controller; 6-Heating tape; 7-Waste plastics; 8-Fixed bed furnace; 9-Quartz wool; 10-Activated carbon catalyst; 11-Condensor; 12-Liquid product collector; 13-Non-condensable gas collector; 14-Control panel of the furnace (Zhang *et al*., 2019).

5. IDENTIFIED GAPS FOR FUTURE RESEARCH

From the researches reviewed so far, the followings are some of the areas that require further work:

a) The common catalyst used for waste plastics pyrolysis is zeolite. Zeolite is very expensive (Butler *et al*., 2011). An alternative to zeolites or zeolite produced locally will greatly reduce the cost of production.

b) Catalyst recovery after use is another issue due to the deposition of carbonaceous matter on the catalyst during the pyrolysis. This can lead to the deactivation of the catalyst (Syamsiro *et al.,* 2014).

c) Integrating a catalyst regenerating unit into the design would be very useful in reducing the cost and also minimize the waste from spent catalyst.

6. CONCLUSION

This paper reviewed different works done in the production of transportation fuels via pyrolysis. Thermal and catalytic pyrolysis has been suggested to be the possible routes for obtaining high grade aviation fuels. Catalytic pyrolysis has the advantage of reducing the activation energy for the process; it has also been reported to contribute to high selectivity of the products. The high cost of catalyst and the contamination of feed stock are challenges facing the commercialization of aviation fuels via catalytic pyrolysis. There is therefore need for more comprehensive work to be done towards developing a catalyst that is cheap possibly from renewable sources such as activated carbon from biomass that would not increase operational cost.

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PREDICTION OF REFRACTORY FAILURE RESULTING FROM CHEMICAL CORROSION IN CARBON BLACK REACTOR

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ABSTRACT

Refractory design is important as it helps to define specification for optimum temperature, furnace life and even cost of high temperature reactors. Failure to produce technically or operationally durable refractory design could lead to premature deterioration of the refractory lining and subsequent collapse with its numerous implications. The main wear mechanisms of refractory ladle are chemical corrosion and mechanical erosion. The chemical potential difference between the refractory and the slag under high temperature conditions is the driving force for the chemical wear mechanism. The objective of this work was to analyse the wear mechanism of refractory wall by the reaction of Magnesium oxide and elemental Carbon in Carbon Black Reactor where MgO is the major refractory material. Models were developed in this work to predict the failure of MgO - C refractory based on the Hasselman's model of crack extension. The models gave consistent profiles for crack extension and consequent failure of the refractory, whence can be deployed in the prediction and/or analysis of similar systems.

Keywords: *Refractory; Chemical Corrosion; Carbon Black*

1. INTRODUCTION

Carbon Black is essentially elemental carbon in the form of extremely fine particles having small amounts of other gaseous compounds like water vapour, hydrogen and even sulphurous gases. By its annual production in tonnes, Carbon Black is amongst the first 50 industrial chemicals manufactured worldwide. Statistics shows that 90% of carbon black is used in rubber applications, 9% as pigment, and the remaining 1% as an essential ingredient in diverse applications (Voyles, 2001). Different types and grades of Carbon Blacks including Acetylene Black, Channel Black, Furnace Black, Lampblack and Thermal Black are often produced by the Oil Furnace Process which uses heavy petroleum fractions such as tar and other Asphaltic residue from refinery and allied processes (Buchel, 2007).

An important feature of Carbon Black Reactors is the internal refractory lining usually made of different metallic oxides for heat conservation. Refractory failure is a common problem in Carbon Black Reactors and other furnace applications which is of great concern in the design and operation of high temperature processes. Different factors responsible for refractory failure include slag penetration and corrosion, thermal shock, spalling, installation curing and drying (Yamaguchi, 2001). The type and degree of failure is therefore dependent on the refractory material and its design and installation. Chemical resistant oxides such as CrO fail under thermal shock and mechanical wear than chemical attack while MgO and Silicates fail under chemical attack more readily (Pfeifer, 1990).

This research work is aimed at developing simple mathematical models for prediction of refractory failure caused by chemical reaction in Carbon Black Reactor. The importance of refractory efficiency cannot be overemphasized, as it is at the heart of most high temperature processes such as furnace operations. A failed refractory almost always leads to process shutdown. Understanding refractory dynamics for timely prediction of failure thus averts unscheduled process shutdown and improves process efficiency and operability. While there is considerable literature on refractory failure through mechanical action such as thermal shock, the same is not true of failure caused by chemical corrosion. The present work which uses the thermal shock model of Hassalman (1969) to predict failure resulting from chemical action therefore is not only novel but presents a viable alternative to previous models.

2. THEORETICAL PRINCIPLES

There are a number of theories which attempt to explain refractory failure generally but most common of these are temperature related. This is because most refractory structures are usually exposed to severe thermal loading conditions (i.e. effect caused by variation of temperature) in the form of rapid temperature changes (thermal shock). While failure is caused by a myriad of conditions including thermal, mechanical, electrical, chemical activity etc, it is most readily determined using thermal and mechanical properties. Resonant frequency measurement can allow refractory manufacturers to predict the degree of damage that a material can sustain without complete fracture (buzzmac, 2016). Also, Hasselman(1969) used resonant frequency measurement of Young's Modulus to determine failure in a composite bar as depicted in figure 1.

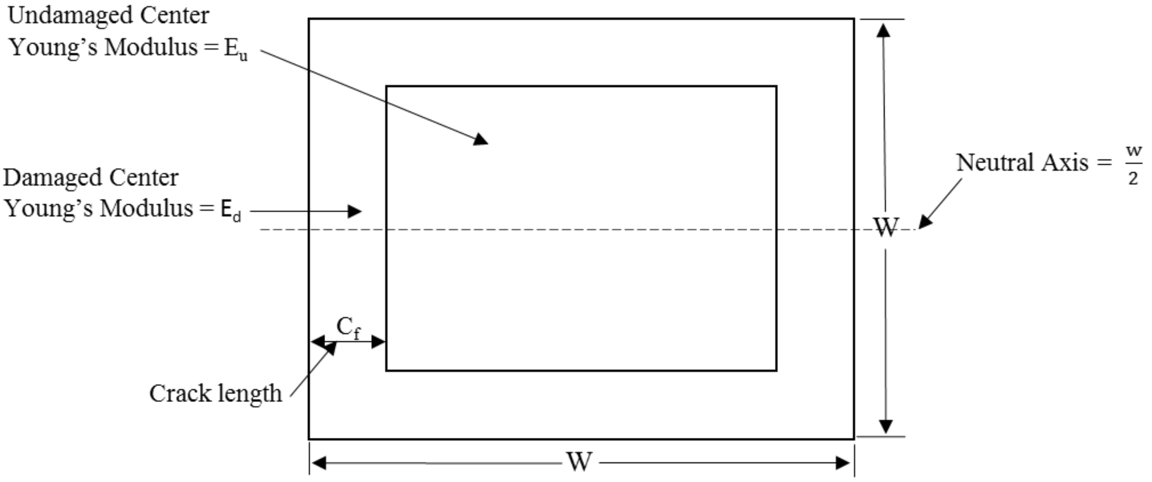


Figure 1: Cross-section of square bar after water quenching

Failure in the Hassalmen's model was assumed to be the result of extension of an initial crack (C_o) caused by thermal shock to the inner core. Crack Length (C_f) was given as;

$$C_f = C_o \left[\frac{\Delta T}{\Delta T_c}\right]^{\frac{2}{3}} \quad (1)$$

Assuming further that the crack length is half of the length of bar, i.e refractory thickness, crack length becomes;

$$C_f = \frac{w}{2} \quad (2)$$

Failure and total damage of the bar was thus predicted by equation (3) below (Buzzmac 2006):

$$E = E_u \left[\left(1 - \frac{2C_O}{W} \left(\frac{\Delta T}{\Delta T_C} \right)^{3/2} \right)^4 + \left(\frac{\Delta T_C}{\Delta T} \right)^{3/2} \left(1 - \left(1 - \frac{2C_O}{W} \left(\frac{\Delta T}{\Delta T_C} \right)^{3/2} \right)^4 \right) \right] \quad (3)$$

In reactive systems like the Carbon Black Reactor, chemical reaction accounts for a considerable part of refractory failure or decay which chemistry is given in Section 2.1.

2.1 Reaction Stoichiometry

In a typical Carbon Black Reactor, the following reactions take place:

a. Combustion of hydrocarbon in presence of air

$$C_nH_n + O_2 \quad \rightarrow \quad CO + H_2O$$

b. Coking Reaction of hydrocarbon

$$C_nH_n \quad \rightarrow \quad nC + \frac{n}{2}H_2$$

c. Oxidation of Elemental Carbon

$$2C(s) + O_2(g) \quad \rightarrow \quad 2CO(g)$$
$$MgO(s) + C(s) \quad \rightarrow \quad Mg + CO(g)$$

A consequence of the MgO reaction is an increase in porosity of the refractory material as elemental Mg corrodes away from the refractory material. Ghosh et al.(2003) showed that Aluminium reacts with Carbon as an anti – oxidant in refractories of Carbon Black Reactors according to the scheme;

$$4Al(l) + 3C(s) \quad \rightarrow \quad Al_4C_3(g)$$

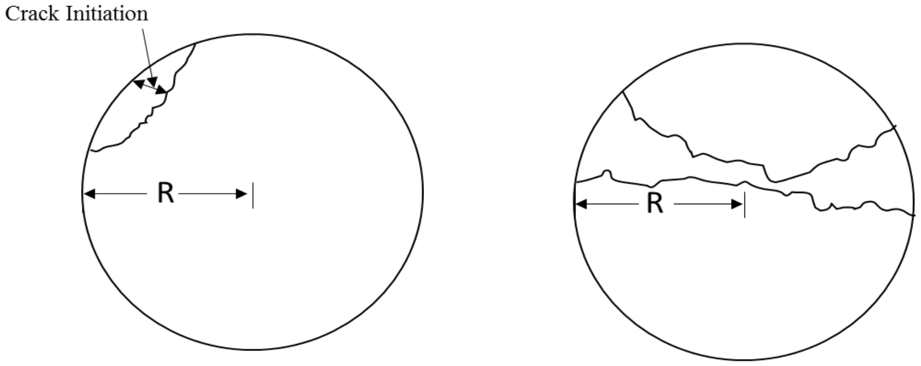
The formation of Aluminium Carbide removes Aluminium from its Oxide which is a common material in refractory composites. MgO and Al_2O_3 in the refractory forms a magnesia-alumina spinel during pre-heating (Ganesh, 2002) which has positive effect on slag erosion and penetration resistance of the refractory. However, Kawahara et al.(2006) attributes the improved corrosion resistance to the higher volumetric stability and blockage of the pores in the refractory by the composite of $MgAl_2O_4$.

Reaction induced decay of refractory especially of Alumino – Magnesia composites are analysed in this work based on experimental observations described by Levenspiel (2002) and Rosenquist (1987) and involves chemical reaction at the interface amongst others phenomena. Also, experimental works documented by Langlias (1991) showed that in most refractory composites especially those containing Aluminium, bulk diffusion of Mg to the interface and its subsequent reaction is the rate determining step in these high temperature processes. But in a solid lattice like refractory wall, bulk diffusion (such as of Mg) is negligible compared to interfacial reaction.

$$MgO(s)+Al_2O_3(s) \quad \rightarrow \quad MgAl_2O_4(s)$$

2.2 Assumptions for Present Model Development

i. The rate of depletion of refractory is similar to that given by Flores et al.(1998).
ii. Crack initiation occurs when atomic nucleus is completely depleted (R = 0)as depicted in figure 2.
iii. Crack extension in refractory to inner core follows the same phenomena whether it is initiated by thermal shock or chemical corrosion.



CRACK INITIATION OF ATOMIC NUCLEUS

DEPLETION OF ATOMIC NUCLEUS

Figure 2: Crack Initiation by depletion of molecular Nucleus

Representing interfacial chemical phenomena for Carbon Black refractory as;

$$\frac{\partial^2 C_{Mg}}{\partial R\partial t}+\frac{\partial C_{Mg}}{\partial t}+\frac{\partial C_{Mg}}{\partial R}=0 \qquad (4)$$

and defining the following as process conditions

$$t=0,\ ;\ C_{Mg}=\ C_{Mgmax};\ R=R_{max} \quad (5a)$$

$$t=t_{max}\ ;\quad C_{Mg}=\ 0; R=0 \qquad (5b)$$

From kinetic studies of Flores et al. (1998), the rate of removal of Mg from refractory wall was given as;

$$-\frac{VdC_{Mg}}{dt}=k(C_{Mg}+C_{Mg(eq)})^n S \qquad (6)$$

For a unit length of refractory lattice and assuming $\mathbf{C_{mgeq}}$ = 0 and n = 1, which was the experimental order of the reaction (Flores et al., 1998) and (Escobedo et al.2003), Equation (6) simplifies to;

$$-\frac{dC_{Mg}}{dt}=kC_{Mg} \qquad (7)$$

Equations (4) and (7) yields Equations (8) and (9) in terms of time and atomic radius respectively.

$$\frac{C_{Mg}}{C_{Mg}^o}=e^{-kt} \qquad (8)$$

$$C_{Mg}=e^{(\frac{k}{1-k})R} \qquad (9)$$

Replacing the temperature factor ($\Delta T/\Delta T_c$) in Equation (3) with the concentration factor (C_{Mg}/C_{Mg}^o) from Equations (8) and (9), crack extension due to chemical corrosion in terms of time and atomic radius respectively becomes;

$$E=\mathrm{E_u}\left[\left(1-\frac{2\mathrm{C_O}}{\mathrm{W}}\mathrm{e}^{-3/2\mathrm{kt}}\right)^4+\mathrm{e}^{3/2\mathrm{kt}}\left(1-\left(1-\frac{2\mathrm{C_O}}{\mathrm{W}}\mathrm{e}^{-3/2\mathrm{kt}}\right)^4\right)\right] \qquad (10)$$

$$E = \mathrm{E_u}\left[\left(1-\frac{2\mathrm{C_O}}{\mathrm{W}}e^{\frac{3}{2}(\frac{k}{1-k})R}\right)^4 + e^{-\frac{3}{2}(\frac{k}{1-k})R}\left(1-\left(1-\frac{2\mathrm{C_O}}{\mathrm{W}}e^{\frac{3}{2}(\frac{k}{1-k})R}\right)^4\right)\right] \qquad (11)$$

3. RESULTS AND DISCUSSION

The kinetics of depletion of Magnesium in refractory composites was demonstrated experimentally by Flores et al.(1998) using Electron Backscatter Diffraction (EBSD) in Secondary Electron Microscope (SEM) analytical techniques. Rate profiles of the work were reproduce in terms of % wt of Mg shown in Figure 3.

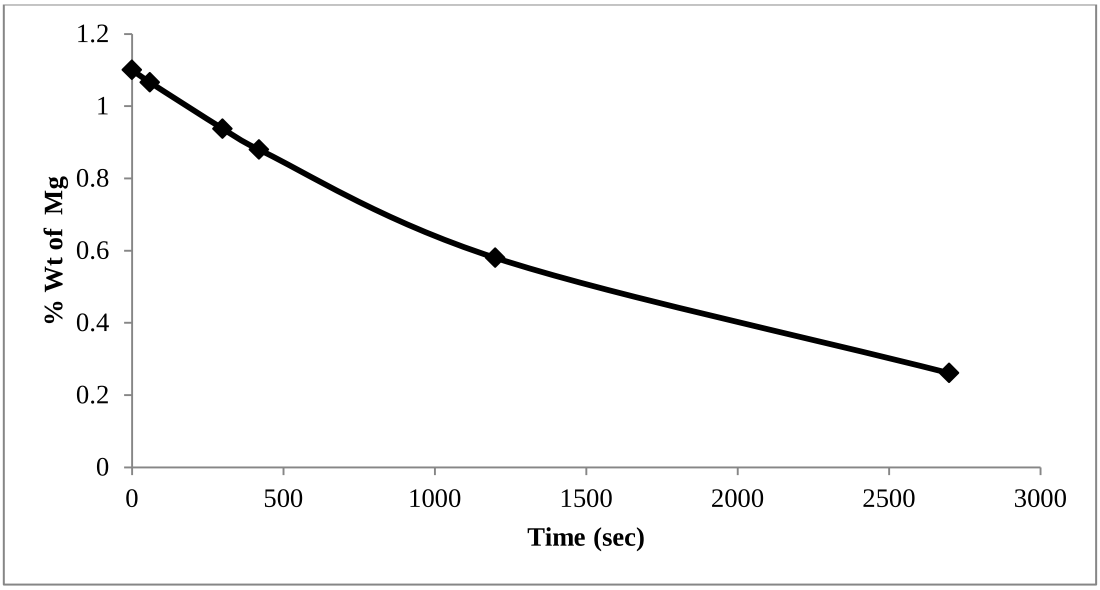


Figure 3: Variation of Mg with Time (Flores et al., 1998)

Table 1: Parameters used for Models validation

1	$C_o = R_{max} = 2.12\,X\,10^{-10} m$ (The Sodeso, 2016)
2	$W = 2.5\,X\,10^{-2} m$ (Buzzmac, 2006)
3	$C_{Mg}^{o} = 3.58\,X\,10^{5} kg/m^3$ (The Sodeso, 2016)

Using the parameters given in Table 1 and kinetic data from Figure 3 above, the crack extension model of the present work was tested. Young's Modulus as a measure of crack resistance was determined as shown in Table 2 and Figure 4. The profile reveals a relatively small change in Young’s Modulus compare to change in time, which implies high resistance of the refractory to chemical corrosion using the present model. Also noteworthy is the steady rise of Young’s Modulus to a peak at 420 sec before a rather sharp drop to 1200 sec implying the occurrence of failure at the peak. Determination of the variation of Young's Modulus with atomic radius using Equation (11) gave similar profile with the former as shown in Figure 5.

Table 2: Variation of Young's Modulus with Time and Atomic Radius

$\mathrm{E/E_u}$	Time (sec)	R (μm)
1	2700	45904.89
1	1200	43306.44
1.000000115	420	41955.24
1.000000105	300	41747.37
1.000000087	60	41331.62
1.000000082	0	41227.68

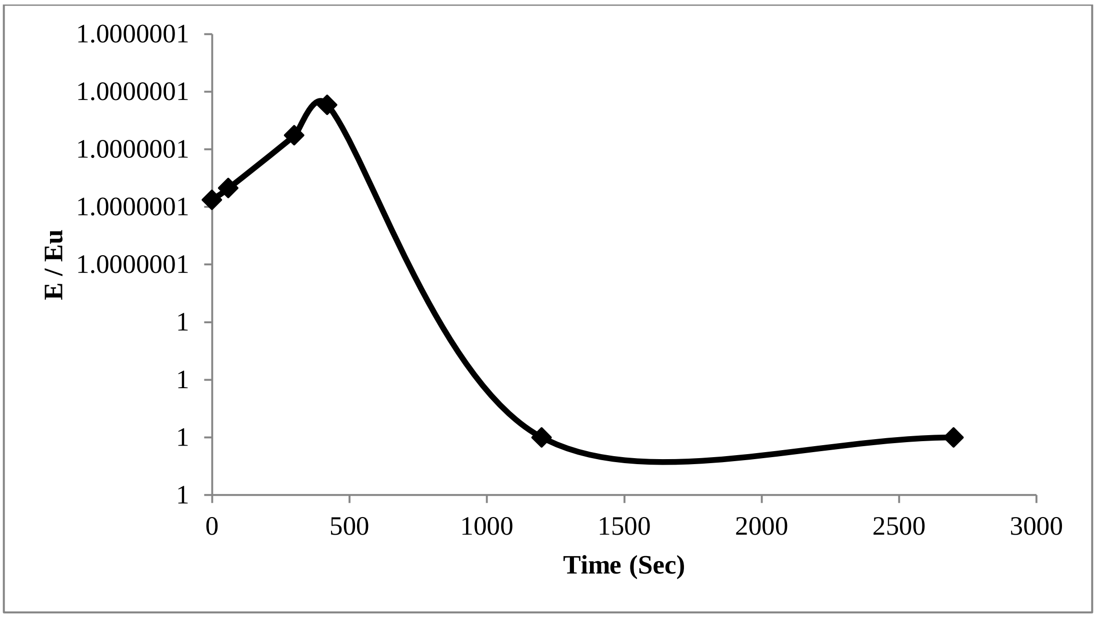


Figure 4:Variation of Young's Modulus with Time

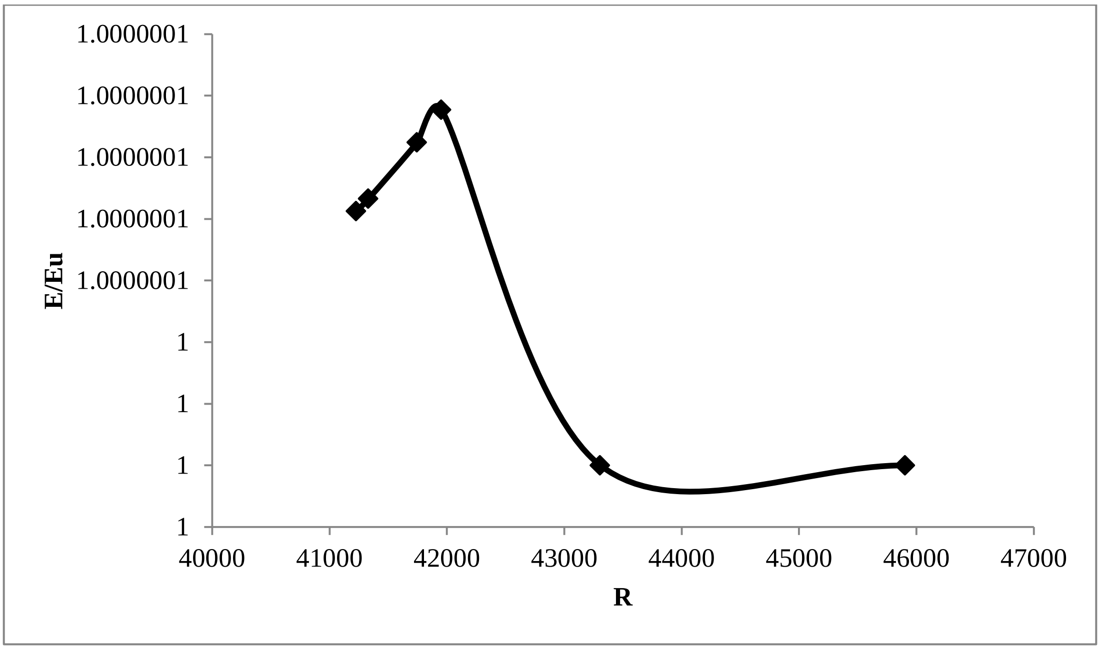


Figure 5: Variation of Young's Modulus with Atomic Radius

From Figure 4 and 5, it is observed that crack extension values on the y-axes are seemingly constant. This is somewhat misleading as the real values are taken to the 9th decimal place as shown in Table 2.

