

# FEDERAL UNIVERSITY OF AGRICULTURE ABEOKUTA NIGERIA



# CHEMISTRY, INDUSTRY AND DEVELOPMENT

by

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(Professor of Industrial Chemistry) Department of Chemistry College of Physical Sciences (COLPHYS) Federal University of Agriculture, Abeokuta, Nigeria

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#### FUNAAB INAUGURAL LECTURE Series No. 67

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# FUNAAB INAUGURAL LECTURE

# Series NO. 67

by

**Prof. Catherine Oluyemisi Eromosele** (Professor of Industrial Chemistry)

# The 67<sup>th</sup> Inaugural Lecture was delivered under the Chairmanship

of

The Vice-Chancellor

# **Professor Felix Kolawole Salako**

B. Agric (Soil Science), M.Sc (Soil Physics/Soil Conservation)(Nigeria), Ph.D (Ibadan), FSSN, FASN

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# CHEMISTRY, INDUSTRY AND DEVELOPMENT

The Vice-Chancellor,

Deputy Vice-Chancellors (Academic and Development),

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Dean, College of Physical Sciences,

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Head, Department of Chemistry and other Heads of Department,

Distinguished Members of the University Senate,

All Academic and Non-teaching Staff,

My Lords Spiritual and Temporal,

Members of my family,

All Special Guests and Friends of the University,

Distinguished ladies and gentlemen,

Gentlemen of the press, and

Great Funaabites.

## CHEMISTRY, INDUSTRY AND DEVELOPMENT

# **1.0 INTRODUCTION**

I am immensely grateful to Almighty God for the grace to stand before this distinguished audience today to deliver the 67<sup>th</sup> Inaugural Lecture of the Federal University of Agriculture, Abeokuta, Nigeria. I deeply appreciate the Vice-Chancellor, Professor Felix Kolawole Salako, for the institutional approval of and support for the Inaugural Lecture. This Inaugural Lecture is the fourth from the Department of Chemistry since creation out of the defunct Department of Chemical Sciences in 2001. The preceding three lectures from the Department of Chemistry, then under the defunct College of Natural Sciences, were delivered by Professors I. C. Eromosele, F. O. Bamiro and O. O. Odukova in this order. It is, therefore, a singular honour and pleasure for me that I deliver the first Inaugural Lecture from the College of Physical Sciences of which I had the privilege of being the pioneer Dean. To God be the Glory! This Inaugural Lecture gives me the opportunity to share with you the over thirty-five years of my experience in the academia, twenty years of which have been at the Federal University of Agriculture, Abeokuta. The title of my Inaugural Lecture is: Chemistry, Industry and Development and in the treatise I shall attempt to provide historical perspectives to Chemistry as a discipline which has had ubiquitous influence on civilization, prompting the question, what is not Chemistry? I shall then situate my modest research efforts as an Industrial Chemist, followed by matters arising and the imperatives of good governance.

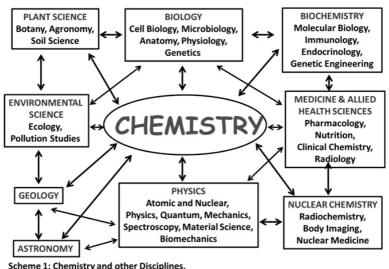
# 2.0 CHEMISTRY IN PERSPECTIVES

Chemistry is the study of matter, its chemical and physical properties, the chemical and physical changes it undergoes and the energy changes that accompany these processes. Matter means anything that has mass and occupies space (Caret et al.,1977). Thus, Chemistry is the central science underscored by its

connectivity to all other sciences and resultant inter-disciplines as shown in Scheme 1 (McMurry et al., 2010).

Historically, Chemistry and civilization are inextricably linked, animated by the inherent desire of man to seek to **identify**, **utilize** and **change** materials in the environment. The manifestations of these attributes can be gleaned from the fact that:

- Early potters found beautiful glazes to decorate and preserve their wares.
- Herdsmen, brewers and vintners used fermentation techniques to make cheese, beer and wine respectively.
- Housewives leached the lye from wood ash to make soap.
- Smiths learned to combine copper and tin to make bronze.
- Grafters learned to make glass.
- Leatherworkers tanned hides.