Profiles of the crack extension models in this work were compared with those of the damage model of refractory materials by Xiaoting et al.(2007). While quantitative validation of the models were not carried out due to lack of sufficient experimental data, suffice to note that the profiles showed similar pattern with those of Xiaoting et al.(2007). Consequently, it can be inferred that the model herein developed for analysis of crack extension resulting from chemical corrosion can be used to study refractory phenomena that have similar features.

CONCLUSION

Various studies have been carried out on refractory failure resulting from chemical reaction especially on gasifiers (Kinkar, 2015) and (Kasimagwa, 2010), but these analysis are often too complex and rigorous for easy comprehension. The crack extension model given here therefore present good alternative that describes the phenomena of chemical reaction on refractory using the Carbon Black Reactor as case study.

NOTATIONS

$C_f = Crack\ length$

$C_o = Initial\ crack\ length$

$C_{Mg} = Concentration\ of\ Magnesium$

$C_{Mg(eq)} = Equivalent\ Concentration\ of\ Magnesium$

$E = Young's\ Modulus\ for\ crack\ extension\ to\ inner\ core$

$E_u = Young's\ Modulus\ for\ undamaged\ Centre$

$k = Reaction\ Rate\ Constant$

$T = Temperature\ of\ reaction$

$T_c = Critical\ temperature\ of\ reaction$

$R = Molecular\ radius\ of\ Magnesium$

$S = Surface\ area\ of\ reaction\ on\ refractory\ lattice$

$t = Time$

$W = Total\ thickness\ of\ refractory$

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STRATEGIES FOR DEVELOPING ONION VALUE-CHAIN IN NIGERIA – AN APPRAISAL

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ABSTRACT

Onions are grown in very large quantity in Nigeria. However, dehydrated powdered onions are currently imported mainly from China and India. The powdered onions have industrial applications as additive in production of sauce (Maggi, Knorr, etc), food condiment, noodles, etc. Development of onion value chain is envisioned to link the growing of onions to the industrial needs in Nigeria. In this appraisal, we suggest strategies to develop onions value chain in Nigeria. In achieving the objective, the focus should be on three important areas; (1) Domestication of powdered onion production technology, (2) Development of framework for best agronomy practice in onion cultivation and (3) Linking entrepreneurs to onion cultivation and powdered onion production in Nigeria. It is envisaged that the implementation would spur the domestication of powdered onion production in Nigeria thereby reducing the importation of powdered onions. In addition, a clear framework to improve the current agronomy practices in onion cultivation to meet the specifications for industrial applications were also suggested.

1. INTRODUCTION

Nigeria government is actively pursuing economic diversification. The recent Economic Recovery Growth Plan (ERGP) is intended at growing national output via broadening production (ERGP, 2017). Along this line, the Nigerian Industrial Revolution Plan (NIRP), which is focused specifically on industrial transformation, is designed to accelerate industrial capacity and diversification (NIRP, 2014). To achieve this objective, the plan is centered on developing four key industrial groups in which Nigeria already possesses clear advantage: agri-business and agro-allied; solid minerals and metals; oil and gas related industries; construction, light manufacturing and services (NIPR, 2017). Agri-business and agro-allied industrial sector is envisaged to build an end-to-end integrated value chain via boosting local production to meet domestic demand and reducing country’s requirement on import of processed food products.

Agricultural sector is gradually and steadily being transformed in Nigeria. This is evidenced from the successful Central Bank of Nigeria Anchor Borrowers’ Programme, which provides linkages between companies involved in processing rice and smallholder farmers, have spurred the production of rice in Nigeria (CBN, 2016). Consequence of this initiative and the progress recorded, according to PricewaterhouseCoopers (2018) report, rice production peaked at 3.7 million tons in 2017 and with appropriate agricultural practice in the next 5 years rice production in Nigeria is expected hit 7.2 million tons.

The success achieved in rice production in Nigeria can be replicated for major crops such as sorghum, soya beans, maize, onions, etc. which when processed serve direct industrial applications. For example, Onions when dehydrated into flakes or powder form are used as additive in production of sauce (Maggi, Knorr, etc) and food condiment and so on.

Onion is most commonly grown in North-west and North-central regions of Nigeria with states like Kebbi, Sokoto, Kano, Kaduna, Jigawa and Plateau states. From 2012 data, Nigeria ranks sixth nation behind major producers such as China and Japan with 240 thousand tons of green onions and 1.3 million tons of dry (Indorama, 2014).

In Nigeria postharvest and poor storage are the major challenges associated with the production of onions. For Nigeria to maximize the benefit of growing onions and drastically reduce the 50% postharvest best agronomy practices must be introduced. The farmers must be provided with extension services to choose the appropriate varieties that have long shelf life, suitable soil condition and application of fertilizer at correct time and use the correct quantity. After harvesting, the onions must be classified to remove undeveloped onions that may potential be the source of spoilage (Olanipekun, 2018).

Postharvest losses in onions could also be reduced by transforming via value addition to products such as onion powder, onion flakes, onion sauce, etc. Despite the huge potential likely to be achieved through the development and deployment of an onion powder production process, there is no existing onion powder production plant in Nigeria.

The goal is to demonstrate the technical and economic viability of domesticating production of powdered onion from local onion raw material. The production of powdered onions from local raw material will entail the following key objectives:

1. Domestication of powdered onion production technology in Nigeria.
2. Spur import substitution of powdered onions currently imported.
3. Develop framework to improve the current agronomy practice in onion cultivation to meet the specifications for industrial application.

2. APPRAISAL

2.1 Domestication of Powdered Onion Production Technology

Currently in Nigeria, the powdered and flake onions utilized by the industries are imported predominantly from India and China. Although no data available from the key government agencies (Central Bank of Nigeria and National Bureau of Statistic) on the quantity and amount of powdered onion imported into the country, however, companies that produce sauce, food condiment and so on, import the product from Asia.

Maggi, Knorr, etc. produced by various companies are collectively referred to as bouillon cubes. In production of bouillon, powdered onion is a key raw material. At this moment, the following companies produce the bouillon in Nigeria (Table 1); Nestle Nigeria Limited, Unilever Nigeria Limited, PZ Nigeria, etc.

Table 1: Companies Producing Bouillon Cubes

S/No	**Company**	**Bouillon Cubes** **Brand Name**
1	Nestle Nigeria Limited	Maggi
2	Unilever Nigeria Limited	Knorr and Royco
3	PZ Nigeria	Mamador
4	Pramasidor	Onga
5	Doyin Group of Companies	Doyin and Prime
6	Daily Nigeria Limited	Suppy
7	NASCON Allied Industries Plc, (a subsidiary of the Dangote Industries Limited)	Dan-Q
8	TGI Distri Limited	Terra

According to Nestlé, the Central West Africa Region is the largest MAGGI cube producing market in Nestlé and sells over 100 million cubes in the Central West Africa Region daily. Nigeria is the major contributor in the growth of bouillon cube market in this region.

Another group of companies in Nigeria that utilize powdered onions is the producers of noodles. Noodles are now very common instant meal in Nigerian homes. According to World Instant Noodles Association (WINA), Nigeria is currently 12th largest consumer of noodles in the world with 1.82 billion serving noodles in 2018 (WINA, 2019). In-fact, Nigeria consumes 7 times than the amount consumed in South Africa.

The sauce that normally comes along with the noodles contains powdered onions. There are several companies in Nigeria that produce noodles, hence, these companies import the powdered onions additive. Indomie noodles produced by Dufil Prima Foods Plc are reported to control about 75% of the market share. Other notable producers of noodles are Golden Noodles Company Limited (Golden Noodle).

In essence, there is a large market demand for powdered onions in West Africa, particularly Nigeria that is being supplied for primarily by importation. Therefore, domestication of this technology will not only improve the shelf lives of onions and reduce their wastages in the country, but will also go a long way in providing import substitution for the product and ultimately create jobs for the vast unemployed populace in the country.

Strategies

The key strategies in domestication of production of powdered onions (DPPO) in Nigeria are presented in in Table 2:

Table 2: Strategies for Domestication of Powdered Onion Production Technology

S/No.	Strategies	Key Activities	Stakeholders	Lead Agency
1	Formation of RMRDC Stirring Committee for the DPPO	1. Selection of RMRDC staff for DPPO Stirring Committee 2. Inauguration of the DPPO committee 3. Meeting to adopt the work plan for DPPO 4. Harmonize the DPPO activities with the current effort of RMRDC in Sokoto 4. Reengineering and developing of the Sokoto Plant in Zaria	RMRDC, Consultant	RMRDC
2	Stakeholders Meeting to Review the Plan for the DPPO	1. Workshop to review and adopt the work plan for DPPO	RMRDC, FMARD, FMST, CBN, NIRSAL, BOI, BOA, SON, NAFDAC, State Governments, related food industries, organized onion farmers association, Agricultural research institutes, NACIMA	RMRDC

Outcomes

The outcomes from the domestication of the production of powdered onions in Nigeria are:

1. A functional plant for the production of powdered onions from local raw materials.
2. Demonstration of economic and technical viability of production of powdered onions in Nigeria.

2.2 Development of Framework for Best Agronomy Practice in Onion Cultivation in Nigeria

The onion cultivation in Nigeria is associated with huge postharvest loss. As stated earlier, about halve of the onion produced are lost to poor agronomy practices by farmers such as lack of appropriate storage facilities (Olanipekun, 2018). In meeting the need of onion processors, postharvest loss must be drastically reduced and the problem of storing onions for extended time needs to be addressed.

The reduction of the postharvest loss begins at the start of cultivation and application of appropriate agronomy practices. Suitable varieties with longer shelf life must be made available to the farmers and application of appropriate fertilizer (Olanipekun, 2018).

Strategies

The key strategies in development of framework for best agronomy practice in onion cultivation in Nigeria are presented Table 3:

Table 3: Strategies for Development of Best Agronomy Practice

S/No.	Strategies	Key Activities	Stakeholders	Lead Agency
1.	To develop appropriate framework for onion cultivation in Nigeria.	1. Meeting of the Stirring Committee Members with key stakeholders (State Goverments, FMARD, IAR and CBN) 2. Preparation of a draft document for the workshop. 3. Validation of the draft financial package document	Sokoto, Kebbi, Zamfara, Kano, Jigawa and Kaduna State Governments, FMARD, RMRDC, IAR Zaria, UDU Sokoto	FMARD
2.	Demonstration of best practices of onion cultivation to onion farmers at the proposed Sokoto site.	1. Identification of farmers that will be involved in the demonstration farm. 2. Provision of appropriate onion variety to the farmers. 3. Extension services to the farmers' prior-cultivation, during cultivation and after harvesting. 4. Demonstration of appropriate storage techniques	Sokoto State Government, FMARD, RMRDC, IAR Zaria, UDU Sokoto	IAR Zaria

Outcomes

The outcomes from the development of framework for best agronomy practice in onion cultivation in Nigeria are:

1. A document clearly stating the best approach in cultivation of onions in Nigeria.
2. Demonstration of the best agronomy practice at the Sokoto site of the proposed plant.

2.3 Linking Entrepreneurs to Onion Cultivation and Powdered Onion Production

There are several government agencies with experience and expertise in developing financial packages that link entrepreneurs with appropriate funding arrangements. Some of these agencies include CBN, BOI and BOA. It is paramount to tap into these know-how and skills in development of financial packages for the entrepreneurs that will take-up the production of powdered onions and also cultivation of onions.

The public-private company, The Nigeria Incentive-Based Risk Sharing system for Agricultural Lending (NIRSAL), is well suited in providing tailor made financial solution for agriculture enterprises. NIRSAL have already demonstrated this with its acclaimed successes achieved in the rice value chain. It is expected to be at center of providing solution for the onion value chain.

Strategies

The key strategies in linking entrepreneurs to onion cultivation and powdered onion production in Nigeria are shown in Table 4:

Table 4: Strategies in Linking Entrepreneurs to Onion Cultivation and Powdered Onion Production

S/No.	Strategies	Key Activities	Stakeholders	Lead Agency
1	To develop appropriate financial packages for onion cultivation and powdered onion production.	1. Meeting of the Stirring Committee Members with financial stakeholders (CBN, NIRSAL, BOI and BOA) 2. Preparation of a draft document for the workshop. 3. Validation of the draft financial package document	CBN, NIRSAl, BOI, BOA and RMRDC	NIRSAL

Outcomes

The expected outcomes from linking entrepreneurs to onion cultivation and powdered onion production in Nigeria are:

1. Development of financial instruments for potential investors in onion cultivation and powdered onion production.

3.0 CONCLUSION

In this appraisal of development of onion value chain in Nigeria, it envisaged that best agronomy practice, appropriate onion powder technology and linking entrepreneurs to opportunities is envisioned to lead into production of powdered onion locally and reduce current loss associated with growing onions in Nigeria. This could be replicated in the value chain for other crops such as ginger, pepper, etc.

Acronyms

ABU: Ahmadu Bello University
BOA: Bank of Agriculture
BOI: Bank of Industry
CBN: Central Bank of Nigeria
DPPO: Domestication of Production of Powdered Onions
FMARD: Federal Ministry of Agriculture & Rural Development
FMST: Federal Ministry of Science and Technology
IAR: Institute of Agriculture, Ahmadu Bello University
NIPR: Nigerian Industrial Revolution Plan
NIRSAL: Nigeria Incentive-Based Risk Sharing system for Agricultural Lending
UDU: Usman Danfodio University
RMRDC: Raw Materials Research and Development Council

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SUGARCANE BAGASSE AND GROUNDNUT SHELL DENSIFICATION FOR THERMAL ENERGY APPLICATIONS

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ABSTRACT

As part of the efforts towards increasing the economic prospects across agricultural value chain, efficient utilization of associated wastes and by-products is of significant importance. In that regard, densification is widely used as a means of increasing the energy density of loose biomass, to improve its effectiveness when used as a fuel for energy generation. However, owing to the differences in across the densified materials, not all densified biomass (commonly called briquettes) exhibit the same performance characteristics when used as fuels. This is because the required properties for a briquette – including mechanical strength and burning characteristics – is largely dependent on the biochemical composition and physio-chemical properties of the biomass and the binder material used, as well as the briquetting conditions. In this work, two of the common wastes associated with major cash crops of Nigeria - sugarcane bagasse and groundnut shells, were densified into briquettes, using starch and gum Arabic as binders. Different combinations (in varying proportions in mass) of sugarcane bagasse and ground shells, were tested to achieve the best quality of briquettes. The materials were densified using a hydraulic press using a compaction pressure of 5 bar, and the resulting briquette samples were assessed by evaluating their physical, mechanical and burning characteristics. Overall, the briquette sample made from equal proportions of groundnut shells and sugar cane bagasse, with gum arabic as the binder showed the most desirable combination of characteristics including good physical appearance, a bulk density of 0.7918 g/cm^3, low ash content (3.9%), relatively high calorific value (16.382 MJ/kg), appreciable moisture content (15.52%) and adequate burning rate (0.93 g/min). It was however observed that the groundnut shells-sugarcane bagasse briquette sample, produces significant smoke on ignition, due to high percentage of volatile matter (79.19%).

1.0 INTRODUCTION

Due to the current socio-economic and environmental reasons associated with the use of fossil based fuels, the utilization of biomass for a variety of energy applications is becoming increasingly popular. However, biomass in general, and especially agricultural wastes and by-products, have very low energy density. Hence, densification is employed to significantly increase the energy density of different biomass materials (Olorunnisola, 2007), to improve their pliability for both domestic (like cooking and space heating) and industrial like (steam and power generation) applications.

Densification is an easy and environmentally friendly means of compacting loose biomass and wastes into higher density (Wilaipon, 2007; Kaliyan and Morey, 2009), low-cost replacements of fire wood, twigs, coal and charcoal (Olorunnisola, 2007). Considering the fact that traditional biomass and related waste materials are the major sources of domestic energy in Nigeria (Osueke and Ezugwu, 2011; Kwadzah and Ogbeh, 2013; EIA, 2016; EnergyPedia, 2020), improvement in their means of utilization will proffer a significant socio-economic benefit to the nation. Furthermore, apart from turning the biomass and wastes into improved sources of energy, productions of the briquettes will help in deterring cutting off of trees (Arevalo *et al*., 2017), which is a major contributor to soil erosion and desert encroachment (Olorunnisola, 2007).

In general densification of a wide variety of biomass into briquettes have been significantly studied over the last two decades (Chin and Siddiqui, 2000; Ndiema *et al.*, 2002; Roy and Corscadden, 2012; Stolarski *et al.*, 2013; Obi, 2015; Arévalo *et al.*, 2017; Shuma and Madyira, 2017). Chin and Siddiqui (2000) investigated the densification of sawdust, rice husks, peanut shells, coconut fibres and palm fruit, while Roy and Corscadden (2012) studied 15 biomass briquettes produced from a range of feedstock including hay and switch grass. Likewise, Rupinderjit *et al.* (2012) investigated the densification of rice husk, coffee husk, saw dust, ground nutshell and cotton stalks. Stolarski *et al.*, (2013) produced and compared the quality and productions costs of eight types of briquettes from different biomass sources including pine sawdust, perennial energy plants, rape straw, and de-oiled cake of rapeseed. Also, Obi (2015) investigated the effect of temperature and percentage of binder, on the quality of briquettes made from saw dust and rice husk. In line with that, Arévalo *et al.*, (2017) proposed a model of briquette production from rice husk, while Shuma and Madyira (2017) reported on the various production methods, procedures and processes that are deployed to process loose biomass into biomass briquettes.

Due to the wide variations in both the biochemical composition and physio-chemical properties of the variety of biomass used in briquetting, not also briquettes end up with the required quality and characteristics for the intended application (Stolarski *et al.*, 2013). This is because the required properties for a briquette – including mechanical strength and burning characteristics – are largely dependent on the nature and type of the biomass, the binder material used (to help in sticking the biomass materials together), and the briquetting conditions (Ndiema *et al.*, 2002; Rupinderjit *et al.* 2012). Thus, different binders (Shuma and Madyira, 2017) and varying operating conditions (Obi, 2015) have been investigated for production of briquettes with the desired mechanical and burning characteristics. These characteristics include improved energy density and calorific value, low moisture content, adequate burning rate, good handling and storage characteristics (Chin and Siddiqui, 2000; Shuaibu *et al.*, 2016; Shuma and Madyira, 2017).

To ensure continuity in the production of briquette from waste biomass materials, it is important to assess the impact of using a mixture of different biomass on the quality of the briquettes. This is important because the exact availability of any of the materials under consideration is not strictly controllable, and thus the ability to use a combination of the different biomass materials available will be an advantage. However, this prospect in biomass briquetting is not fully exploited, and very limited literature is available on it. Stolarski *et al.*, (2013) produced briquette from equal amount of rape straw and rapeseed oilcake, but it turned out to be of inadequate quality compared to all other briquettes studied by the authors (Stolarski *et al.*, 2013).

This study is focused on investigating the quality of briquettes produced from sugarcane bagasse and groundnut shell as well as different combinations of two in varying proportions, using a hydraulic press machine, with starch and gum Arabic as binding materials.

2.0 MATERIALS AND METHOD

2.1 Materials Collection and Preparation

Groundnut shell was gathered from local farmers in Samaru and Bagasse was obtained from sugar cane juice point in Danfodio hostel, ABU Zaria.

Groundnut shells and bagasse were sun-dried for 1 week to remove moisture. The bagasse was further oven-dried for 4 hours at 70°C to aid size reduction. Both groundnut shells and the sugarcane bagasse were grinded using Thomas Wiley Laboratory mill, and sieved to have uniform particle sizes using a 2mm sieve.

Table 1: Description and Composition of Briquette Samples

Sample number	Label	Weight of Groundnut shell (g)	Weight of Bagasse (g)	Volume of Starch (mL)	Volume of Gum Arabic (mL)	Biomass to Binder Ratio (mass)	Composition
1	GG1	320	-	-	300	3:1	Groundnut shell with gum Arabic
2	GG2	320	-	-	200	5:1	Groundnut shell with gum Arabic
3	GS1	320	-	450	-	3:1	Groundnut with starch binder
4	GS2	320	-	250	-	5:1	Groundnut with starch binder
5	BG1	-	180	-	300	3:1	Bagasse with gum Arabic
6	BG2	-	180	-	200	5:1	Bagasse with gum Arabic
7	BS1	-	180	450	-	3:1	Bagasse with starch binder
8	BS2	-	180	250	-	5:1	Bagasse with starch binder
9	GBG1	50	200	-	250	2:1	Groundnut shell, bagasse and gum Arabic
10	GBG2	150	150	-	250	3:1	Groundnut shell, bagasse and gum Arabic
11	GBG3	200	50	-	250	1:1	Groundnut shell, bagasse and gum Arabic

2.2 Methodology – Briquette Production

The first briquette sample was prepared by weighing out and thoroughly mixing 320g of the powdered groundnut shell, and about 107g of gum Arabic (dissolved in water to make 300 ml). The mixture was then poured into a mold and compressed by applying a pressure of 5.0 bar,


Plate 1: Briquette Samples

using a hydraulic press. Ten more briquette samples were made by weighing out the required amounts of biomass (powdered groundnut shell, sugarcane bagasse or both) and binder based on the given quantities in Table 1 above. The briquettes made were then detached from the molds (Plate 1), weighted and sun-dried for 14 days.

2.3 Briquettes Samples Analysis

Briquettes are generally evaluated by assessing their physical properties, mechanical strength, and burning characteristics including percentage moisture content (PMC), percentage volatile matter (PVM), percentage ash content (PAC), bulk density, and calorific value (Chin and Siddiqui, 2000; Shuaibu *et al.*, 2016; Onokuk *et al.*, 2017; Shuma and Madyira, 2017)

2.3.1 Bulk density

Bulk density is an indication of the total amount of energy contained after compaction, and thus provides a hint of the briquette's burning rate (Shuma and Madyira, 2017).

The bulk density was calculated by measuring the diameter of the overall briquette as d_o, diameter of the hole created at the centre of briquette (see plate 1), the height of the briquette and the weight of each briquette sample.

Using the values of length and diameter for each briquette, the volume of the overall briquette was calculated, and the bulk density of each briquette was calculated using

$$\rho_B = \frac{mass\ of\ briquette\ sample}{volume\ of\ briquette\ sample}$$

ρ_B is the bulk density in $^{g}/_{cm^3}$

2.3.2 Percentage volatile matter (PVM)

To determine the PVM of each sample, 5g of the dried, pulverized sample was heated in an oven (at 500 ^oC), for 10 min, and weighed after cooling. The PVM was calculated by

$$PVM = \frac{(weight\ of\ heated\ sample - weight\ of\ dried\ sample)}{weight\ of\ heated\ sample} X\ 100$$

2.3.3 Percentage moisture content (PMC)

For the moisture content determination, 5g of each of the samples was dried in an oven and weight again after the drying. The PMC was calculated by

$$PMC = \frac{(weight\ of\ \ sample - weight\ of\ dried\ sample)}{weight\ of\ sample} X\ 100$$

2.3.4 Percent ash content (PAC)

To determine the ash content of the samples, 5g of each sample was measured and poured into different crucibles. The samples were burned to ash in a Carbolite Furnace. Weight of crucibles plus the ash formed measured were measured using analytical balance with draft shield. The PAC was calculated from

$$PAC\ = \frac{Weight\ of\ ash}{weight\ of\ sample}$$

2.3.5 Calorific value

0.5g of each sample was taken and placed in a crucible. A presser was used to press each sample in the crucible. An e2k O-Bomb Combustion Calorimeter was used for the determination of the calorific value. A burning wire was attached to lid assembly of the machine and was coupled with the crucible containing sample. This was then placed carefully inside the vessel of the machine. Oxygen gas was pumped into the vessel and everything was loaded into the machine for 10 minutes. Galvanometer deflections were taken for deflections without sample and with sample respectively. Readings of calorific values in MJ/kg were recorded.

2.3.6 Burning rate

For the burning rate, 3g of each sample was taken and placed on an insulated wire gauze, and then placed on a burner to burn. The sample and the insulated wire gauze were measured at 20 seconds interval. The burning rates were recorded (in g/min) as time taken for each sample to burn completely was recorded.

3.0 RESULTS AND DISCUSIONS

3.1 Nature and Physical Appearance of the Briquettes Samples

Plate 1 shows the briquettes produced from Groundnut shell and sugar cane bagasse with gum Arabic and Starch binders. The briquettes produced from the compaction machine were strong and well formed, with a light brown coloration. From a physical examination of the briquettes, the higher amount of binder give the briquette a smooth and consistent appearance. The briquette with lesser amount of binder appear rough, with inconsistent surface. This indicates that the briquettes compaction and strength increased with binder concentration. Also, by visual observation, the briquettes produced from bagasse appear to be weaker, lighter in weight, and easier to disintegrate, compared to the groundnut shell briquettes (Table 2).

Table 2: Visual observation of briquettes' appearance

Samples	Relative Strength of the briquette samples			Degree of cracking		
	Poor	Average	Good	Severe	Average	No crack
GG1			✓			✓
GG2			✓			✓
GS1			✓			✓
GS2		✓			✓	
BG1			✓			✓
BG2	✓				✓	
BS1		✓			✓	
BS2	✓			✓		
GBG1			✓			✓
GBG2		✓				✓
GBG3	✓					✓

Again, it was noticed that there appears to be a growth of some sort of microorganism (like fungi) with higher concentration of starch binder, and it is more pronounced on the briquette samples made from sugarcane bagasse.

3.2 Bulk Densities of the briquette Sample

Bulk density is one of the important quality indicators of a briquette. High-quality solid fuels are required to have high bulk density in order to burn for a longer time and generate a higher energy. The higher the density, the better the briquette's quality (Onukak *et al.*, 2017). From Figure 1, the briquette same made from groundnut shells with gum Arabic as the binder in a ratio of 3:1 by mass (GG1), has the highest bulk density of 1.16 g/cm^3. The second and third samples in terms of bulk densities are GS1 and GG2 with 1.02 and 0.99 g/cm^3 respectively. This goes on to show that groundnut shells have a tendency to generate briquettes o high bulk density, in spite of the nature of material used as a binder. This is in line with the findings of Shuma and Madyira (2017) where five different materials (including thatching grass, groundnut shells, sugarcane and Mopani leaves) were studied and groundnut shells based briquettes exhibited the highest bulk density. Also, all samples with higher ratios of gum Arabic as the binder (GG1, BG1, GBG1), show relatively higher densities than those with similar biomass composition but lower ratios of the gum Arabic (GG2, BG2, GBG2) respectively. Contrastingly, the briquettes samples containing sugarcane bagasse are

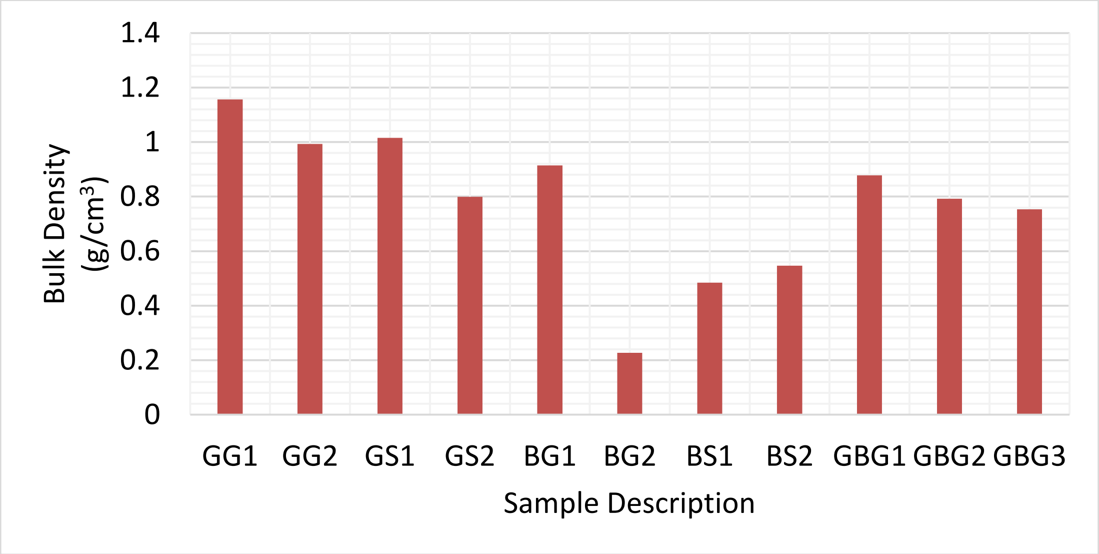

Figure 1: Bulk densities of the briquette samples

generally low in bulk density, most especially where starch is used as the binder. The combination of ground shells and bagasse shows obvious improvement in bulk density (GBG1, GBG2 and GBG3), relative to when bagasse alone is used (and not much lower than for groundnut shells alone) – thus indicate a justification for combining the two.

Since briquette density influences their burning rates, as high density briquettes tends to have a longer burning time and releases more heat, the combination of groundnut shells and sugarcane bagasse, is a positive development. Furthermore, denser briquettes occupy less volume, hence making storage and transportation easier (Arevalo *et al*., 2017) and less expansive.

3.3 Percentage Volatile Matter of the briquette Sample

Lower volatile matter is associated with higher energy value. Hence, the briquette sample with the least volatile matter is expected to have the highest energy value, because samples with higher volatile matter will require more energy to burn off the volatile matter before the release of its usable heat energy (Onukak *et al.*, 2017). In this regards, same GG2 – made from groundnut shells and lower ration of gum Arabic has the best quality.

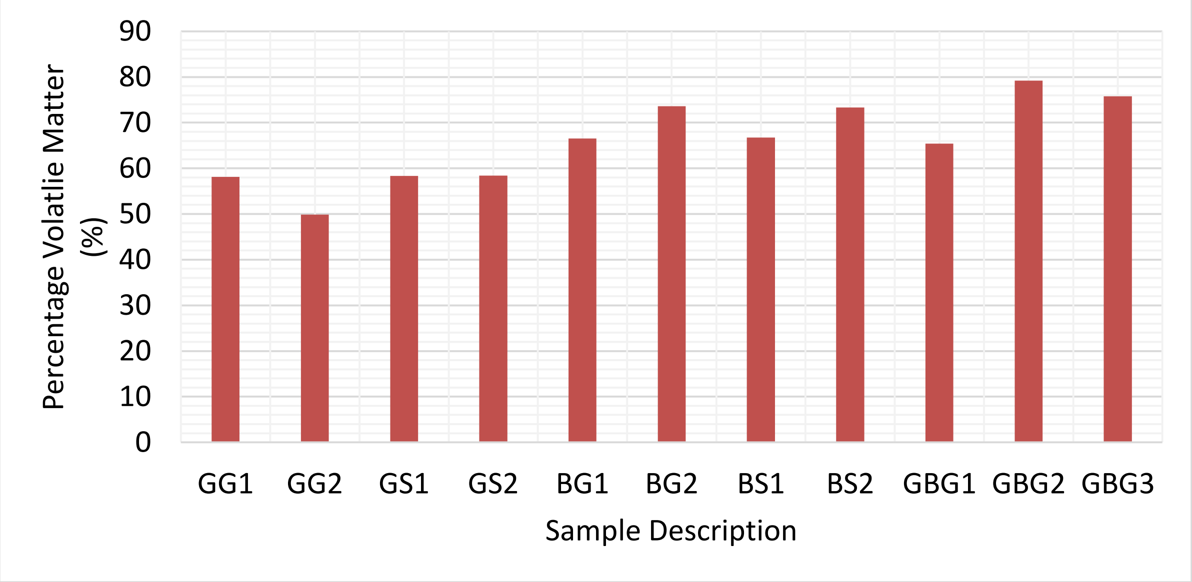

Figure 2: Percentage volatile matter of the briquette samples

3.4 Percentage Moisture Content of the briquette Sample

Moisture content facilitates starch gelatinization, protein denaturation and fiber solubilization during briquetting, but when it is high, it reduces the binding strength of the fuel as well as the density (Onukak *et al.*, 2017). Also, high moisture content in briquettes can cause them to crumble too quickly during combustion, hence briquettes with relatively lower moisture content is preferable (Cutz *et al.*, 2016). The optimum moisture content for a briquette is around

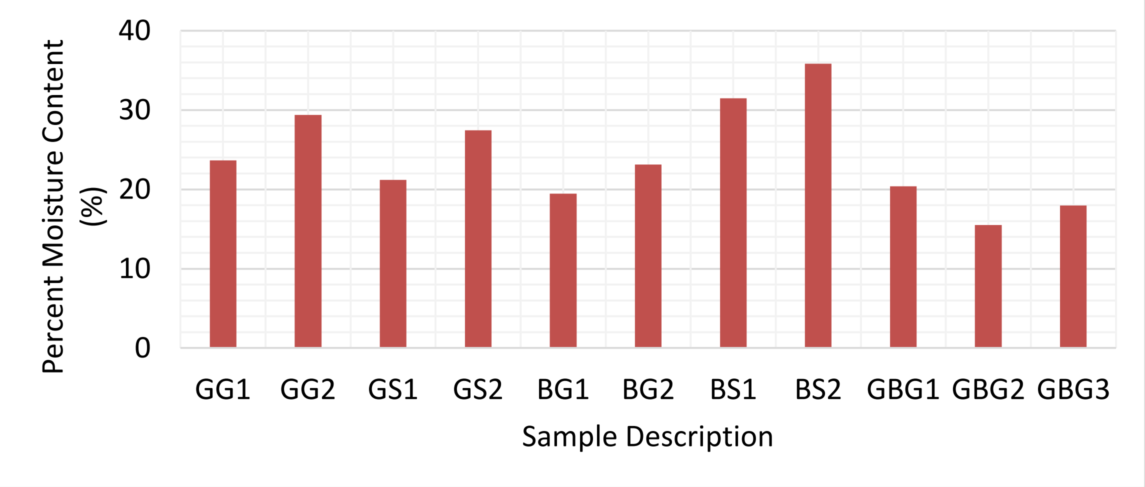

Figure 3: Graph showing percent moisture content of samples

10 -18% (Siddiqui, 2000). When the moisture content is lower than 10% or higher than 18%, the particles will not be consistent and briquette may show tendencies of falling into pieces.
From Figure 3, only GBG 2 and GBG 3 fall between this acceptable range with GBG 2 having the lowest moisture content (15.52 %). This may be due to the combined effects of the two different materials used (groundnut shells and sugarcane bagasse). Again, this is another indication that the combined groundnut shells and sugarcane bagasse briquette sample, can outperform the sample made from the individual biomass (groundnut shells and sugarcane bagasse).

Generally, more energy will be required for burning briquettes with higher moisture content because the moisture has to be exhumed. This will lead to overall decrease in the total energy to be obtained. And in a furnace, a damp fuel will lead to the excessive emission of fumes and risk of explosion. A further disadvantage of high moisture content is the facilitation of a breeding ground for fungi and other microorganisms (Onukak *et al.*, 2017). This explains the observation in section 3.1 where it was observed that growth of microorganism was more eminent in the briquette samples made from sugarcane bagasse with starch binder. These are the same with highest moisture content (BS1 and BS2 in Figure 3).

3.5 Percentage Ash Content of the briquette Sample

Ash content is one of the factors affecting the quality of briquettes. Low ash content is desired for briquette so that low amount of waste will be generated, hence reducing environmental pollution. Also, knowledge of the ash content expresses the extent of clogging up of the burning medium. High ash content decreases the burning rate and reduces the heating value of fuel, because it significantly affect their burning rate and ignition time. The tolerance level of ash content for fuel is below 4% (Onukak *et al.*, 2017).

From Figure 4, GBG 2 has the lowest ash content (0.04%), which again signifies the benefit of combining the groundnut shells and sugarcane bagasse. As shown (Figure 4), each of the two used alone exhibit higher ash content (relative to when the two are combined), regardless of the binder used.

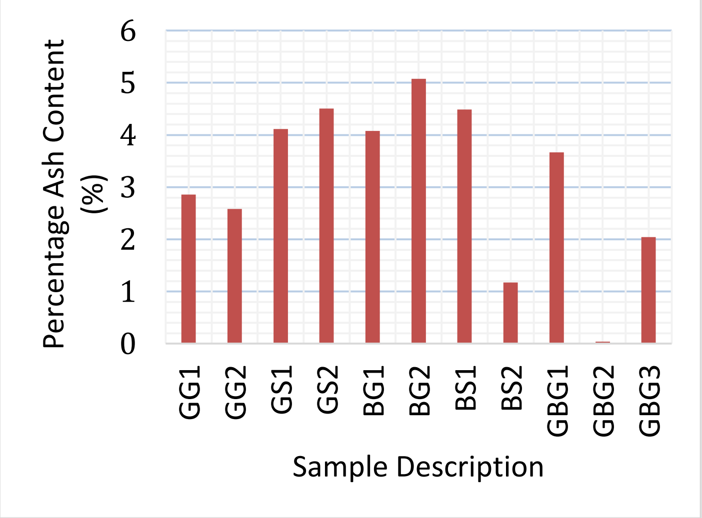

Figure 4: Percentage ash content of the briquettes samples

On the basis of the standard tolerance level of ash content only six of the briquette samples (GG1, GG2, BS2, GBG1, GBG2 and GBG3) are within acceptable range.

3.6 Calorific Value of the briquette Sample

Calorific value indicated the amount of energy obtainable from a unit mass of fuel. Calorifc value is therefore one of the most important characteristics of a fuel. The higher the calorific value the better, and more efficient an energy system will be (Onukak *et al.*, 2017). Generally, briquettes with calorific values above 16.0 MJ/kg are considered acceptable (Lubwama & Yiga, 2017).

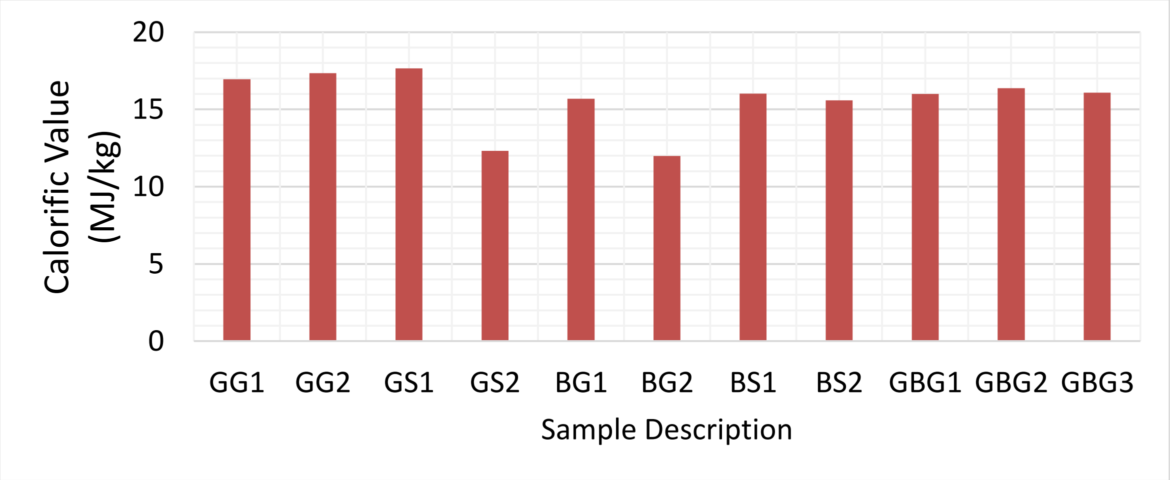

Figure 5: Plot of calorific values of briquettes

From Figure 5, briquette samples GG1, GG2, GS1, BS1, GBG2 and GBG3 are above within the acceptable range of calorific value above 16.0 MJ/kg. The briquette showing the highest calorific value was GS1, likely because of the high concentration of starch binder which has been shown to improve calorific quality of briquettes (Ismaila & Sadiq, 2013). From the Figure, it can be seen that the higher calorific value samples are all associated with higher ratios of binder. This is consistent with the findings of David and Jason (2013).

3.7 Burning Rates of the briquette Sample

The burning rate of a fuel refers to the rate at which its specific mass is burnt in air. The quality of any fuel briquette depends on its ability to provide sufficient heat at the necessary time, to ignite easily without any danger, generate less ash as this will constitute nuisance during cooking. The burning rate has a significant effect on briquette application, because briquettes with high burning rate will require higher amount of the briquettes in combustion, as they burn off quickly (Onukak *et al.*, 2017). It can be observed from the Figure (Figure 6) briquette samples with lower proportion of binders (GG2, GS2, BG2, BS2, and GBG3) burn relatively faster than their counterparts with higher proportion of binder (GG1, GS1, BG1, BS1, and GBG1). A similar observation has been made in a previous study (Onukak *et al.*, 2017) and it indicates an additional reason for using binders in biomass briquetting.

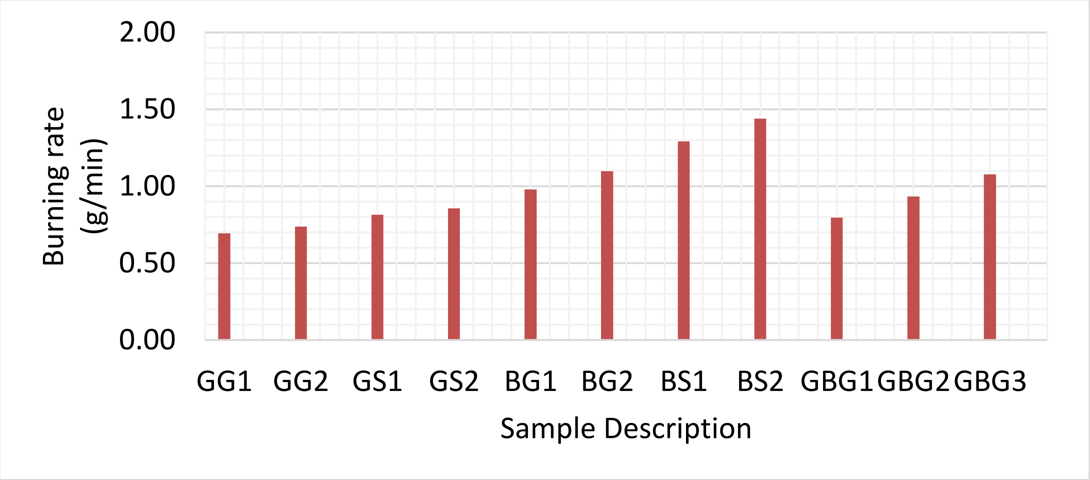

Figure 6: Graph showing burning rates of briquette samples

CONCLUSION

Biomass briquettes were developed from groundnut shells and sugar cane bagasse, using starch and gum Arabic as binders. This was accomplished by varying the amount of the binders and also varying the relative mass ratios of the two biomass materials (groundnut shells and sugar cane bagasse). Overall, the briquette sample made from equal proportions of groundnut shells and sugar cane bagasse, with gum arabic as the binder showed the most desirable combination of characteristics including good physical appearance, a bulk density of 0.7918 g/cm^3, low ash content (3.9%), relatively high calorific value (16.382 MJ/kg), appreciable moisture content (15.52%) and adequate burning rate (0.93 g/min).