[Source: Fundamentals of General Organic and Biological Chemistry]

But in all these, Chemistry has its root in the works and beliefs of the alchemists, notably the Arabic alchemist Jabir ibn Hayyan, who recognized four Aristotelian elements namely, air, earth, fire and water in addition to two philosophical elements, sulphur and mercury. These were recognized as irreducible components of the universe (en. Wikipedia.org). He is believed to be the author of 22 scrolls which described methods of distillation, crystallization, sublimation and evaporation. A major draw back in the activities of the alchemists was the absence of a systematic naming of compounds and agreement on scientific methods for ease of reproducibility of experiments. In this regard, the English Chemist, Robert Boyle (1627 - 1691) is generally believed to be the founder of modern Chemistry in pioneering modern experimental scientific methods and by his law on the inverse relationship between absolute pressure and volume of gas at constant temperature within a closed system. A flurry of remarkable developments by Chemists followed which include:

- Discovery that air is a combination of gases, and isolation of oxygen and seven other discrete gases by Joseph Priestly, an English Chemist (1733 1804).
- Establishment of the law of Definite Proportions, stating that a chemical compound will always have its own characteristic ratio of elemental components by Joseph Proust, a French Chemist (1797–1804).
- The discovery of the law of conservation of mass by Antoine Lavoisier (1743 1794).
- Isolation of carbon dioxide by a Scottish Chemist, Joseph Black in 1754 which he called 'fixed air'.
- Isolation of hydrogen by the English Chemist, Henry Cavendish in1766 which he called 'inflammable air'.
- The enactment of modern atomic theory by the English meteorologist and Chemist, John Dalton in 1803, stating that all matter was composed of small indivisible particles

called atoms, and that, atoms of a given element possess unique characteristic and weight.

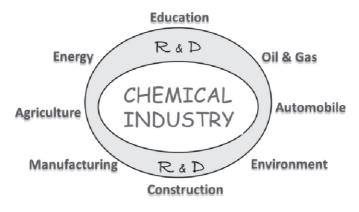
- The establishment of the structure of benzene by the German organic Chemist, Friedrich August Kekule, later known as Friedrich August Kekule von Stradonitz, in 1865 as consisting of a six-carbon ring with alternating single and double bonds, laying the foundation for the profound development of the chemical industry in Germany in later part of the 19<sup>th</sup> century.
- The construction of the Periodic Table by the Russian Chemist, Dimitri Mendeleev in 1871 in which all the known chemical elements were arranged in order of increasing atomic weight, now appropriately, atomic number, which then showed a recurring pattern or periodicity of properties within groups of elements. This singular act has been described as the most potent icons of science, in the embodiment of the most fundamental principles of Chemistry.

The foregoing developments were foundational for the evolution of the chemical industry, strengthened and sustained by research and development.

## 3. THE CHEMICAL INDUSTRY

Analogous to Chemistry as the central science, is the centrality of the Chemical Industry to all other industries as shown in Scheme 2.The Chemical Industry is concerned with conversion of raw materials to intermediates or products for domestic and industrial utilization and applications. It is concerned with making three categories of products, namely, inorganic chemicals, organic chemicals and specialized products (Ikoku, 1981). The unique features of the Chemical Industry in Scheme 2 are:

- Production of materials that are used by other industries to make products e.g., agricultural, industrial and consumer goods.
- Utilization of intermediates and by-products of synthetic processes of the Chemical Industry by other industries as raw materials.
- Utilization of waste products from other industries for production of useful chemicals and products, enhancing environmental waste management regime.



Scheme 2: Chemical Industry and Sectorial Connectivity

The pivotal role of the Chemical Industry in the development of countries may be appreciated by the economies of Singapore, Malaysia and South Korea.