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REVIEWING THE CHEMICAL ENGINEERING CURRICULUM FOR RELEVANCE

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ABSTRACT

This paper reviews the case of the chemical engineering curriculum and proposes ways and areas that need urgent attention. It recommends the need to develop an appropriate action plan for the review, the introduction of new courses that are in consonance with new trends in the chemical industry and the need to develop instructional materials to make the implementation of the curriculum easier for both the lecturers and the students and the reintroduction of the periodic industrial attachments for lecturers to keep them abreast with the new developments in the industry. It further calls for an implementable timetable to ensure regular reviews of the curricula of the programmes of Nigerian tertiary institutions and for all institutions to strengthen their strategies and specific initiatives designed to support the development of quality teaching since pedagogy is a central enabler of the implementation of all academic curricula. The paper finally recommends that Nigerian tertiary institutions consider the hiring of adjunct lecturers from critical industries to join regular staff for a period of time as this will go a long way in inculcating the appropriate real life skills and competences in students. Such symbiotic collaboration between industry and academia are key ingredients of a successful curriculum implementation.

Key words: Curriculum Revision, Industrial Trends, Chemical Engineering,

DEFINITION OF CURRICULUM

According to United Nations Educational, Scientific and Cultural Organization (UNESCO), Curriculum is a systematic and intended packaging of competencies (i.e. knowledge, skills and attitudes that are underpinned by values) that learners should acquire through organised learning experiences both in formal and non-formal settings. Good curriculum plays an important role in forging life-long learning competencies, as well as social attitudes and skills, such as tolerance and respect, constructive management of diversity, peaceful conflict management, promotion and respect of Human Rights, gender equality, justice and inclusiveness.

Curriculum development is defined as a planned, purposeful, progressive, and systematic process to create positive improvements in the educational system. Every time there are changes or developments happening around the world, the curricula are affected. There is a need to update them to address the society's needs. According to Bilbao et al. (2008), curriculum is considered the "heart" of any learning institution which means that the Polytechnics or Universities cannot exist without a curriculum for each of their programmes. Since there are constant changes in the society, curriculum development has become a dynamic process. The curriculum can therefore be considered the total learning experiences of individuals not only in the institutions but the society as well. The critical question we need to ask is, do we have to wait for society to change before we prepare a curriculum to match it or can we be innovative enough to keep pace?

The truth is that we have to develop the curriculum around the challenges in the Chemical Industry. Wrongly defined trends lead to wrongly defined challenges to non-relevant curriculum. What type of Curriculum are we preparing? Is it a community curriculum, regional curriculum, national curriculum or global curriculum?

IMPORTANCE OF CURRICULUM DEVELOPMENT

Curriculum development has a broad scope because it is not only about the Institution, the learners, and the teachers; It is also about the development of society in general. In today's knowledge economy, curriculum development plays a vital role in improving the economy of a country. It also provides answers or solutions to the world's pressing conditions and problems, such as environment, politics, socio-economics, and other issues of poverty, climate change, and sustainable development. There must be a chain of developmental processes to develop a society. First, the curriculum must be developed to preserve the country's national identity and to ensure its economy's growth and stability. Thus, the president of a country must have a clear vision for his people and the country as well. For instance, in Nigeria, Mr. President in his Change Agenda may want the country to be self-sufficient in food and also produce its fuel so as not to rely on importation. The curriculum should therefore be reviewed to support these initiatives by, for example, the introduction of storage and processing systems and bio-fuel studies.

There are issues of illegal processing of stolen crude oil. The mineral sector needs to be developed to enable us move from oil dependency. How will this influence the curriculum development and review? Then the curriculum must be developed along that line. Curricula programs for higher education can be crafted in such a way that graduates can fit easily in the relevant sectors to boost the food, oil industry and mineral sector. For example, different models may arise such as a curriculum that emphasizes renewable energy, bio-energy, returning to coal energy, producing fuel from methane. Questions like, will there be more emphasis on gas. Should government and industry support the building of more modular refineries? How about the introduction of mineral processing systems or emphasizing multidisciplinary approaches in the curriculum? In Singapore, for example, water is a key issue and there are more water related programmes and research. Poor curriculum means precious time is wasted by industry for on-the-job training

If Polytechnics or Universities have curricular programmes that are innovative and in demand in the local or global markets, many students even from foreign countries will enroll. A higher number of enrollees would mean income on the part of the Institutions. As a result, if the income is big, it can be used for teachers' promotion, scholarship, and remuneration. It can also be used in funding research and development endeavors, and in putting up school facilities, libraries, and laboratories. The country's economy can improve the people's way of life through curriculum development. And to develop it, curriculum experts or specialists should work hand in hand with lawmakers such as senators, the local government officials, governors among others.

Likewise, business communities and industries, and other economically oriented players in society may be engaged in setting and implementing rules and policies for educational reforms. Hence, curriculum development matters a lot in setting the direction of change in an Institution, not only at the micro but also at macro levels. As long as the goals and objectives of curriculum development are clear in the planner's mind, cutting-edge achievements in various concerns can be realized. Why is Massachusetts Institute of Technology (MIT) or Harvard University, etc, considered a brand? This can be traced to, among others, the quality of the programmes they run, which can further be traced to the curricula they use.

DEVELOPMENT RELEVANCE OF CURRICULA

The following are key considerations when developing a curriculum:

1. What does the country/community want to achieve with regard to the personal development of learners and societal well-being and advancements? And how well does the curriculum reflects that education vision?
2. What are the mechanisms for making the curricula to respond to national development policies and strategies? Is there evidence that the mechanisms work effectively?
3. How well are the key/core/cross-cutting competencies identified in the curricula aligned to education policy goals?
4. Is there evidence that such key competencies have been at the core of curriculum development?
5. How are education stakeholders (teachers, learners, private sector, and civil society) involved in developing the curriculum vision and appropriate curriculum policies?
6. Is there evidence of their involvement having made a difference?

STAKEHOLDERS IN CURRICULUM DEVELOPMENT

As we all know, curriculum development is a complex and iterative process with a great number of activities that involve many stakeholders. This therefore means that a variety of stakeholders should be consulted in order to collect invaluable feedback regarding their needs and requirements related to education processes. Two distinct groups of stakeholders have been indentified: curriculum stakeholders and professional stakeholders. Curriculum stakeholders are key informers and drivers of the content, method of delivery, evaluation requirements and scope of curriculum that qualifies for a certain profession. Professional stakeholders have a broader interest in specific professions, professional attributes of graduates, their work capabilities and conditions, specialty career development, knowledge and competencies. Curriculum stakeholders are essential to curriculum development. Collaboration with stakeholders and an open dialogue that calls for recommendations, feedback, critique and advice that can provide a significant contribution in combining the content and method of delivery of the curriculum to meet the needs of the wider community (Matkovic *et al*., 2014).

A modified curriculum development master process based on analysis, design, development, implementation and evaluation model was proposed by Matkovic *et al*. (2014). The model recognize the importance of different stakeholders, how to identify and select key curriculum stakeholders whose contribution can be of great importance for the curriculum development process, how to collect and process their requirements, the activities of the analysis phase, and utilize their input for curriculum innovation.

In identifying the stakeholders involved in curriculum development, the following pertinent question must be answered:

a. Why do you need to develop or review the curriculum?
b. Who is developing the curriculum?
c. Who will use the curriculum?
d. Where is it to be used?
e. Who will deliver the curriculum?
f. Where will the students who use the curriculum go to when they graduate?
g. The students you enroll, where are they coming from (pre-knowledge of the field)?
h. How is the curriculum development team selected?

Curriculum development for programmes in Nigerian tertiary institutions has not been a regular exercise in many cases. Why this is so can be traced to many factors but the most important is not the funds to conduct the exercise but to the lack of the knowledge of the importance of such exercise by the institutions administrators and supervisor agencies to the institution in particular and the country in general. It is important for all tertiary institutions to assess themselves by asking the following questions:

a. Who is the primary initiator of curriculum development?
b. Is the Institution reviewing or developing a curriculum because the supervisory bodies (National Universities Commission (NUC) or National Board for Technical Education (NBTE) say so?
c. What internal quality assurances measures do Nigerian tertiary institutions have to improve the curriculum of their programmes?
d. Do Nigerian tertiary institutions have tracer programmes for graduates to see if the skills and competencies imparted are relevant to their future endeavors?
e. Are Nigerian tertiary Institutions ready to phase out programmes that the skills and competences are no longer required by industry?
f. Are tertiary Institutions innovating enough to produce graduates for the industry of the future or we only think about past and present gaps?
g. Are Nigerian tertiary Institutions' curricula producing regional, national or global graduates?

NATIONAL BOARD FOR TECHNICAL EDUCATION (NBTE) CURRICULUM CRITERIA: POLYTECHNICS

Before any programme in the Polytechnic in Nigeria can be accredited, the National Board for Technical Education (NBTE) has laid down the following conditions:

a. The curriculum in use for the programme should be adequate and therefore, not inferior to the NBTE's approved minimum curriculum and course specification for the level of training.
b. It should reflect the requirements of the relevant industry and employers, and adequate in content to prepare students at the appropriate level in the particular field to acquire skills, that is, sound theoretical background and competences to fulfill the requirements for specific job objectives, in addition to social and communication skills necessary to understand the environment and to live, work and make useful contributions as a citizen.
c. There is a curriculum for the programme designed by the department/institution. Its structure includes professional and general education courses and students' industrial work experience scheme (SIWES).
d. The curriculum developed by NBTE is just a minimum requirement. Additional curriculum content must be developed by the Department to meet local/regional needs.
e. The content of each course should be adequate and similar to those contained in the NBTE curriculum.
f. The curriculum content is clear to the lecturers teaching the courses.
g. Skill and professional components are adequate for the level of programme.
h. The mode of teaching the curriculum is effective and includes lecture/recitation, practical exercises/projects and written exercise.

It is further expected that general studies courses should be included so that students may improve their communication skills, oral and written and their understanding of themselves, and their environment where they will live, work and make useful contributions as worthy citizens of the country and the world at large. General studies courses will also inform the student on how to relate his skills to the society and the economy. The general studies courses account for 10% - 15% of the contact hours allocated to the programme distributed by courses in the arts and humanities, social and behavioral sciences, mathematics and basic sciences and physical and health education. All students in all programmes are expected to take all the modules in Use of English, Communication in English, Physical and Health Education, Contemporary Social Problems and Outline History of Nigeria (Citizenship).

Other courses are taken as elective courses depending on the professional programme and the resources available to the institution to mount them. Students' practical/project works are of good standard and quality. They reflect adequate preparation of the students for entry level employment in his chosen field.

In addition, the Board shall confirm that:

a. All laboratory/workshop/farm practical exercises listed for each course were accomplished by the end of each semester;
b. Simulated work related problems in each core modules are solved;
c. Projects undertaken by the students are related to the discipline, useful in the Nigerian environment and are of good standard;
d. All new equipment, are properly installed and commissioned;
e. All equipment in the laboratories, workshops and farm/field facilities are functioning;
f. Safety provisions are adequate and are being maintained; and;
g. Adequate volumes of books, journals, periodicals and non-book items are available in the library for the programme.

NATIONAL UNIVERSITIES COMMISSION (NUC): CURRICULUM CRITERIA: UNIVERSITIES

Before any programme in the University in Nigeria can be accredited, the National Universities Commission (NUC) has laid down the following conditions:

a. The Curriculum of the programme to be accredited should be adequate to prepare graduate at an appropriate level in the particular field;
b. It should include adequate theoretical knowledge and skills to fulfill the requirements for the specific job objectives;
c. It should be designed to equip the graduates with adequate communication skills (written and oral) and a sound knowledge of the social, political and economic environment in which the graduate shall live, work and make useful contribution as a citizen;
d. The curriculum must be in compliance with the NUC Benchmarks Minimum Academic Standards (BMAS);
e. The environment of the university must be suitable for the implementation of the curriculum;
f. The must adequate infrastructure such as lecture rooms, theatres, laboratories and workshops with the relevant equipment, etc to support the implementation of the curriculum;
g. There must be evidence of individual course content, textbooks, students' work, lecture notes and descriptive materials and annual external examiners' reports of final examinations for three years preceding the accreditation visit.

PRESENT DAY TRENDS ISSUES THAT AFFECTS CURRICULUM DEVELOPMENT

Scanning the present day industry and socio-economic landscape, the following are predominately the catch phrases or words trending:

a. Climate change,
b. Changing ecology,
c. Nanotechnology,
d. Increasing population,
e. High speed computers,
f. Fracking,
g. Global warming,
h. Job loss due to the influence of technology,
i. Deforestation,
j. Desertification,
k. Multidisciplinary approach and team work,
l. Sustainable development,
m. Equity,
n. Finite resources,
o. New sustainable energy sources, etc.

Is the current chemical engineering curriculum in use abreast with these new trends? A review shows that it is highly deficient.

SCOPE AND EMERGING CAREER OPTIONS IN CHEMICAL ENGINEERING

The chemical and related industries including pharmaceuticals and health, agriculture and food, phosphate and fertilizers, environment, oil and energy production, textile, iron and steel, bituminous, building materials, glass, surfactants, cosmetics and perfume, and electronics, etc; are today in a phase of rapid evolution. Engineering, Procurement and Construction (EPC) companies, which are contractors who complete projects from start to finish for their clients, routinely hire chemical engineers for design related jobs such as designing petrochemical, industrial plants, refineries, etc using various software tools. Electronics companies also hire chemical engineers for jobs such as material development, production and process control equipment design. In case you are good at number crunching and analytics, you may also join banks or analytics companies and be involved in their financial modeling and quantitative research work. A glance at the Chemical Industry identifies the following fields, some emerging (*https://books.google.com.ng/books?isbn=0309165806)*:

a. Upstream Oil and Gas, Energy

Many integrated oil companies consist of an upstream organization and a downstream organization. The former focuses on exploration and production and the latter refines crude petroleum into usable products (gasoline, lubricants, etc.). Within upstream, processes and departments are often separated by subsurface work and surface facility work. Generally, most Chemical Engineers upstream are found on the facility side, managing projects related to tanks, pumps, pipelines and separators. Besides, there are options in sub stream as well. As we attempt to tackle the current national energy challenges, oil and gas will continue to be a key factor in the equation.

b. Chemical Engineering Informatics

Chemical engineering informatics is the application of information technology to help engineers investigate new problems and organize, analyze and understand scientific data in the development of novel compounds, materials and processes. Chemical informatics is the application of information technology to chemistry and chemical engineering. Major aspects of chemical informatics are information acquisition, information management, information use, chemical computation and biopharmaceutical computation.

c. Genetic farming and consumer goods

Chemical engineers who work in the food industry can work in agriculture or in manufacturing. Those working in agriculture may study the genetic modification of fruits and vegetables and attempt to increase yields and make them more desirable and thus more profitable. The career may also include researching methods of making agriculture more environment friendly, trying new methods of processing waste and conserving soil and water. Farmers of the future will not only raise livestock and agricultural crops, they will also grow plants that have been genetically engineered to grow therapeutic proteins, pharmaceuticals and chemicals. All consumer products involve chemicals; consumer product development depends upon research to develop and improve a product – work that would fall to a chemical engineer. Such a career may involve improving such consumer goods as hygiene products, chemical cleaning products, and electronics.

d. Bio-technology

Chemical engineers working in biotechnology typically work in conjunction with researchers in molecular biology, biochemistry, genetics, embryology, and cell biology. A career in biotechnology may overlap with work in health care, crop production, agriculture, and the environment. A researcher may use chemical engineering to advance procedures in genetic testing and gene therapy. Chemical engineers in medicine may also work on engineering organisms and microorganisms to be used in applications, such as degrading wastes and converting chemicals into more useful ones.

e. Green Processes

The focus of all chemical engineers is to work sustainably. Corporations and consumers worldwide are increasingly embracing green technology and celebrating achievements in sustainable technology, water management and energy efficiency. Every organization would have a role of green process engineer who will develop environmentally benign chemical processes and products, select processes that minimize pollution, use less hazardous materials and develop alternative reactions. This will all need to be done while meeting emerging regulations and laws.

THE CHANGING WORK ENVIRONMENT: TRENDS TO INNOVATION

The emerging trend is toward open innovation: solutions to problems are externalized more, instead of having all the people inside a company available to work on every problem. There is more effort to reach out to the world to get answers. Companies are emerging around this idea, such as *Nine-Sigma* and *Intercentive.* These are places where problems can be posted for a bounty. Some 20 or 30 years ago, this might have been impossible to manage or handle. Now it is very easy. A web page can be accessible to almost everyone who might be interested in providing a solution.

Digitalization will drive a tremendous wave of innovation. Recent advancements in digital technology offer unprecedented levels of connectivity, granularity, and speed in accessing, processing, and analyzing huge amounts of data. Besides mobility, cloud and in-memory computing, the Internet of Things, machine learning and block-chain will start acting as game-changers in the chemical industry. All three trends are coming together to challenge existing strategies and create a perfect storm for the chemical industry. In addition, computer modeling is changing how chemical engineering and experimentation are thought about. They can quickly pinpoint how something is going to react, where it is going to react, and what issues the reaction presents. It is remarkable how this is changing.

Supply centers are shifting due to the challenges in the Niger-Delta Region of Nigeria, advent of shale gas in the U.S. or coal to olefins in China. Also, demand centers are shifting thanks to a rapidly growing middle class in the emerging countries. In addition, new market entrants drive shrinking lifecycles and rapid commoditization of products. Key raw materials are getting scarce. Regulatory requirements exponentially increase as the environmental impact of emissions and waste becomes more and more evident. Chemical companies are in the driver’s seat to respond to this, and some are already extending their ecosystems with the purpose to establish end-to-end concepts.

CHALLENGES FOR THE NEW GRADUATES

As markets change swiftly and as many other fields also move quickly, people who cannot go from one field to another become stranded in the company. They are experts, with expertise that is no longer needed. To perform well in the commercial process in a global environment, people have to understand how they fit into the whole value-creation process and how they connect to people around the world. Obviously, for top talent, international people skills and being able to lead diverse teams are going to be essential for personal growth and success. Broader language skills are also desirable but not requisite. When chemical engineers need all these high-value skills to perform well in a company, however, a lot is asked from them. Most at the top of the company now cannot provide this sort of capability, but it will be expected of the next generation. They will have to be better.

To address these challenges, institutions must be ready to answer these questions: What role can or should the polytechnics and universities play in selecting and developing students, or is it solely the role of industry to find the right people? Are engineers being prepared to use teams and external resources to supplement what they can do and what they are doing? Does the entire graduate-school process take students down a slightly different path that must be unlearned once they go into industry? Is industry making full use of the new skills and capabilities that new graduates have, and how well are chemical engineers being trained to understand how their craft will be practiced when they get into industry?

GREEN PROCESS ENGINEERING

Capentier (2016) pointed out that today’s industries are confronted by 4 challenges:

a. The globalization of the markets,
b. Acceleration of partnerships and innovation,
c. Fight against environmental destruction and
d. Non-sustainable behaviour of the today world production

Capentier (2016) proposed that the chemical and related industries militate for the evolution of chemical engineering in favour of a modern process engineering voluntarily concerned by sustainability **(**the green process engineering**).** New challenges and stakes arise because of the complex systems at the molecular scale**,** at the product scale and at the process scale. Therefore existing and the future processes will be progressively adapted to the principles of the “green chemistry” which involves a modern approach of chemical engineering that satisfies both the market requirements for specific nano and microscale end-use properties of competitive targeted green (sustainable) products, and the social and environmental constraints of sustainable industrial meso and macroscale production processes at the scales of the units and sites of production.

These last constraints require an integrated system approach of complex multidisciplinary, non-linear, non-equilibrium processes and transport phenomena occurring on the different time and length scales of the chemical supply chain. This means a good understanding of how phenomena at a smaller length-scale relates to properties and behaviour at a longer length-scale, from the molecular and active aggregates-scales up to the production-scales. This modern scientific multiscale approach of chemical engineering " the green approach of process engineering" that combines both market pull and technology push is strongly oriented on process intensification and on the couple green products/green processes "to produce much more and better in using much less", and to sustainably produce molecules and products responding to environmental and economic challenges, with the help of technical innovation and sustainable technologies for efficient mass and energy utilization and for a better quality of life. This modern green approach of chemical and process engineering will concern the eco-efficient "Factory of Future".

The success of this integrated multiscale approach for process innovation is mainly due to the considerable developments in the analytical scientific techniques coupled with image processing, in the powerful computational tools and capabilities (clusters, supercomputers, cloud computers, graphic processing units, numerical codes parallelization etc.) and in the development and application of descriptive models of steady state and dynamic behaviour of the objects at the scale of interest **(**Capentier, 2016).

QUALITIES OF A GOOD CHEMICAL ENGINEER

a. What will be the qualities of the future workforce for those operating in this increasingly global environment? This has to do with know-who and know-how.
b. To be a good engineer in the future will mean competing with an extraordinary number of good engineers around the world. To be differentiated from the rest, it will be important to have expertise, of course, but it will also be necessary to have the ability to go out and find things and to connect with others.
c. Willingness to be a team player is essential. This is where communication Skills comes in. There are only a few jobs and a few opportunities for people who are lone experts. In most industrial companies, value is created by multifunctional teams. The ability to perform and provide knowledge and expertise to such teams is critical.
d. Flexibility is another important quality for success as a chemical engineer of the future. One must be able to adapt to new areas and learn to integrate knowledge from other fields. That is manifested in terms of a low-growth environment. The narrow people, however, are not as fortunate.

THE PRESENT HND CHEMICAL ENGINEERING CURRICULUM

The success of any chemical engineering curriculum will depend on the realization of the following students outcomes (*maeweb.ucsd.edu/.../AE%20STUDENT%20OUTCOMES*):

a. An ability to apply knowledge of mathematics, science, and engineering,
b. An ability to design and conduct experiments, as well as to analyze and interpret data,
c. An ability to design a system, component, or process to meet desired needs within realistic constraints such as economic, environmental, social, political, ethical, health and safety, manufacturability, and sustainability,
d. An ability to function in multidisciplinary teams,
e. An ability to identify, formulate, and solve engineering problems,
f. An understanding of professional and ethical responsibility,
g. An ability to communicate effectively,
h. The broad education necessary to understand the impact of engineering solutions in global, economic, environmental, and societal context,
i. A recognition of the need for, and an ability to engage in life-long learning,
j. A knowledge of contemporary issues,
k. An ability to use the techniques, skills, and modern engineering tools necessary for engineering practice.

The present ND and HND curricula were reviewed as far back as 2002 and there is little hope that the above listed outcomes can be achieved with the present curriculum. The curriculum for the HND Chemical Engineering is presented in Table 1. A look at the content of the curricula shows that many aspects in the emerging areas in chemical engineering were left out. This shows that the curricula are grossly deficient. Of course, this can be traced to the lack of regular review of the chemical engineering curriculum. More importantly, the ICT components are scanty and in a very dynamic area as Information technology *vis-a-vis* the rapid changes taking place in the chemical industry, a review is needed at least every two years. Table 2 presents a list of new courses that can be considered for addition to the curriculum during review. In coming up with the list, the trends in chemical industry have been considered and the peculiar need of the country.

There is therefore the need to constantly review the content of each course to keep up with new developments in the industry. To ensure this is done, an implementable plan of action for regular value-added curriculum review should be put in place and followed religiously. Since the curriculum of the NBTE is just the minimum standard, there must be a forum for institutions to share what each has added to the curriculum. This type of cross fertilization will help those institutions that are weaker in this area.

Table 1: The Present HND Chemical Engineering Curriculum: 2002

CODE	**COURSE TITLE**	**CU**
MTH 311	Advanced Algebra	2.0
MTH 312	Advanced Calculus	2.0
CHE 301	Engineer in Society	2.0
CHE 303	Unit Operations 111	2.0
CHE 305	Chemical Engineering Laboratory 111	3.0
CHE 307	Heat Transfer 11	2.0
CHE 309	Chemical Engineering Thermodynamics 11	2.0
CHE 311	Mass Transfer 11	2.0
MTH 313	Engineering Statistics	2.0
GNS 301	Use of English 11	2.0
		21.0
MTH 321	Advanced Numerical Methods	2.0
COM 321	Computer Programming	3.0
GLT 301	Instrumentation	2.0
CHE 302	Unit Operations IV	2.0
CHE 304	Fluid Mechanics 11	2.0
CHE 306	Chemical Reaction Engineering 11	2.0
CHE 308	Chemical Engineering Laboratory IV	3.0
CHE 310	Polymer Science and Technology	2.0
CHE 312	Strength of Materials	2.0
GNS 302	Communication in English	2.0
		22.0
CHE 401	Process Design	3.0
CHE 403	Chemical Plant Economics Unit Operations V	2.0
CHE 405	Food Science & Technology Chemical Engineering Laboratory V	2.0
CHE 407	Chemical Engineering Analysis Project	2.0
CHE 409	Engineering Management	3.0
CHE 411		2.0
CHE 413	Elective 1	2.0
CHE 415	Pulp and Paper Technology Process Metallurgy	2.0
CHE 417		
CHE 419		
		22.0

CODE	COURSE TITLE	CU
CHE 402	Unit Operations VI	2.0
CHE 404	Equipment Design	2.0
CHE 406	Chemical Process Dynamics & Control	2.0
CHE 408	Health, Safety & Environment II	2.0
CHE 410	Chemical Engineering Entrepreneurship	2.0
CHE 412	Plant Services and Maintenance	2.0
CHE 414	Petroleum Refining and Petrochemical Technology	2.0
CHE 416	Project	2.0
	Elective II	
CHE 418	(i) Biochemical Engineering	
CHE 420	(ii) Gas Processing Technology	
CHE 422	(iii) Reservoir Engineering.	
		20.0

A look at the content of the curriculum shows that it is highly deficient. Key areas trending in the chemical Engineering field are not covered. A complete review of the curriculum is very necessary to correct these anomalies.

CHALLENGES FOR REVIEWING THE CHEMICAL ENGINEERING CURRICULUM

In reviewing the chemical engineering curriculum, it is important to note the following challenges:

a. The need to keep core chemical engineering knowledge;
b. The need to emphasize fundamentals: basis life-long learning;
c. The need to modernize the curriculum and add flexibility by emphasizing the following;
    i. Increase exposure molecular level,
    ii. Increase exposure to energy (alternative/renewable) sustainability issues,
    iii. Expose students to new process technology,
    iv. Introduce product design as complement of process design,
    v. Emphasize process operations, enterprise planning,
    vi. Increase link to other industrial sectors (e.g. pharmaceuticals and electronics).
d. The need to recognize that “bio-area” While important will not be dominant force in chemical engineering, emphasis should be on bio processing;
e. Environmental engineering increasingly important and requires chemical engineering (water use efficiency, pollution control, etc.);
f. Need closer interaction with industry; otherwise risk being irrelevant;
g. Need to provide excitement to recruit the very best young people to join chemical engineering.

Table 2: List of New courses to be considered when reviewing the Chemical Engineering Curriculum

S/NO	NEW COURSES TO BE INTRODUCED OR MODIFIED
1	Energy Technology and Management
2	Renewable Energy Engineering
3	Energy Engineering and Technology
4	Industrial Pollution Prevention
5	Industrial Pollution Control
6	Introduction to Biochemical Principles
7	Programming Using MATLAB
8	Biology for Engineers
9	Biochemical Process Design
10	Enzyme Engineering and Technology
11	Bioreactor Analysis
12	Bioreactor Design
13	Fertilizer Technology
14	Petroleum Refining Technology
15	Polymer Technology
16	Drug and Pharmaceutical Technology
17	Pulp and Paper Technology

S/NO	NEW COURSES TO BE INTRODUCED OR MODIFIED
18	Petrochemical Technology
19	Food Technology
20	Chemical Plant Safety and Occupational Hazard
21	Electrochemical Engineering
22	Computational Fluid Dynamics
23	Introduction to Statistical Thermodynamics
24	Equilibrium Stage Operations
25	Chemical Plant Utilities
26	Chemical Process Optimization
27	
28	
29	Basic Mechanical Engineering
30	Basic Electrical Engineering
31	Basic Electronics Engineering
32	Value Education
33	Basic Civil Engineering
34	Classical and Instrumental Methods of Analysis Laboratory
35	Computational Methods
36	Chemical Process Equipment Design & Drawing Laboratory
37	Chemical Reaction Engineering & Process Control Laboratory
38	Chemical Process Equipment Design & Drawing Laboratory
39	Process Modeling and Simulation
40	Sustainable Refinery and Bio-Refinery.
41	Process and Product Design
42	Biological Systems Engineering
43	Food Engineering Operations
44	Food and Pharmaceutical Separations
45	Environmental Engineering
46	Mineral Processing Technology
47	Bioprocess Engineering
48	
49	Autocad P&ID
50	Computer Aided Process Dynamic and Control
51	Project & Business Management
52	Communication

CHALLENGES OF CURRICULUM DEVELOPMENT

To carry out a thorough review of the curriculum, we must strive to overcome the following challenges:

a. The infusion of the ICT gene into the workers of the future who are the present students.
b. The lecturers cannot afford to be analogue and trying to raise digital graduates.
c. Be innovative on how to tackle the conservatives (If it is not in Levenspiel, it is bad CRE)
d. What to do with lecturers who do not have the knowledge to implement the revised curriculum: (*Reskilling and Upskilling?)*
e. Deciding on the best way for selecting the appropriate team for curriculum development

IMPORTANCE OF PEDAGOGY IN CURRICULUM IMPLEMENTATION

Despite the frenetic call for regular curriculum review for most programmes in Nigerian tertiary institutions, it is highly questionable to what extent classrooms have changed as little attention has been paid to teacher development. It is important that all institutions should strengthen their strategy and specific initiatives be designed to support the development of quality teaching. Therefore pedagogy can be viewed as a central enabler of the implementation of all academic curricula.

Pedagogy can be considered as the dynamic relationship between learning, teaching and culture. Teachers' actions in the classroom, in relation to learning and teaching, are underpinned by the ideas and values that they have about education. Pedagogy interacts with and draws together beliefs about learners and learning, teacher and teaching, and curriculum. It also includes consideration of the context in which learning and teaching takes place. Pedagogy is often shaped by a teacher's own experience of learning. For many this was simply knowledge being transmitted by their teacher. Their role as students was to receive this knowledge without question or other interaction (https://www.unesco.org.uk/wp-content/uploads */2017/06/pedagogy.pdf).*

Teachers' own beliefs about learning and teaching, teachers' experience of and expertise in alternative learning and teaching approaches and the alignment between curriculum, pedagogy and assessment expectations (leading, for example, to 'teaching to the test') are considered critical challenges in realizing education targets. In addition, learning and teaching space and resources, the quality of teacher education and ongoing support for teachers' professional learning; and teacher educators' understanding of different pedagogical approaches are also important considerations

To improve pedagogy which will ensure that the curriculum is well implemented, teachers need support in the following areas *(*https://www.unesco.org.uk/wp-content /uploads /2017/06/pedagogy.pdf)*:*

a. High quality pre-service and in-service teacher education. Teacher education and mentoring must be viewed as an on-going process, continuing throughout a teacher's career and helping teachers to understand and apply different pedagogical principles.
b. Alignment of curriculum, pedagogy and assessment. Examinations need to be designed to ensure a better fit of the assessment to the different types of knowledge and skills required for the 21st century globalised world.
c. Alignment of new pedagogical approaches sensitively with existing cultural practices. Educational stakeholders and community leaders should develop equal partnerships and joint visions to meet the educational targets.

IMPORTANCE OF INDUSTRIAL TRAINING FOR LECTURERS IN CURRICULUM IMPLEMENTATION

Teachers are seen to be vital in not only developing greater understanding about industry needs and expectations but also in the transfer of those workplace-related skills and competencies to their work with students. Concerns have been expressed about teachers' knowledge and abilities to make this link effective. This has resulted in a significant focus being placed on teacher professional development programmes that increase teachers' understanding about the world of work (Perry and Ball, 1998). Whilst there has been an increasing recognition of the value of programmes that create links or partnerships between education and industry, the main emphasis of these programmes has been on provision of work placements for students. There has been less emphasis placed on school-industry link programmes that focus on teacher professional development. Those programmes that do involve linking teachers and industry more often relate to curriculum materials production and seminar or liaison group discussions with industry personnel than they do on focusing on teachers actually working in industry. It is therefore paramount that the programme of lecturers spending quality time in the industry be reintroduced and followed religiously.

THE ROLE OF ADJUNCT POSITIONS IN THE SUCCESS OF CURRICULUM IMPLEMENTATION

Industry managers think that Nigerian tertiary institutions are not properly preparing students to enter the workforce. However, it is important that industry managers appreciate the enormity of the task of inculcating skills and competencies to students. It is easy to criticize the quality of the product of tertiary institutions but it is more productive if industry managers are more involved in improving the quality of the graduates. It will do industry managers a world of good if they can spend some quality time in tertiary institution to teach students real life experiences.

Many tertiary institutions abroad hire adjunct lecturers who are currently employed in the industry they are teaching about. This allows the institution to gain the insight of the person's practical knowledge and allows the professional to share their real-world experience with students because they want to, not because they have to *(https://www.cornerstoneondemand.com/rework/adjunct-solution-using-industry-knowledge-teach-must-have-skills-workplace).* With a strong understanding of how skills are being used in their industries on a practical level, adjunct lecturers are quickly becoming the norm in tertiary institutions abroad. The key to getting students the best education possible lies in striking the right balance between adjunct and full-time academic staff. Adjunct staff gives the student real-world examples which are critical ingredient of an industry compliant graduate.

It is therefore important that Nigerian tertiary institutions are encouraged to hire adjunct lecturers from critical industries to join regular staff for a period of time as this will go a long way in inculcating the appropriate real life skills and competences in students. Such symbiotic collaboration between industry and academia are key ingredients of a successful curriculum implementation.

LESSONS FROM UNESCO-NIGERIA TVE REVITALISATION PROJECT

During the years 1998 – 1999, NBTE, recognized that most Technical and Vocational Education (TVE) curricula have been operated for more than a decade without updating and were far out of synchrony with the world of work. Subsequently, a Project Document and Plan of Operation were signed on 15 December 2000 by UNESCO and the Federal Government of Nigeria for the “Support for Revitalisation of Technical and Vocational Education in Nigeria – Phase I”. The Phase I was instrumental to the first ever review of TVE curricula in the country, about 57No curricula were reviewed and updated to international standards, as well as integrating industry needs and current technologies. These curricula and their formats were adopted by other ECOWAS countries. In the Phase II of the Project, a total of 346 learning/training e-packages for thirteen programmes at the National Diploma level were produced in the areas where the curricula have been developed. At the same period, about 25 additional curricula were reviewed or developed in new and emerging fields, which are being adopted by West African countries through collaboration with the ECOWAS Commission. Furthermore, some 500 new Learning, Teaching and Training Materials (LTTMs) were developed for other subject areas. More importantly, the Project had a well-structured approach to curriculum review and development.

RECOMMENDATIONS

In order to come up with a workable and implementable chemical engineering curriculum, the following recommendations have been made:

a. Developing an action plan for the immediate review of not only the chemical engineering curriculum but the curricula of all engineering programmes in the polytechnics and universities. The last review of the chemical engineering curriculum was done in 2002.
b. Requesting Tertiary Education Trust Fund (TETFund) and other sponsors to support the development of curricula of new programmes identified in this study and the review of the old ones. This will ensure that they support Institutions whose programmes contribute to the growth of the economy.
c. To ensure that the revised curriculum is satisfactorily deployed, TETFund and other sponsors should support Instructional Materials development to assist the lecturers in the implementation of the new curricula. Textbook are scarce these days.
d. The lessons learnt in the curriculum development programme of the UNESCO-Nigeria Technical and Vocational Education (TVE) Project should be evaluated and those that can assist the curriculum development process implemented.
e. There is the need to identify the redundancies and gaps in the chemical engineering workplace and then deciding which new programmes to introduce and which old ones to phase out. This will require identifying knowledge gaps which need to be filled for an evidence-based policy and practice of curriculum development.
f. There is the need for a special team to identify the key areas and binding constraints to be addressed urgently to achieve major improvements in the quality of the curricula.
g. The need to develop an innovative approach to curriculum development by identifying the skills and knowledge required for the future chemical engineering industry.
h. Identifying key electives with the immediate regions in mind.
i. Ensuring that research and design activities are industry related and ICT tools are appropriately used.
j. An implementable timetable should be developed to ensure regular review of the curricula of the programmes of Nigerian tertiary institutions.
k. The need for proper funding, the provision of the required equipment and facilities to support the implementation of the curriculum and maintenance of infrastructure and policies that ensure a serene environment conducive for teaching and learning is available.
l. The upgrading of virtual library facilities to support the implementation of the curriculum.

CONCLUSION

This paper has analyzed the present chemical engineering curriculum used by Nigerian tertiary institutions and has found it to be deficient and therefore cannot be used to produce employable graduates for Nigerian industries in particular and the world of work in general. This is because a critical review of the curriculum has revealed that the curriculum is out of tune with the state of the present industry. The deficiency is traced to the lack of regular review and revision of the curriculum. It was noted that regular review is important in order for the curriculum to keep pace with the developments of the industry and the lack of it has led to the production of graduates with obsolete skills and competencies which make them work-place and industry non-compliant. It is further revealed that, in many cases, industry has to spend huge resources retraining new employees before they could be useful in the industry. The paper points out that the classrooms have not changed significantly as little attention has been paid to teacher development. It therefore calls for all institutions to strengthen their strategies and specific initiatives designed to support the development of quality teaching since pedagogy is a central enabler of the implementation of all academic curricula. Major recommendations proposed include the development of a curriculum review plan with set timelines, the selection of knowledgeable curriculum review teams and updating of the curricula of not only the chemical engineering curriculum but the curricula of all engineering programmes of tertiary institutions so that new areas and trends occurring in the industry and workplace are captured.

The paper further recommends the development of an appropriate action plan for the review and introduction of new courses that are in consonance with new trends in the chemical industry and proposes the development of curriculum-linked instructional materials to make the implementation of the curriculum easier for both the lecturers and the students. Other recommendations include the development of an implementable timetable to ensure regular review of the curricula of the programmes of Nigerian tertiary institutions and the reintroduction of the periodic industrial attachments for lecturers to keep them abreast with the new developments in the industry.

The paper finally recommends that Nigerian tertiary institutions consider the hiring of adjunct lecturers from critical industries to join regular staff for a period of time as this will go a long way in inculcating the appropriate real life skills and competences in students. Such symbiotic collaboration between industry and academia are key ingredients of a successful curriculum implementation.

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DEVELOPMENT OF Ni-Fe-Bi-O/γ-Al_2O_3 CATALYST FOR THE OXIDATIVE DEHYDROGENATION OF N-BUTANE

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ABSTRACT

Butadiene is an important petrochemical used for the production of polymers such as synthetic rubbers, plastics, automobile fuels etc. Ni-Bi-O/γ-Al_2O_3 catalyst was found to be effective for oxidative dehydrogenation of n-butane to yield butadiene. The effect of substituting Ni with Fe in Ni-Bi-O/γ-Al_2O_3 catalyst during oxidative dehydrogenation of n-butane to butadiene has been investigated in this work. The reaction was carried out over partially and fully substituted Ni-Bi-O/γ-Al_2O_3 catalyst to identify the best combination for an enhanced selectivity. The catalysts were synthesized and characterized using Brunauer-Emmett-Teller (BET) technique and x-ray diffraction (XRD). The metal oxides reducibility was determined by H_2-temperature programmed reduction (TPR) and NH_3/CO_2-temperature programmed desorption (CO_2/NH_3-TPD) was used in the determination of the acidic and basic sites in the catalysts, respectively. Ni substitution up to 50% with Fe improved mainly the butadiene selectivity by increasing the basic sites present in the catalyst which enhances the H_2-abstraction and adsorption of 1-butene intermediate.

Keywords: *oxidative dehydrogenation, n-butane, butadiene, metal oxides, catalysts.*

1. INTRODUCTION

Butadiene is an important intermediate used in petrochemical industries for the production of polymers such as synthetic rubbers, resins, plastics, automobile fuels and other important products. It is mainly obtained during production of ethylene and propylene obtained from naphtha cracker as a byproduct. The change of feedstock into lighter feed (ethane) limited the production of butadiene, and hence cannot satisfy the ever-increasing demand of this raw material. This necessitated the search for an on-purpose production method to complement the conventional production method (Li *et al*., 2018; White, 2007).

Butadiene is obtained in commercial quantities using the direct dehydrogenation method. Some of the direct dehydrogenation processes that have been commercialized include Catofin process that utilizes CrO_x-Al_2O_3 catalyst, Oleflex process which uses Pt/Sn/Al_2O_3 catalyst and Linde/BASF process that uses Pt-Sn/Zr catalyst. All these processes have major drawbacks such as high temperature operation and frequent catalyst regeneration due to coke deposition (Ajayi *et al*., 2013; Bender, 2014).

Oxidative dehydrogenation (ODH) of n-butane is a thermodynamically favorable process that can be conducted at relatively low temperatures. Moreover, the use of gas-phase oxygen reduces catalyst deactivation thereby extending the catalyst life. However, the major challenge of the ODH process is selectivity control mainly due to deep oxidation of n-butane to yield combustion products (carbon oxides) (Armenda *et al*., 1992). Efficient catalyst design is required to enhance the selectivity of the reaction at the desired product step (only dehydrogenation to butadiene).

The activity and selectivity of a catalyst for ODH depends on its acidic/basic properties and reduction-oxidation (redox) characteristics. The catalyst is reduced by losing its lattice oxygen which is used in the reduction reaction with water as the byproduct, it then adsorbs molecular oxygen from the feed to regain its earlier oxidation state via the Mars Van Krevelen mechanism. The interaction between the metal components of the catalysts (active species and support) plays an important role in the availability or otherwise of the lattice oxygen for the reaction. Several researchers have studied the ODH of n-butane over different catalysts such as zinc-iron oxide (Armenda *et al*., 1992), zinc-chromium-ferrite (Armendariz *et al*., 1994), VO_x/Al_2O_3 (Blasco and Nieto, 1997)' VO_x/SBA-15 (Liu *et al*., 2008), Modified activated carbon (Malaika et al., 2010), $Mg_3(VO_4)_2/MgO-ZrO_2$ (Lee *et al*., 2012), V_2O_5/MO-Al_2O_3 (M= Mg, Ca, Ba, Sr) (Xu et al., 2015). Most of these studies however focused mainly on production of butenes with little or no attention to butadiene formation.

Ni-based catalysts have been utilized for several reactions that require hydrocarbon activation because it is readily available, less expensive and has high activity for cleavage of C-C and C-H bonds. Nickel only catalysts suffer from fast deactivation and low selectivity towards oxidation reactions (Li *et al*., 2018). Jermy *et al*. (2015) reported that NiO when promoted with Bismuth oxide results in an improved performance;

this is due to the participation of Bi_2O_3 as oxygen mobile oxides which is critical in the formation of electrically active grain boundaries in the NiO. The redox system by the Ni species is better stabilized with bismuth oxide (which act as controlled supplier of O_2-) as hierarchical nanoparticle cohabitation hence making the system highly efficient. Modification of Ni with FeO_x is considered as an efficient way to improve the activity, selectivity and stability of the Ni-based catalysts. This is because Fe oxides have the ability to easily switch from Fe^{+2} to Fe^{+3} and vice versa in the redox cycle thereby making it suitable and selective for butadiene formation.

Present work focuses on investigating the effect of substituting Ni with Fe in Ni-Bi-O/γ-Al_2O_3 catalyst in the oxidative dehydrogenation of n-butane to yield butadiene. The reaction was carried out over partially and fully substituted catalyst to identify the best combination for an enhanced selectivity.

2. MATERIALS AND METHODS

2.1 Materials

2.1.2 Catalyst preparation

The supported Ni-Bi-O substituted with Fe catalysts were prepared using co-impregnation technique described elsewhere (Tanimu *et al.* 2017). The synthesized catalysts were abbreviated using letters shown in Table 1.

Table 1. Abbreviations of the synthesized catalysts

Catalyst abbreviation	Description
A	Ni-Bi-O/γ-Al_2O_3
B	75% Ni-25% Fe-Bi-O/γ-Al_2O_3
C	50% Ni-50% Fe-Bi-O/γ-Al_2O_3
D	25% Ni-75% Fe-Bi-O/γ-Al_2O_3
E	Fe-Bi-O/γ- Al_2O_3

2.2 Characterization of the catalysts

All the calcined catalysts were characterized using the following techniques: x-ray diffraction (XRD) was conducted with a desktop x-ray diffractometer Rigaku Miniflex II for phase analysis; Specific surface area and pore structure measurements (pore surface area, pore volume and pore diameter) were carried out using a Micrometrics ASAP 2020 equipment (Norcross GA). The pore surface area, pore volume and pore diameter were determined using BJH adsorption calculation method. For redox and acidic/basic properties of the catalysts, temperature programmed reduction (TPR) and temperature programmed desorption (TPD) were conducted in a chemisorption apparatus (BELCAT-A-200). NH_3 and CO_2 temperature programmed desorption (NH_3 and CO_2-TPD) were carried out using the same equipment (BELCAT system) for acidity and basicity measurements, respectively.