# 3.1 SINGAPORE

Singapore, a country of less than six million in population, has no natural resources as feed stocks; no mineral deposits; no crude oil and no natural gas. Yet, Singapore is home to some of the world's largest chemical plants (American Institute Chem. Eng., 2013). In 2010, the Chemical Industry, including pharmaceuticals, produced the largest share (37%) of the country's manufacturing output with

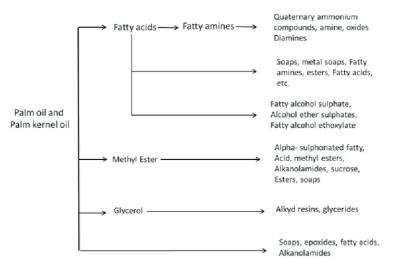
a value of USD81 billion. With four major refineries, Singapore, by 1970, had become one of the largest refining centers in the world with a capacity of more than 1.2 million barrels per day, producing products such as naphtha, gasoline, oils, paraffin, etc. Development of the down stream sector resulted in the conversion of naphtha to basic chemicals like ethylene, propylene, C4s, aromatics and a wide variety of higher-valued finished products. These include polymers – plastics, fibres, personal and home care products and additives. As at 2020, the GDP per capita of Singapore was USD59,797.8 (The World Bank, 2020)

#### 3.2 MALAYSIA

Malaysia, on the other hand, with a population of 32.36 million (2020) is richly endowed with natural resources including petroleum with a total reserve of 18.82 billion barrels oil equivalent and production rate of 600,000 barrels per day. The country has the 14<sup>th</sup> and 25<sup>th</sup> largest gas and oil reserves respectively in the world. Gas production as at 2005 was approximately 5.7 billion standard cubic feet per day (Razmahwata, 2005). Deploying a series of industrial strategies and policies, the Malaysian government has helped to kindle manufacturing industries and to attract foreign investments paving the way for a robust Chemical Industry. The country is the second largest exporter of liquefied natural gas (LNG) in the world. The plastics industries are well established underscored by ready availability of feed stock from the petrochemicals industry. The bulk of the plastics produced in the country are in their nonprimary forms - household goods, acrylic sheets, packaging, etc (Fov, 2015). But beyond petroleum, Malaysia is the 2<sup>nd</sup> largest producer of palm oil accounting for 39% of global production while export of the commodity accounts for 44%. In 2016, the country's total palm production was 2.1 million metric tons valued at USD39.3 billion.In 2018, for the period, January - August,

Malaysia's export of palm and palm oil-based products amounted to USD7.23 billion (Malaysian External Trade Stat., 2018). This is against the backdrop, as of 2014, of palm plantation which covered 5.3 million hectares of land producing 19.67 million tons of crude palm oil, mostly exported (Fov, 2015). There are more than 15 oleo-chemical plants producing raw materials for the manufacturing industries – food, pharmaceuticals, cosmetics, detergents, etc.

Furthermore, Malaysia was the world's 5<sup>th</sup> producer of natural rubber at 0.67 million tons in 2016. Through value-addition, Malaysia is an exporter of rubber products which include gloves, surgical gloves, latex thread, wires, cables and other electrical conductors, catheters, seal and gaskets, farm products, belting amounting to USD4.59 billion in 2017 (Malaysian Rubber Export Promotion Council). In all these, there is value-addition to the commodities - palm oil, palm kernel oil and natural rubberthrough sustained research and development programmes in much the same way as it is for petroleum crude. Thus, the Chemical industry of Malaysia is foremost in the world in the production and export of oleo-chemicals derivable from palm oil as shown in Scheme 3. The aftermath of all these is a productive populace engaged in economic activities with GDP per capita of USD 10,401 (2020); foreign exchange reserve of USD108 billion and un-employment (3.4%) (2018).