2.3 Catalytic evaluation

All the catalysts testing were done in a fixed bed reactor fully integrated with a continuous flow system (BELCAT). The details of the reactor has been reported previously (Tanimu *et al.* 2017). The reactor contains a quartz tubular reactor fixed into a stainless steel furnace passing through reactor furnace thermo well wall. 300 mg of catalyst was loaded into the reactor and calcined in-situ under air atmosphere. The reaction started under nitrogen atmosphere, feed contact time was fixed at 0.42 h.g/mol with total feed flow rate maintained at 31.2 ml/min. the catalysts were tested at 400 ^oC (O_2: n-butane ratio of 1, 2 and 4 mol/mol) and 450 ^oC, 500 ^oC (O_2: n-butane ratio of 2 mol/mol). Online GC system (Agilent, 7890N) was used for product analysis. Hydrocarbons and oxygenates were analyzed using FID and GC-Gas Pro capillary column; while gases were detected using TCD and shin carbon 80/100 mesh SS column (He carrier) and MS5A 60/80 mesh SS column (Ar carrier). The products were confirmed by comparing with standard samples. The feed (n-butane) conversion and products selectivity were determined using carbon balance.

3. RESULTS AND DISCUSSION

3.1. Characterization of the catalysts

3.1.2 Specific surface area and pore structure of the catalysts

The specific surface areas, pore volumes and the average pore diameters of all the synthesized catalysts are presented in Table 2. Ni substitution with Fe improves the surface area of the resulting catalysts while the pore volumes and the average pore diameters of all the catalysts exhibit slight changes.

Table 2: Physical properties of the catalysts

Catalysts	BET surface area [m^2/g]	Pore volume [cm^3/g]	Average diameter [nm]
A	136	0.38	9.6
B	134	0.37	9.6
C	169	0.42	8.8
D	149	0.38	9.1
E	169	0.45	9.4

3.1.3. X-ray diffraction

The x-ray diffraction (XRD) patterns of the catalysts are presented in Fig. 1. The substituted catalysts showed a varying degree of crystallinity due to the effect of FeO_x interaction with the Bi_2O_3 phases. Jermy *et al* (2015) reported that the characteristic peaks of the support appeared at $2\theta = 46°$ and 67° (JCPDS 10-425), which are present also in all the substituted catalysts. NiO and FeO_x peaks however were not identified in the XRD patterns of the catalysts due to their high dispersion and small crystal sizes. This was ealier confirmed by TEM measurement of the Ni-Bi-O supported catalyst (Jermy et al., 2015).

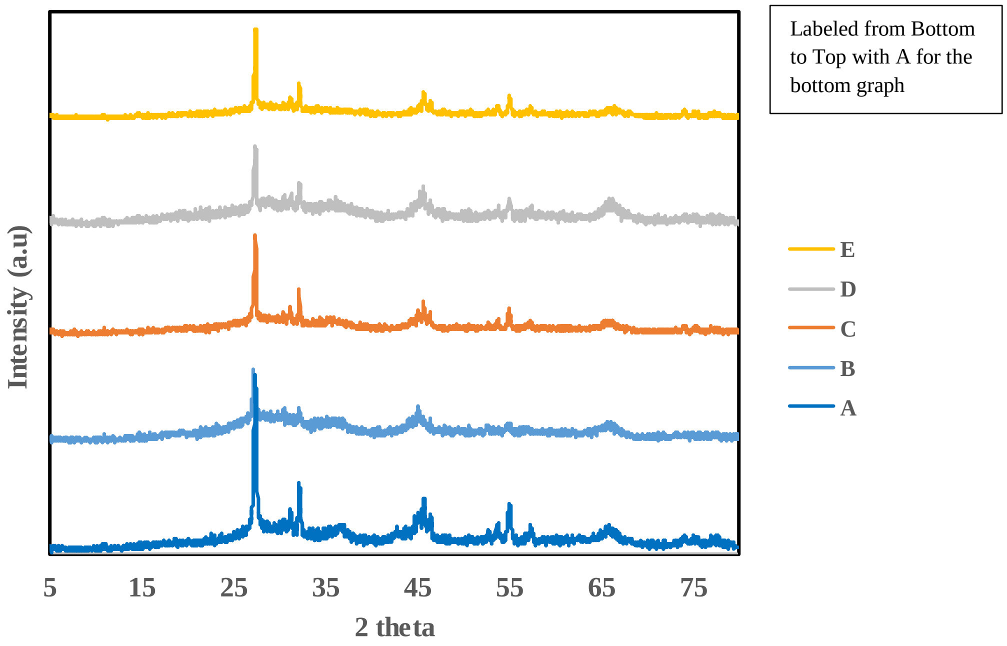

Fig. 1: X-ray diffraction patterns of the catalysts

3.1.4. Temperature programmed reduction (TPR)

Active species reducibility plays a great role in catalyst performance during ODH reaction. Therefore, H_2-TPR was used to measure the extent of reducibility of the substituted catalysts, and the H_2-TPR profile is shown in Fig. 2. TPR profiles are conveniently divided into three regions: low temperature region signifying easily reducible species, moderate temperature region and high temperature region signifying moderately reducible and highly difficult to reduce species respectively (Adamu et al., 2017; Tanimu et al., 2017). It can be concluded from Fig. 2 that Ni substitution by Fe increases the catalyst reducibility as seen from the decrease in the maximum reduction temperature peaks. This in turn will accelerate the redox cycle thereby improving the catalyst performance.

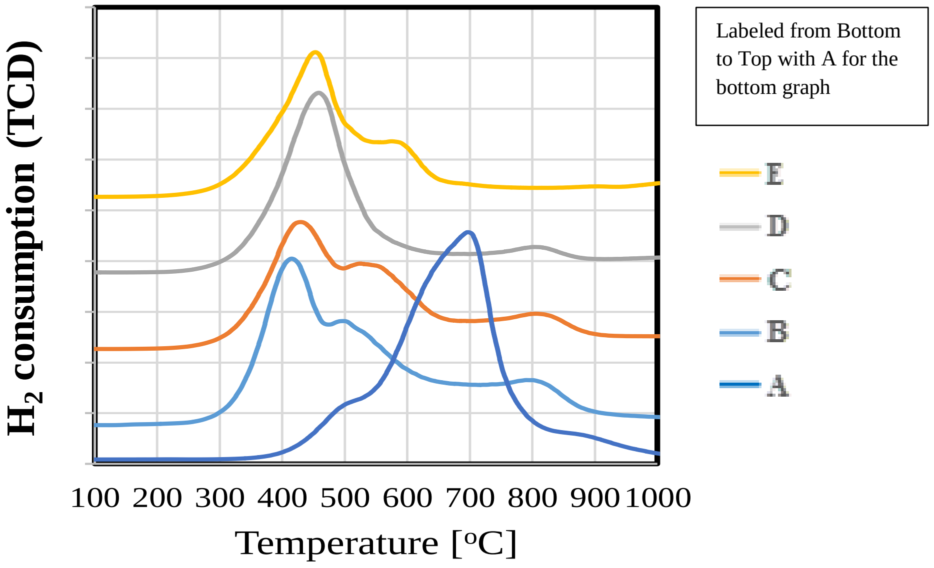

Fig. 2: TPR profile for the substituted catalyst

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3.1.5. Temperature programmed desorption (TPD)

NH_3/CO_2-TPD were used to measure the acidic and basic sites present in the catalysts respectively. The amount of NH_3/CO_2 desorbed in mmol/g for A, C and E catalysts are presented in Table 3. The TPD profiles of the catalysts are presented in Fig. 3 and the profiles are decomposed into three regions representing weak, moderate and strong acidic/basic sites for NH_3/CO_2 respectively. Moderate and strong basic sites are required for efficient hydrogen abstraction from n-butane and 1-butene. Weak acid sites are required for adsorption of intermediate butenes for subsequent conversion to butadiene (Jermy *et al.*, 2015; Tanimu, Asaoka, *et al.*, 2017). From Table 3, it can be observed that catalyst A has both acidic and basic sites while catalysts C and E have only weak and medium acidic sites with no strong acidic sites. Catalyst C has the highest strong basic sites which enabled an improved butadiene selectivity. Catalyst E has the least strong basic sites which resulted to its relatively low performance compared to the other catalysts.

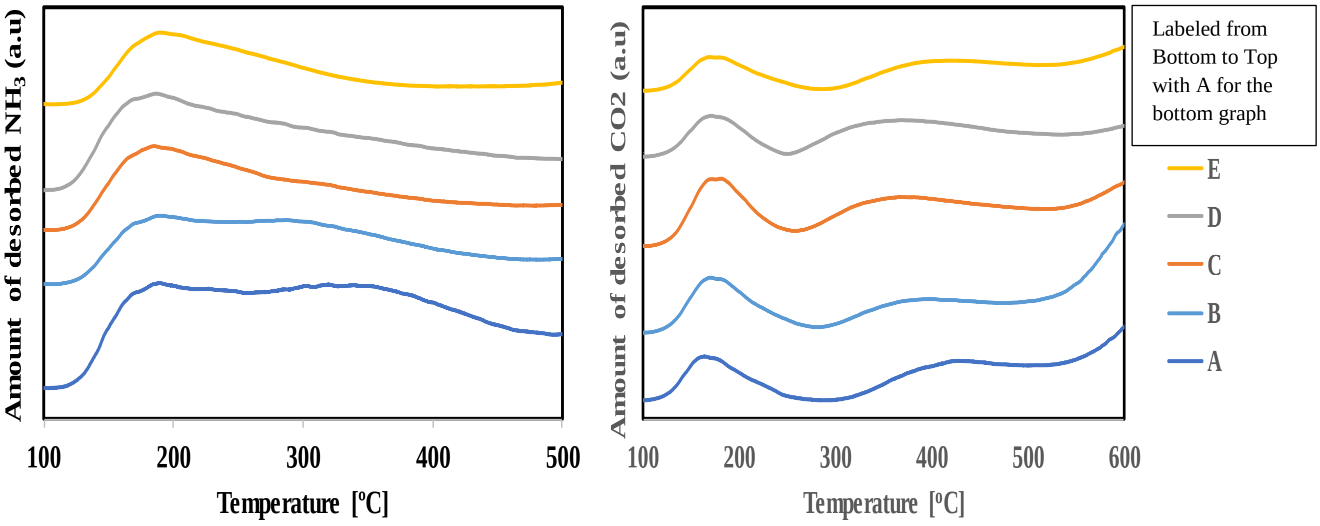

Fig. 3: NH_3 and CO_2-TPD profiles of the catalysts.

Table 3: Temperature programmed desorption analysis

Catalyst	NH_3-TPD Acid amount [mmol/g]				CO_2-TPD Base amount [mmol/g]			
	I	II	III	Total	I	II	III	Total
A	0.115	0.169	0.097	0.381	0.073	-	0.173	0.246
C	0.077	0.056	-	0.133	0.107	-	0.254	0.361
E	0.072	0.049	-	0.121	0.061	-	0.123	0.184

3.2. Catalytic evaluation

3.2.1. Effect of O_2/n-C_4H_{10} ratio

The effect of O_2/n-C_4H_{10} ratio (1.0, 2.0 and 4.0 mol/mol) on the catalytic performance (n-butane conversion, dehydrogenation and butadiene selectivities) of the substituted catalysts is shown in Fig. 4. It can be seen that the conversion at 400 °C for all catalysts A to E is greater at the ratio of 4.0 with the highest value at 50% Fe substitution indicating that n-butane conversion increases with increase in feed ratio. Dehydrogenation (DH) selectivity decreases continuously from A to E with increase in feed ratio while butadiene (BD) selectivity showed a different trend. For O_2/n-C_4H_{10} ratio = 4.0, BD selectivity showed an irregular pattern with an overall decrease from A to E. O_2/n-C_4H_{10} ratio = 1.0 and 2.0 showed the same pattern with the highest value at 50% Ni substitution. O_2/n-C_4H_{10} ratio = 2.0 was selected for further catalytic investigation because it gave a high overall yield (conversion X selectivity) compared to O_2/n-C_4H_{10} ratio = 4.0 that showed very high conversion with decreasing DH selectivity due to over reaction to deep oxidation products.

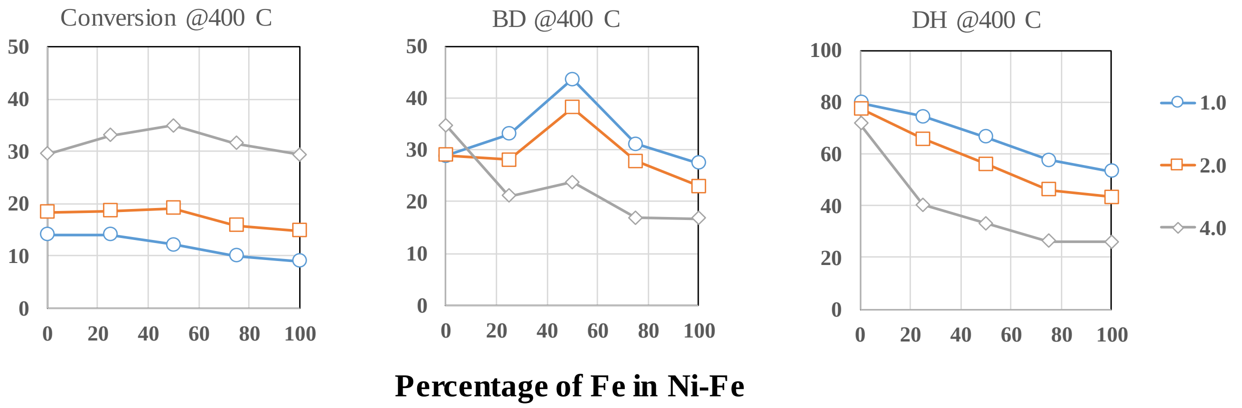

Fig. 4. Effect of O_2/n-C_4H_{10} ratio and Fe content of the catalysts on n-C_4H_{10} conversion, butadiene selectivity (BD) and dehydrogenation (DH) selectivity at 400 °C

3.2.2. Effect of reaction temperature

The effect of process temperature (400-500 °C) on the performance (n-butane conversion and BD selectivity) of the A to E catalysts during n-butane ODH is shown in Fig. 5. It can be observed that n-butane conversion increases with increase in reaction temperature due to C-C and C-H bonds activation at higher temperatures resulting to both cracking and dehydrogenation products. At 500 °C, the BD selectivity decreases continuously from A to E catalysts. At 450 °C and 400 °C, the selectivity increases up to 50% Ni substitution (catalyst C) and then decrease. The catalytic performance is higher at 450 °C than 400 °C.

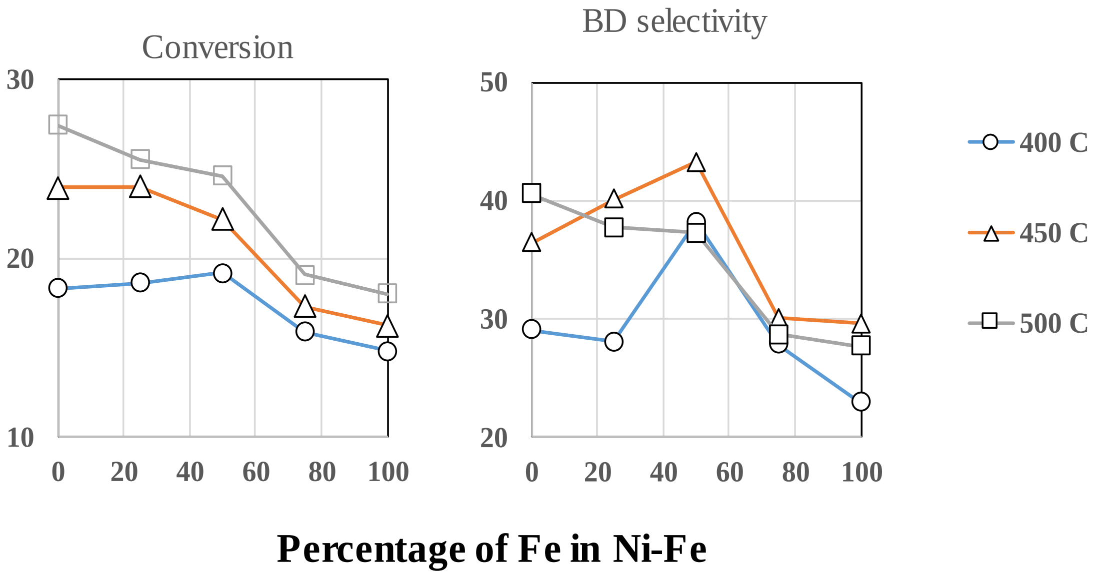

Fig. 5: Effect of reaction temperature on the performance (n-butane conversion and BD selectivity) of the catalysts

The catalytic performance of the various catalysts for oxidative dehydrogenation of n-butane to butadiene at 450 °C and O_2/n-C_4H_{10} = 2.0 is shown in Table 4. The products of the ODH reaction are mainly categorized into dehydrogenation products (butenes and butadiene), cracking products (C_1, C_2, $C_2^=$, C_3, $C_3^=$) and partial oxidation products which are represented in the reaction scheme presented in Fig. 6.

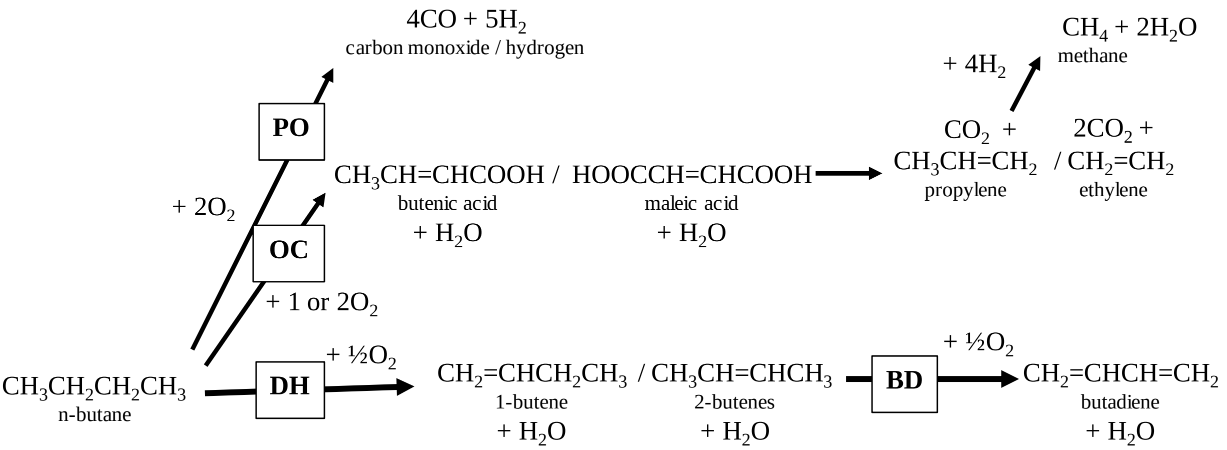

Fig. 6: ODH reaction scheme

From Table 4, it can be observed that the n-butane conversion decreases from catalysts A to E. A similar trend was also observed in the dehydrogenation selectivity. On the contrary, oxygenate and cracking products selectivity increases from A to E which means the combination of FeO_x only and Bi_2O_3 is not selective for dehydrogenation. Butadiene selectivity, butadiene yield and BD/DH all showed an improvement for partial Ni substitution up to 50%. This enhanced selectivity is mainly due to the moderation in redox property and acidic-basic sites of the catalyst resulting from the metal combination. This agrees with the reports by Koike *et al.* (2012) and Kim *et al.* (2017) which state that the improvement is dependent on the percentage of Fe substituting the Ni in the catalysts (Koike et al., 2012; Kim *et al.*, 2017) .

Table 4: Comparison of catalytic performance at 450 °C and O_2/n-C_4H_{10} =2.0

Catalyst	A	B	C	D	E
nC4 conversion	24.0	24.0	22.2	17.3	16.2
Selectivity					
DH	75.1	60.0	54.0	44.4	43.3
1-C4=	15.7	7.3	3.8	4.8	3.9
BD	36.4	40.1	43.2	30.1	29.6
OC	23.7	39.5	45.7	54.2	54.9
PO	1.2	0.5	0.3	1.3	1.8
BD/DH	48.5	66.8	80.1	67.7	68.3
BD yield	8.7	9.6	9.6	5.2	4.8

4. CONCLUSIONS

The synthesized catalysts (A to E) showed varying activities and selectivities to the desired butadiene product. Catalyst C which has 50% Ni substituted by Fe gave an improved butadiene yield mainly due to increased active sites reducibility and a combination of weak acidic sites and moderate/strong basic sites. These contributed to the abstraction of terminal H in both n-butane and butenes and also enhanced intermediate adsorption.

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DESIGN OF AMMOXIDATION PROCESS FOR THE PRODUCTION OF FIFTY THOUSAND TONS PER ANNUM OF ACRYLONITRILE

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ABSTRACT

Propylene, the raw material for the production of acrylonitrile is in production at olefins plant, Eleme, Nigeria in liquid form and fluid catalytic cracking Units of Nigerian Petroleum refineries in the form of propylene rich feed but acrylonitrile is yet to be produced in Nigeria. Varying its polymeric composition result in many other raw materials due to the reactivity and polar nature of acrylonitrile. Nigeria needs acrylonitrile for raw materials that cannot be produced from polyethylene and polypropylene e.g. acrylic fibre, adiponitrile, etc. If a petrochemical plant for production of acrylonitrile is set-up in Nigeria, Nigeria will begin to be earning the foreign exchange it would have used for importing these raw materials. Study reveals that ammoxidation process technology is the most suitable. With this technology, 3739.70 kg of acrylonitrile could be produced from 4,200 kg propylene, 1,700 kg of ammonia and 20,600.12 kg of air besides other useful secondary products such as water, carbon monoxide, carbon dioxide, Hydrogen cyanide, methyl cyanide, acetonitrile, acrolein (Propenal), ammonium sulphate and sulphuric acid. A pay-back period of 2 years and a rate of return of 50.48 % show that an acrylonitrile production process plant if well managed could be economically viable in Nigeria.

KEYWORDS*: Acrylonitrile; Propylene; Ammoxidation ; Pay-back period; Rate of Return on Investment; Petrochemical; Process-flow*

1.0. INTRODUCTION

1.1. Nigerian Economic Policy

The Nigerian government has initiated economic policies aimed at stimulating export of non-oil and value added products, thus encouraging private investors to establish petrochemical process plants (Louis *etal*., 2019; Ekpo, 2014).This could help Nigeria earn the foreign exchange it could have used for importing raw materials for local industries. Nigeria will no longer depend on exportation of crude petroleum alone but also on exportation of petrochemicals.

Acrylonitrile is an important petrochemical not yet produced in Nigeria. Although Olefins plant in Eleme in Rivers State, Nigeria is producing polymer grade ethylene and propylene for manufacture of polymer resins, Nigeria still need acrylonitrile for raw materials which cannot be produced from ethylene and propylene.

1.2. Reactivity of Acrylonitrile

The versatility in uses of acrylonitrile polymers result from the Polar nature and characteristic reactivity of acrylonitrile.

Mark *et al*. (1988); othmer (2007) stated that many raw materials can be produced by varying the polymeric compositions of acrylonitrile. The polar nature and reactivity of acrylonitrile is illustrated in figure 1.

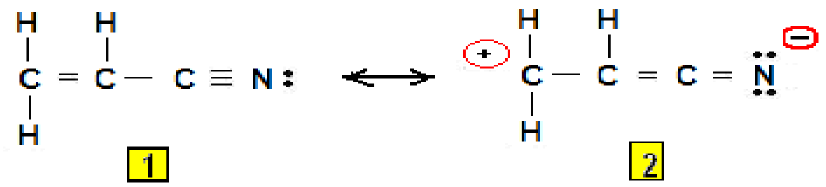

Fig. 1: Resonance Structure of Acrylonitrile
Source: Lewis (2019)

From this resonance structure, the (+) and (-) poles make acrylonitrile attract and be attracted to ions of other elements and compounds. The dots represent active interaction sites. The characteristic double and triple bonds are due to its unsaturation and show the high degree of reactivity of acrylonitrile molecules.

Acrylonitrile is a better source of higher quality plastics and resins than ethylene and propylene because of its versatile uses. Conversion of propylene to acrylonitrile helps improve the physical and chemical properties of the resultant polymer.

1.3. Acrylonitrile and its Uses

Acrylonitrile is a petrochemical in the sense that it is produced from the products of natural gas and petroleum refining e.g. propylene and ammonia. The major product (Acrylonitrile) is a colourless liquid with faint pungent odour of peach pits. Acrylonitrile with chemical formular C_3H_3N, molecular weight 53.064 is an unsaturated molecule having carbon-carbon double bond conjugated with a nitrile group

$$CH_2 = CH\text{-}C{\equiv}N{:}\longleftrightarrow CH_2{=}CH - \bar{C}{=}\underline{\ddot{N}}{:}\leftrightarrow \bar{C}H_2\text{-}CH = C{=}\underline{\overline{N}}{:}$$

Acrylonitrile undergoes a wide range of reactions at its two chemically active sites, the nitrile group and the carbon-carbon double bond. Acrylonitrile has versatile uses because of its high chemical reactivity. Acrylonitrile is used for the manufacture of acrylic fibre which is used for the manufacture of apparel e.g. sweaters, fleece wear and sportswear as well as home furnishings including carpets, upholstery and draperies. Moreover, co-polymerisation with other monomers improves the use of acrylonitrile.

Acrylonitrile is used for making Nitrile rubber. Nitrile rubber is used for the manufacture of rubber hoses, gaskets, seals and oil well components.

Acrylonitrile is used in the manufacture of Adiponitrile which is used in the manufacture of Nylon-6,6. Nylon 6,6 is an excellent fibre as well as an excellent plastic.

Adhesives, binders, antioxidants, medicines, dyes, artificial insulations, emulsifying agents, graphic arts, insecticides, leather, paper, plasticizers, soil modifying agents, solvents, surface coatings, textile treatments, viscosity modifiers, azeotrope distillations, artificial organs, lubricants, asphalt additives, water soluble polymers, hallow spheres, cross linking agents, and catalyst treatments are some of the areas of application of acrylonitrile polymers.

Acrylonitrile co-polymerises with styrene to produce Styrene Acrylonitrile (SAN) which is superior to polyethylene and polypropylene in the areas of toughness, rigidity, chemical and thermal resistance and hence have many commercial applications which implies a wider market.

Acrylonitrile – Butadiene-Styrence (ABS) Polymer can be produced by addition of an elastomeric component (Butadiene) within the SAN matrix. This help increase the impact resistance of the SAN polymer. The ABS has useful SAN properties of rigidity, resistance to chemicals and solvents while the elastomeric component contribute to its high impact resistance.

Polymer database (2015) stated that besides styrene acrylonitrile and acrylonitrile-butadiene – styrene, other co-polymers of Acrylonitrile are Acrylate-Styrene – Acrylonitrile (ASA); Acrylonitrile –Butadiene-Rubber (NBR); Acrylic fibers or Poly Acrylonitrile (PAN); Acrylonitrile Acrylate (ANA) and Methyl methacrylate

– Acrylonitrile – Butadiene – Styrene (MABS) also known as transparent ABS.

ASA has high resistance to ultraviolet radiation, heat, cracking and weathering. NBR is an important elastomer with Acrylonitrile content between 15 and 45 %. NBR grades with high Acrylonitrile content have better oil and abrasion resistance whereas NBR grades with low Acrylonitrile content have better low temperature flexibility and resilience. Acrylic fibers have acrylonitrile content of at least 85 %. Typical co-monomers are vinyl acetate and methyl acrylate. Both co-monomers improve flexibility, toughness and resilience of the rather brittle acrylonitrile fiber. Other synthesized acrylonitrile co-polymers which have found commercial uses are Acrylonitrile Acrylate (ANA) and Methyl methacrylate – Acrylonitrile – Butadiene – Styrene (MABS). Poly acrylonitrile copolymers (ABS; SAN; MABS; NBR and ABS blends) are important thermoplastics. They are produced on a large scale and sold under various trademarks. Important manufacturers include sabic; ineons; Lgchem; Trinseo and Basf to mention but a few.

Polymer database (2015) stated the following as applications of acrylonitrile polymer. ABS is a low cost engineering and commodity plastic that is easy to mold and fabricate. ABS is widely used for applications in kitchen and household appliances (ovens, washing machines, dryers, toaster, refrigerators, vacuum cleaners etc.). It is also extensively used for toys including Lego and Kre-O bricks. Other important industries for ABS include automotive, construction, and electronics. Due to its similar mechanical properties, ASA copolymers are used for similar applications as ABS. However, ASA has superior weathering resistance which makes it more suitable for outdoor applications than ABS. One of the most important markets for ASAs are automotive body parts such as mirror housings and radiator grills. ASA thermoplastics are also extensively used in many other industries including building and construction, appliance, electrical and electronics, and sports goods. Nitrile Butadiene Rubbers (NBR) are mainly used for disposable non-latex gloves and for elastomeric parts such as transmission belts, O-rings, gaskets, hoses, and oil seals whereas amine, carboxy, and epoxy functionalized butadiene-acrylonitrile rubbers are important tougheners for epoxy formulations such as coatings and adhesives. SAN is one of the most important acrylonitrile copolymers. Like ABS, it is widely used for applications in appliances (refrigerators, coffee machines, kitchen utensils, etc.). Other important applications include housings for scales, batteries, computers, and other consumer products. Acrylic fibers are sometimes used in the apparel industry for sweaters, socks, and tracksuits. Other important textiles made with acrylic fibers include blankets, area rugs, upholstery, luggage suitcases, awning, and outdoor furnitures.

1.4. Ammoxidation Process

Ammoxidation process involves the reaction of ammonia, air and propylene to produce acrylonitrile along with several secondary products such as hydrogen cyanide, water, carbondioxide, carbon monoxide, methyl cyanide, acetonitrile, acrolein (propenal) which is toxic, ammonium sulphate and sulphuric acid. Selectivity for acrylonitrile is enhanced by the help of a catalyst NS733A which contains iron, antimony and other compounds.

NS733A catalyst is active and effective resulting in 79.5 % propylene conversion. 80 % acrylonitrile selectivity requires less propylene and ammonia and forms less secondary products. This catalyst act as an initiator of the free radical polymerisation.

Following its generation, the initiating free radical adds to monomer units thereby growing the polymer chain. Polymer growth can be terminated by addition of a chain terminator e.g. water. One of the termination steps for polymer growth is the transfer of free radical to another molecule.

Carraher (2013) gave an example of a chain transfer process as the transfer of hydrogen atom at one end of the chain to a free radical end of another chain. Thus, hydrogen is often used as a chain transfer agent in free radical polymerisation. The polymer chain can be transferred to the initiator or to the monomer or to the chain transfer agent.

1.5. Importance of Locating the Acrylonitrile Production Process Plant in Nigeria

Having studied the principles of ammoxidation process for the production of acrylonitrile and the various uses of acrylonitrile and applications of its polymers, it is imperative that an acrylonitrile production process plant be set-up in Nigeria.

If this Acrylonitrile production process plant is set-up in Nigeria, Nigeria will begin to be earning the foreign exchange it would have used for importing raw materials produced from acrylonitrile. The low pay-back period and reasonable rate of return on investment and the high profitability rate expected are indications that the plant could be economically viable in Nigeria.

As is the usual practice, an Environmental Impact Assessment (EIA) will be carried out before the plant is established in Nigeria. The plant will help increase the Nigerian Gross Domestic Product (GDP) and the Nigerian National income per capital which is a good impact on the Nigerian economy. The setting up of the plant in Nigeria will create more employment hence eliminating social mal-adjustments which has been believed to be a breed of poverty.

This technical paper studies the petrochemical "acrylonitrile", its structure, uses, polymers and applications as well as the ammoxidation process development, mass balances, energy balances, costing and economic evaluation of the acrylonitrile production process.

2.0. MATERIALS AND METHODS

2.1. Materials

2.1.1. Process Equipment

The following process equipment were used for the design:
K-01 : Feed compressor; R-01 : Fluidised bed catalytic reactor; E-01 : Heat exchanger I; R-02:Quench neutralizer; RG-01: Refrigeration compressor I;AB-01: Absorber; D-01:Knockout drum; E-02: Heat exchanger II; C-01: separating column; E-03: Heat exchanger III: C-02: Acetonitrile recovery column; C-03: Hydrogen cyanide gas stripper or lights column; C-04: Acrylonitrile recovery column to mention just a few.

2.2. Methods

2.2.1. Process Description of Ammoxidation Process

The production process is divided into two sections:

a. The reaction and product recovery section
b. The separation and purification section

The block flow diagram shows the various process units followed by the process-flow diagram which shows the various process equipment used in the process. A process description of the process is made.

Ammoxidation process involves the reaction of ammonia, air and propylene to produce acrylonitrile and several secondary products.

The Ammoxidation process technology developed from the Sohio's technology is preferred to the Sohio's technology, the impont technology and oxidative methylation technology for the following reasons:

a. Steam generation is cheaper as the ammoxidation reaction is highly exothermic.

b. The fluidized bed reactor offers better process temperature control.

c. The use of appropriate differential pressures is useful for multiple effect heat recovery for effluent heat recovery system in absorption section to minimize solvent requirements and effluent treatment loading.

d. The major raw material for the ammoxidation process (propylene) is readily available in Nigeria from Olefins plant, Eleme Petrochemicals company and fluid catalytic cracking units of Nigerian petroleum refineries as Propylene Rich Feed (PRF). This lower cost of raw materials gives substantial advantage in the overall production cost.

e. Ammoxidation process technology involves the use of an improved catalyst (NS 733 A) which is more efficient and more selective than Sohio's catalyst 41 as it requires less propylene and Ammonia and forms less Hydrogen cyanide and acetonitrile. This increases the selectivity for acrylonitrile (the major product).

Selection of Materials for Construction

Stainless steel is chosen where corrosion is expected to constitute a major process hazard, otherwise carbon steel is used so as to minimize the cost.

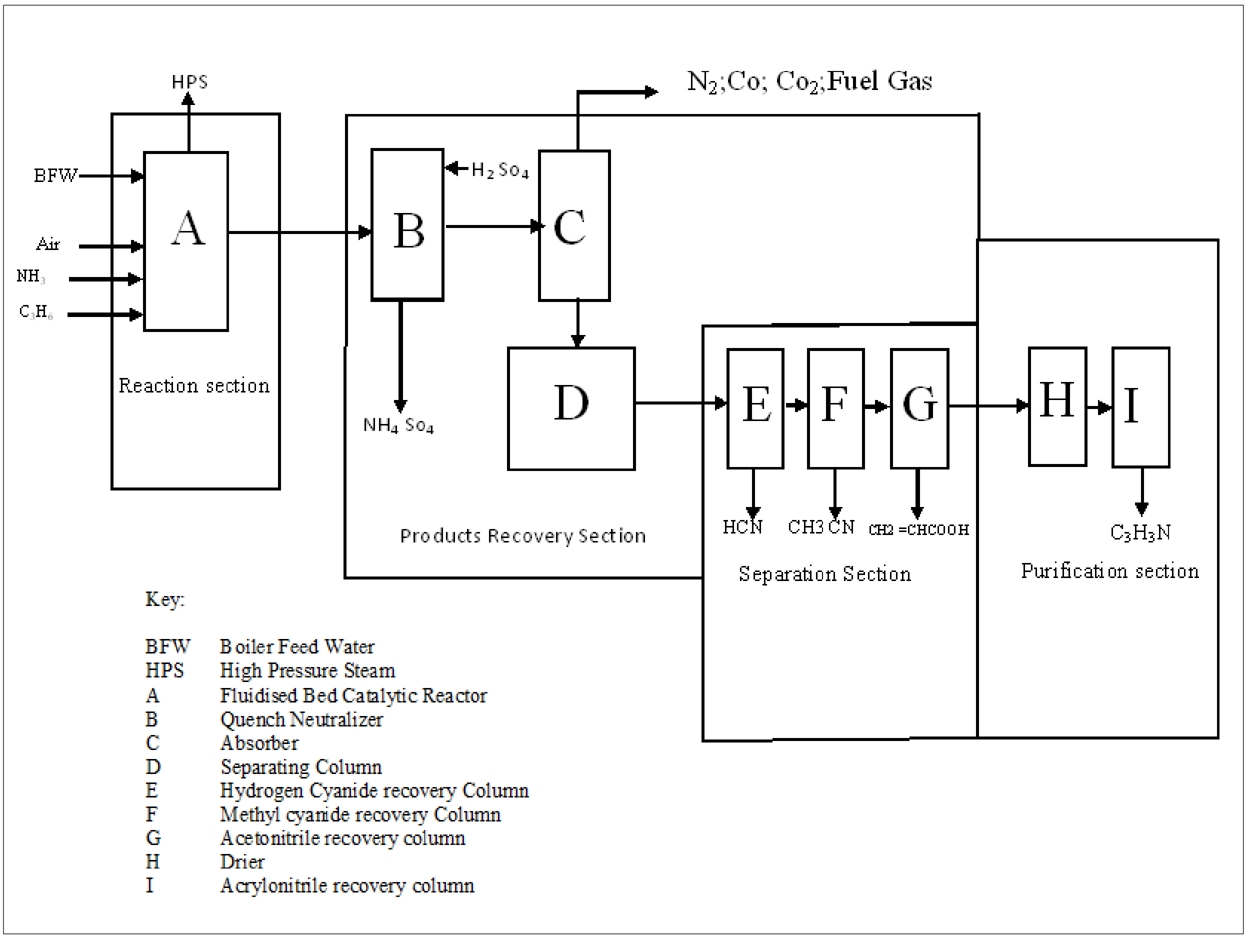

Fig. 2: Block Flow for Ammoxidation Process

2.2.1. The Reaction Section

Propylene, ammonia and air are fed into a fluidised bed catalytic reactor at controlled ratios of 90 % propylene and 100 % ammonia. Air, ammonia and propylene at 400 °C–510 °C and 49–196 kpa (0.5 – 2.0 gcm^{-2} G) contact NS733A solid catalyst in a single pass process with about 98 % conversion of propylene and uses about 1.1 kg propylene per kilogram of acrylonitrile produced.

The equation for the reaction is:

$$C_3H_6 + NH_3 + {}^{3}\!/_{2}\, O_2 \xrightarrow[\text{Catalyst}]{} C_3H_3N + 3H_2O \qquad (1)$$

That is

$$1 \text{ mole } C_3H_6 + 1 \text{ mole } NH_3 + 1.5 \text{ mole } O_2 \xrightarrow[\text{Catalyst}]{} 1 \text{ mole } CH_2 = CHCN + 3 \text{ moles } H_2O \qquad (2)$$

In the fluidised bed catalytic reactor exothermic reactions take place. The reactor temperature is controlled by removing the heat of reaction to generate high pressure steam which is used to drive the air compressor. The effluent gas at 440 °C contains acrylonitrile, hydrogen cyanide (0.1kg/kg of acrylonitrile) used in the manufacture of methyl methacrylate and some carbonyl compounds.

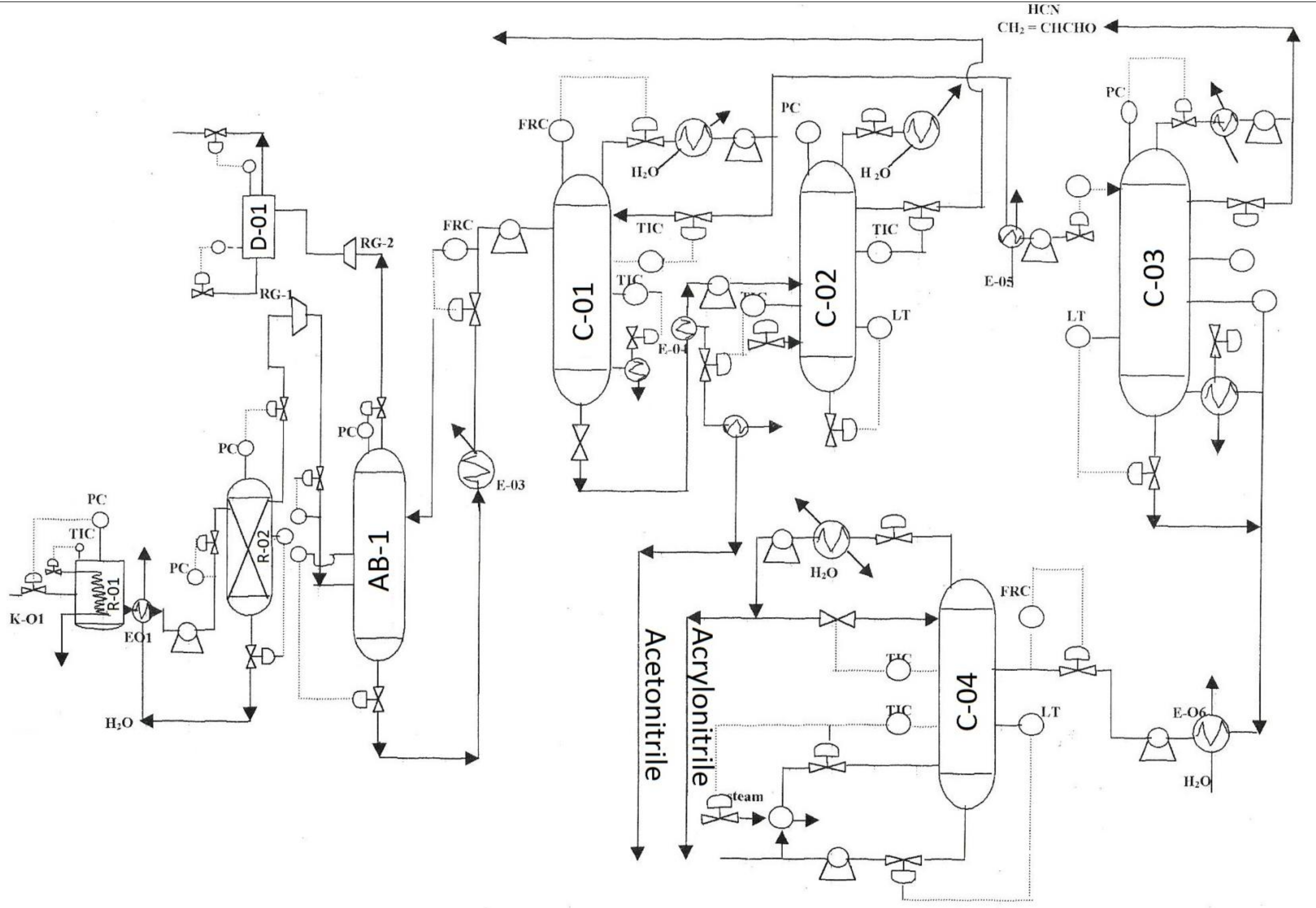

Fig. 3: Process flow for Ammoxidation process

2.2.1.2. The Products Recovery Section

After the heat of reaction has been removed and used for generating high pressure steam, the product overhead gas of the reactor enters into the quench neutralizer where the effluent is scrubbed to remove the catalyst fines and neutralise the small amount of residual ammonia with sulphuric acid.

By this, scrubbing and neutralising takes place in the quench neutraliser. The neutralisation of residual ammonia with sulphuric acid yields ammonium sulphate which is sent to intermediate storage. Ammonium sulphate is useful as fertilizer. The ammonia free gas is then absorbed in water and uncondensed residual propylene, propane, Nitrogen, carbon monoxide and carbon dioxide are vented or used as fuel. The crude acrylonitrile solution from the absorber is passed to a recovery column that produces crude acrylonitrile stream overhead which also contains hydrogen cyanide. This crude passes through a stripper which strips any gases.

2.2.1.3. The Separation Section

The recovery column bottoms are passed to a second recovery column to remove water and produce crude methyl cyanide mixture. The mixture is distilled to remove the by product hydrogen cyanide as gas or liquid and then separate all high boiling carbonyl impurities which are normally incinerated. The remaining is a mixture of acrylonitrile and acetonitrile which need to be separated. This mixture is separated by extractive distillation using water as solvent to generate heterogeneous azeotrope. The separated acetonitrile passes through a stripping column which produces pure crude acetonitrile. The dilute acetonitrile solution is concentrated to recover the acetonitrile.

2.2.1.4. The Purification Section

The acrylonitrile recovered from the separation process is passed though a drier or a dehydration column where it is dried. After being dehydrated, it is sent into the acrylonitrile return column where it is purified to yield high quality acrylonitrile.

2.3. Kinetic Models

Odian (2004) gave rate of polymerisation as:

$$\frac{-d[M]}{dt} = R_i + R_P \qquad (3)$$

Where [M] is the monomer concentration
R_i, the rate of initiation
R_p, the rate of propagation
and t, the time.
Neglecting Ri

$$\frac{-d[M]}{dt} = R_P \qquad (4)$$

$$Rp = kp\ [M^*]\ [M] \qquad (5)$$

Where [M*] is the total concentration of all chain radicals which increases initially and instantaneously reaches a constant, steady state value.

$$R_i = R_t = 2k_i\ [M^*]^2 \qquad (6)$$

$$[M^*] = (\frac{Ri}{Rt})^{1/2} \qquad (7)$$

Substituting this for [M*] in $R_p = k_p\ [M^*][M]$

Gives: $R_p = k_p\,[M]\ (\frac{R}{2ki})^{1/2}$ (8)

Wikipedia (2019) gave the following reaction rates:

$$R_i = {}^{d\ [M^*]}/_{dt} \qquad (9)$$

$= 2k_if\ [I]$ for chain initiation (10)

$Rp = kp\ [M^*][M]$ for chain propagation (11)

$R_t = \frac{-d[M*]}{dt} = 2k_t\ [M^*]^2$ for chain termination (12)

Where f is the efficiency of the initiator. K_i, K_p and K_t are rate constants for chain initiation, chain propagation and chain termination respectively.[I], [M] and [M*] is the concentration of initiator, monomer and the active growing chain respectively. Under Steady State approximation, [M*] remains constant. Hence $R_{i=}\ R_t$ [M*] is expressed in terms of other known species as

$$[M^*] = (\frac{K_i[I]]f}{K_t})^{1/2} \qquad (13)$$

R_p as a function of [I] and [M]

$$= K_p(\frac{fK_i}{K_t})^{1/2}\ [I]^{1/2}[M] \qquad (14)$$

Dynamic chain length without chain transfer:

$$V = \frac{R_p}{R_i} = \frac{K_p[M][M*]}{2fK_i[I]} \qquad (15)$$

$$V = \frac{K_p\ [M]}{2(fK_iK_t[I])^{1/2}} \qquad (16)$$

2.4. Design Equations

2.4.1. Mass Balance Equations

The overall reaction:

$$C_3H_6 + NH_3 + 1.5O_2 \xrightarrow[400 - 460^{\circ}C]{} CH_2{=}CHCN + 3H_20 \qquad (17)$$

The side reactions:

$C_3H_6 + 4.5O_2 \rightarrow 3C0_2 + 3H_20$ (18)

$C_3H_6 + 3O_2 \rightarrow 3C0 + 3H_20$ (19)

$C_3H_6 + 3NH_3 + 3O_2 \rightarrow 3HCN + 6H_20$ (20)

$C_3H_6 + 1.5NH_3 + 1.5O_2 \rightarrow 1.5CH_3CN + 3H_20$ (21)

$C_3H_6 + 1.5O_2 \rightarrow CH_2 = CHCOOH + H_20$ (22)

$C_3H_6 + O_2 \rightarrow CH_2 = CHCHO + H_20$ (23)

$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$ for quench neutralizer (24)

Basis: 100 kmol C_3H_6 taken as the basis

100 kmol C_3H_6 + 100 kmol NH_3 + 150 kmol O_2 → 100 kmol$CH_2 = CHCN$ +300 kmol H_2O (25)

Purity of propylene: 90 %; 10 % for inerts
Conversion: 98 %
Selectivity for Acrylonitrile : 80 % ; 20 % for secondary products
kmols × Molar mass = kg mass (26)

kg of side products = kg of acrylonitrile desired – kg of acrylonitrile produced (27)

Moles of reactant not reacted = moles of Inert + moles of unconverted (28)

Quantity of air supplied = % of oxygen in air × kmoles of oxygen (29)

Quantity of Nitrogen supplied = Quantity of air supplied – Quantity of oxygen supplied (30)

$$\text{kilomole} = \frac{\text{kg mass}}{\text{molar mass}} \qquad (31)$$

Reflux Ratio = $\frac{\text{Overhhead Product}}{\text{Distillate}}$ (32)

ScaleFactor:

$\frac{\text{Production Capacity (kghr}^{-1}\text{)}}{\text{Amount Produced for 335days plant operation from mass balance}}$ (33)

kg product = Amount produced from mass balance × scale factor × number of operational hours per day × number of days of operation per year. (34)

2.4.2. Energy Balance Equations

Work of Compression

$W_{isen} = \frac{RT_1}{\gamma_{AV}-1}\ [\ 1-\ (\frac{P_2}{P_1})^{\gamma_{AV}\,-\,1}/\gamma_{AV}\ ]$ (35)

$\gamma_{AV} = c_p/c_v$ (36)

Actual Work (W_s) = $\frac{\text{Work of Compression}}{\text{Efficiency}}$ (37)

$Cp_{mixture} = A + BT + CT^2 + DT^3$ (38)

Where A, B, C and D are characteristic constants for a particular compound and T, the temperature in Kelvin.

$Cp_{mean} = \frac{\int_{T_1}^{T_2} Cp_{mixture}\, dT}{T_2 - T_1}$ (39)

Volume flow rate = $\frac{\text{Mass flow rate}}{\text{Density}}$ (40)

$Q = MCp_{mean}\Delta T$ (41)

Heat removed to maintain reactor temperature:

$Q = \Delta H_{products} - \Delta H_{Feed} - \Delta H_{reaction}$ (42)

$Q = Ms\lambda s + MsCp\ \Delta T$ (43)

Where λs is the latent heat of vapourization.
Ms, the mass flow rate.

$\Delta Hrxn = \Delta H^0r + \Delta H_{products} - \Delta H_{reactants}$ (44)

Process heat added to maintain the required reactor temperature:

$Q_p = H_2 - H_1 - Q_s$ (45)

Where H_2 is enthalpy of outlet stream
H_1, the enthalpy of inlet stream

Q_s, heat generated in the system which is positive for exothermic processes and negative for endothermic processes.

2.4.3. Cost Analysis Equations

Coulson *etal*. (2009) gave the following costing and economic evaluation equations:

$PEC = a + bS^n \times MF$ (46)

a and b are cost constants obtained from Coulson and Richardson (2009) by taking the size of equipment needed including the shell mass and the rate of inflation over a period of time into consideration. MF is the materials factor ,S the characteristic size parameter and n the index characteristic of equipment size.

Cost in year A = Cost in year B × $\frac{\text{cost index in year A}}{\text{cost index in year B}}$ (47)

$PPC = PEC\ (1 + f_{1+} \text{..........} + f_9)$ (48)

$FC = PPC\ (1 + f_{10} + f_{11} + f_{12})$ (49)
$f_1, f_2 \text{..............} f_{12}$ are cost factors.

WC = 10 % of fixed capital (50)

Total Investment = Fixed Capital +
Working Capital (51)
Operating Cost = Fixed Cost + Variable Cost (52)

Total Cost = Total Investment +
Direct Production Cost (53)

Direct Production Cost = Operating Cost + 20 % of operating cost (54)

Total Cost =Total Investment + 20 % of operating cost + operating cost (55)

2.4.4. Economic Evaluation Equations

Sale of product (Acrylonitrile)
= Mass flow rate of product × Operating time per day × No. of days of operation per year × Cost per kilogram

(56)

Net Annual Profit = Sale of product (Acrylonitrile) – operating cost – Fixed capital (57)

Cash flow for any particular year = Cash in (profit) – Cash out (expenditure) (58)

Cash flow for any particular year = Net Annual Profit (after salaries,
Taxes, charges and fees has been paid as obtained from equation 57)
– [Cost of NYSC and student Industrial Training]
–[Sponsorship of organisations and voluntary donations cost] – [Agricultural development program cost] – [Cost of unforeseen procurement of materials and equipment that were not included in costing] – [Dividends paid to shareholders]
– [Cost of Unforeseen salaries and wages that were not included in costing] (59)

The cost of each item in equation (59) was estimated from expenditure of other companies that embark on similar programs although different companies spend their profit in different ways.

Rate of Return on Investment =

$$\frac{\text{Cumulative net cash flow}}{\text{Plant most Useful Life} \times \text{Total Investment}} \times \frac{100}{1} \quad (60)$$

Pay-back period =

$$\frac{\text{Total Investment}}{\text{Average Annual cash flow}} \quad (61)$$

Average Annual cash flow =

$$[\text{ cummulative net cash flow}] \big/ [\text{Plant most useful life}] \quad (62)$$

Therefore:
Pay-back period =

$$\frac{\text{Total Investment}}{[\text{cummulative net cash flow}] \big/ [\text{Plant most useful life}]} \quad (63)$$

Pay-back period is the inverse of Rate of Return on Investment, Hence:

Pay-back period =

$$\frac{1}{\text{Rate of Return on Investment}} \quad (64)$$

3.0. RESULTS AND DISCUSSION

3.1. The Plant Capacity

50,000 Tons per year of acrylonitrile = 50,000,000 kg per year of acrylonitrile. For 335 days per year and 24 hours per day, the production capacity

$$= \frac{50,000,000}{335 \times 24} = \frac{50,000,000}{8,040}$$

$= 6,218.90547263$ kghr^{-1}

$\approx 6,218.91$ kghr^{-1}

3.1.1. The Scale Factor

$$\text{The scale factor} = \frac{\text{ProductionCapacity}}{\text{Amount Produced}}$$

$$= \frac{6,218.91 \text{ kghr}-1}{3,759.8504} = 1.654$$

3.2 Raw Materials

Propylene: Taking a basis of 100 kmol C_3H_6
From equation (2):

100 kmoles propylene requires 100 kmoles Ammonia and 150 kmoles Oxygen, to produce 100 kmoles of acrylonitrile and 300 kmoles of water .

kg mass of Propylene = kmoles of propylene × Molecular mass of propylene
= 100 × 42 = 4200 kg of Propylene

Ammonia:
kg mass of ammonia = kmoles of ammonia × Molecular mass of ammonia
= 100 × 17 = 1700 kg of Ammonia

Air:
Majorly (21 %) O_2 and N_2 (78 %). Other components are negligible.

O_2 : kg mass of oxygen = kmoles of oxygen × molecular mass of oxygen
= 150 × 32 = 4800 kg of oxygen

N_2: Oxygen = 21% of air. Therefore quantity of theoretical air required = $\frac{150 \; kmols \; of O_2}{^{21}/_{100}}$
= 714.29 kmoles of air.

Quantity of Nitrogen required = 714.29 – 150
= 564.29 kmoles of Nitrogen.
Molar mass of air = 29
kmoles of air = $\frac{714.29}{29}$ = 24.6 kmoles of air.

kg mass of N_2 = kmoles of N_2 × Molecular mass of Nitrogen
= 564.29 × 28 = 15800.12 kg of N_2.

kilograms of air:
kg O_2+ kg N_2
= 4800 + 15800.12
=20,600.12 kg

3.3 Mass and Energy Balances

Mass and energy balances across each equipment in the ammoxidation process is shown on Table 4, appendix 1. The laws of conservation of mass and conservation of energy is being upheld as kg inlet = kg outlet and kJ inlet = kJ outlet.

3.4. Costing and Economic Evaluation

3.4.1. Costing

Table 1: Cost Analysis

Parameter	Amount (£)
Purchased Equipment Cost	8,330,19.94
Physical Plant Cost	2,849,267.796
Fixed Capital	4,131,438.304
Working Capital	4,131,43.8304
Total Investment	4,544,582.134
Fixed Cost	4,473,808.89472
Variable Cost	2,711,799.95152
Direct Production Cost	8,622,730.615488
Operation Cost	7,185,608.84624
Total Cost	13,167,312.749488

Naira could not be used due to instability of the Naira. However, conversion can be made based on the exchange rate at any time the conversion is made. The company is expected to be financially self sufficient as money obtained from sales of secondary products will be kept in the company bank account as company reserve.

3.4.2. Economic Evaluation

3.4.2.1. Cash Flows

Applying equations 58 and 59 for the plant most useful life of 15 years at 3 % rate of increase in Production capacity per annum, the following cash flows were obtained from equation 59:

$$\pounds\ 15{,}142{,}000.00 - \pounds\ 627{,}000.00 - \pounds\ 1{,}253{,}000.00 - \pounds\ 1{,}880{,}104.08899 - \pounds\ 2{,}507{,}000.00 - \pounds\ 3{,}133{,}000.00 - \pounds\ 3{,}759{,}000.00 = \pounds\ 1{,}982{,}895.911$$

Table 2: Cash Flow for each Year

Year	Cash Flow (£)
1	1,982,895.911
2	2,042,382.788
3	2,103,654.272
4	2,166,763.900
5	2,231,766.817
6	2,298,719.822
7	2,367,681.416
8	2,438,711.859
9	2,511,873.215
10	2,587,229.411
11	2,664,846.293
12	2,744,791.682
13	287,135.437
14	2,911,949.496
15	299,307.98
Cumulative	**344,093,98.3**

3.4.2.2. Rate of Return on Investment

The rate of return on investment is given in equation (60)

$$\text{ROI} = \frac{\text{Cummulative Net Cash flow}}{\text{Plant most useful life} \times \text{Total Investment}} \times \frac{100}{1}$$

$$= \frac{344{,}093{,}98.3}{15 \text{ x } 4{,}544{,}582.134} \times \frac{100}{1}$$

$$= \frac{344{,}093{,}98.3}{68{,}168{,}732.01} \times \frac{100}{1}$$

$$= 0.504768 \times 100$$

$$= 50.48\ \%$$

3.4.2.3. Pay – back Period

The Pay-back period is given in equations (61), (63) and (64).

$$\text{PBP} = \frac{\text{Total Investment}}{\text{Average Annual Cash Flow}}$$

The Average annual cash flow

$$= {[\text{cummulative net cash flow}]}\Big/{[\text{plant most useful life}]}$$

Therefore:

PBP =

$$\frac{\text{Total Ivestment}}{[cummulative\ net\ cash\ flow]\Big/[plant\ most\ useful\ life]}$$

$$= \frac{4{,}544{,}582.134}{[344{,}093{,}98.3]\Big/[15]}$$

$$= \frac{4{,}544{,}582.134}{2{,}293{,}959.886667}$$

$$= 1.98 \approx 2 \text{ years}$$

Also: $\text{Pay – back period} = \frac{1}{\text{ROI}}$

$$\frac{1}{[\frac{50.48}{100}]} = \frac{1}{0.5048}$$

$$\approx 2 \text{ years}$$

Table 3: Economic Analysis

Parameter	Value
Market Survey: Cost of 1kg of Acrylonitrile	£ 0.88
Sales of Product	£ 26, 459,125.44
Net Annual Profit	£ 15,142,078.28976
Rate of Return on Investment	50.48 %
Pay-back Period	2 years.

A product sales of £ 26, 459,125.44 is quite high. A net annual profit of £ 15,142,078.29 is extremely high. A pay – back period of 2 years show that the loan can be repaid within a short period of 2 years. A rate of return of 50.48 % is quite reasonable. This show that an acrylonitrile petrochemical process plant if well managed could be economically viable in Nigeria.

4 CONCLUSION

An acrylonitrile petrochemical production process plant of 50,000 Tons per annum capacity has been designed. Economic analysis show that the acrylonitrile petrochemical production process plant if well managed could be economically viable in Nigeria. Government and the private investors are therefore encouraged to invest in the acrylonitrile production project.

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6.0. APPENDIX 1: MASS AND ENERGY BALANCES

Table 4: Mass and Energy Balances

MATERIALS			**ENERGY**	
Component	**Inlet** $kghr^{-1}$	**Outlet** $kghr^{-1}$	**Inlet** $kJhr^{-1}$	**Outlet** $kJhr^{-1}$
Fluidised Bed Catalytic Reactor			**10,416,364 kJhr^{-1}**	**10,416,364 kJhr^{-1}**
Propylene	4200	495.60		
Ammonia	1700	200.61		
Air	20600.12	16366.52		
Water	-	4762.80		
Acrylonitrile	-	3739.70		
Carbon Monoxide	-	162.340		
Carbon Dioxide	-	255.10		
Hydrogen Cyanide	-	156.50		

MethylCyanide	-	118.85
Acetonitrile	-	139.147
Acrolein (Toxic)	-	108.23
Total	**26500.12**	**26500.40**

Quench Neutralizer **163360 kJhr^{1}** **163360 kJhr^{-1}**

Ammonia	578.2	-
Sulphuric acid	1445.5	-
Ammonium Sulphate	-	1854.286
Water	-	169.214
Total	**2,023.5**	**2,023.5**

Absorber **62,794,880.55kJhr^{-1}** **62,794,880.55 kJhr^{-1}**

Carbon Monoxide	162.34	162.34
Carbon dioxide	255.10	255.10
Nitrogen	15800.12	15800.12
Propylene	495.60	495.60
Oxygen	566.40	566.40
Water	9772.93 9772.93	
Hydrogen Cyanide	156.50	156.50
Acrolein	108.23	108.23
Acrylonitrile	3739.70	3739.70
Methyl Cyanide	118.85	118.85
Acetonitrile	139.147	139.147
Total	**31,309.93**	**31,309.93**

Separating Column **7,890,403.034 kJhr^{-1}** **7,890,403.034 kJhr^{-1}**

Acrylonitrile	3739.70	3739.70
Hydrogen Cyanide	156.50	156.50
Acrolein	108.23	108.23
Methyl Cyanide	118.85	118.85
Acetonitrile	139.147	139.147
Water	9772.93	9772.93
Total	**14,035.3613**	**14,035.3613**

Acetonitrile Recovery Column **179,956,567.8 kJhr^{-1}179,956,567.8 kJhr^{-1}**

Methyl Cyanide	116.98	116.98
Water	8771.355	8771.355
Acetonitrile	139.147	139.147
Total	**9,027.482**	**9,027.482**

Gas Stripper **318,766,153.9 kJhr^{-1} 318,766,153.9 kJhr^{-1}**

Acetonitrile	139.147 -	
Water	1001.575	1001.575
Hydrogen Cyanide	156.50	156.50
Acrolein	108.23	108.23
Acrylonitrile	3739.70	3739.70
Methyl Cyanide	1.87	1.87
Total	**5,007.8757**	**5,007.8757**

Acrylonitrile Product Recovery Column **3,828,961.417 kJhr^{-1} 3,828,961.417 kJhr^{-1}**

Hydrogen Cyanide	0.0374	0.0374
Acrolein	0.374	0.374
Acrylonitrile	3739.70	3739.70
Methyl Cyanide	1.87	1.87
Water	954.93	954.93
Total	**4,696.9124**	**4,696.9124**

Feed Compressor (K-01)	2,648,855.50 kJhr^{-1}
Refrigeration Compressor (RG-1)	12,940,644,313 kJhr^{-1}
Heat exchanger (E – O3)	7,976,095.22 kJhr^{-1}
Heat exchanger (E – O4)	4,003,292,780 kJhr^{-1}
Heat exchanger (E – O5)	1,710,980.38 kJhr^{-1}
Heat exchanger (E – O6)	255,354,144.50 kJhr^{-1}
Refrigeration Compressor (RG-2)	1.3313090×10^9 kJhr^{-1}

7.0. APPENDIX 2

Table 5: Nomenclature

SYMBOL	**DEFINITION**	**UNIT**
Cp	Specific heat capacity at constant Pressure	kJ/kg K
Cv	Specific heat capacity at constant Volume	kJ/kg K
CH_3CN	Methyl Cyanide	
$CH_2 = CHCOOH$	Acetonitrile	
$CH_2 = CHCN$	Acrylonitrile	
$CH_2 = CHCHO$	Acrolein or Propenal **(Toxic)**	
CO	Carbon monoxide	
CO_2	Carbon dioxide	
C_3H_6	Propylene	
HCN	Hydrogen Cyanide	
H_2O	Water	
H_2SO4	Sulphuric acid	
ΔH	Change in Enthalpy	kJ/kg K
Ms	Mass flow rate	kg/hr
NH_3	Ammonia	
NH_4SO_4	Ammonium Sulphate	
P_1	Initial Pressure	bars
P_2	Final Pressure	bars
Q	Quantity of heat	kJ/kg
ΔT	Change in Temperature	K
Wisen	Isentropic work	kJ/kg
Ws	Actual work	kJ/kg
£	Currency used in Britain	
γ_{av}	Ratio of Specific heat capacities	
λs	Latent heat of vaporisation	kJ/kg

ABBREVIATION	DEFINITION
ABS	Acrylonitrile – Butadiene – Styrene
ANA	Acrylonitrile Acrylate
ASA	Acrylate – Styrene – Acrylonitrile
DPC	Direct Production Cost
EIA	Environmental Impact Assesment
FC	Fixed Capital
FRC	Flow Recorder
GDP	Gross Domestic Product
LT	Level Transmitter
MABS	Methylmethacrylate-Acrylonitrile-Butadiene – Styrene
MF	Materials Factor
NAP	Net Annual Profit
NBR	Acrylonitrile – Butadiene – Rubber
NYSC	National Youth Service Corps
OPC	Operating Cost
PAN	Poly Acrylonitrile
PC	Pressure Controller
PEC	Purchased Equipment Cost
PFD	Process- Flow Diagram
PIC	Pressure Indicator
PPC	Physical Plant Cost
PRF	Propylene Rich Feed
ROI	Rate of Return on Investment
SAN	Styrene Acrylonitrile
TC	Total Cost
TI	Total Investment
TIC	Temperature Indicator
VC	Variable Cost
WC	Working Capital

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