Scheme 3: Oleochemicals from Palm and Palm kernel oils

# 3.3 SOUTH KOREA

In the 1950s South Korea was one of the poorest countries in the world and the 3<sup>rd</sup> poorest in Asia having the highest population density on a very infertile land (Krueger, 2006). South Korea imports most of its raw materials and the development of the Chemical Industry proceeded in five phases. The first three phases, 1960 -1990s were government-led via economic development plans. But from the 1990s, it has been private-sector driven (Moon, 2011). Development in the petroleum sector is profoundly marked by heavy investment in research and development amounting to 5% of GDP in 2012 by the government. Overall, exports have played a major role in the economy. In 2009, shipments by South Korea's Chemical and petrochemical industries were valued at USD87.7 and USD56.2 billion respectively. The two sectors accounted for 8.9 and 5.7% of South Korea's total manufacturing shipments. In 2012, the country exported USD35.7 billion worth of petrochemicals representing 7.7% of the country's total exports (Moon, 2011). By 2017, South Korea was rated 5<sup>th</sup> exporter of chemicals in dollar terms. Thus, the country with a population of 51.78 million (2020) has GDP per capita of USD31,489.1 and the Chemical Industry now provides for domestic demands in pharmaceuticals, dyes, paints, etc, in addition to meeting export demands.

Mr. Chairman, from the foregoing accounts, it is pertinent and appropriate to examine the Chemical Industry in Nigeria.

# 3.4. NIGERIA

Nigeria has an estimated population of 206.14 million and GDP per capita of USD2,097.1(The World Bank, 2020) and is richly endowed with natural resources which include petroleum crude and 34 types of solid minerals. Indeed, solid mineral exploitation by the colonialist began in 1903 before the amalgamation and tin, coal, columbite, bauxite and lead were exported. Coal production reached 574,758 tons in 1960 (Punch Editorial, 2014). In 2016 and 2017 aggregate production of solid minerals were estimated at 43.94 and 38.53 million tons respectively (CBN: Annual Report, 2017). A notable mineral resource is bitumen spread across Edo, Ondo, Ogun and Lagos. Indeed, there is a huge deposit of bitumen in Irele Local Government Area of Ondo State at proven level of 42.74 billion metric tons, the largest in Africa and second largest in the world. Yet, mining of solid minerals contributes less than 1% of the country's GDP, meaning that the domestic industry on it is under developed with consequent importation of locally available resource. In regard to petroleum crude, Nigeria's aggregate production, including condensates and natural gas liquids averaged 1.72 million barrels per day or 627.80 million for the year 2017. The estimated average capacity utilization of the country's four refineries, in Warri, Port Harcourt and Kaduna, was 20.9% in 2017 (CBN: Annual Report, 2017) with aggregate production of petroleum products of 3.7 billion litres made up of premium motor spirit(PMS) (31.3%), automotive gas oil(AGO) (23.7%), fuel oil

(22.3%), dual purpose kerosene(DPK) (14.6%), fuel and losses (5.2%), liquefied petroleum gas(LPG) (2.8%) and asphalt (0.1%) [15]. But consumption of petroleum products for 2017 was estimated at 15.87 billion litres with PMS taking the lion share of 83.9%. It is noteworthy that ab initio, the installed refining capacity for the four refineries – two in Port Harcourt, one each in Warri and Kaduna – was 445,000 barrels per day of crude oil.

Unable to refine it over the years with operating capacity averaging 20.9%, over 300,000 barrels of crude oil per day is sold or swapped by Nigerian National Petroleum Corporation for importation of fuel to meet domestic demands of petroleum products (Sayne, et al., 2015). Accordingly, Nigeria's import bills on petrol were N1.97 trillion and N2.99 trillion in 2017 and 2018 respectively (National Bureau of Statistics). As seen in Section 3.1, Singapore with four refineries has the capacity to refine 1.2 million barrels of crude oil per day to meet both domestic and export demands. Proven crude oil reserve as at 2017 for Nigeria was 37.45 billion barrels and for gas, 5.6 trillion  $m^3$  (Eman, 2015; Annual Statistics Bull., OPEC, 2018). Total estimated volume of gas produced in 2016 was 1,147.20 million standard cubic ft (msct), out of which 86.3% was utilized and 13.7% flared (CBN: Annual Report, 2017). It must be noted however that the low flare of gas is a recent development because in 2006. United Nations Industrial Development Organization (UNIDO) reported that Nigeria flared 76% of its associated gas everyday, the highest in the world, the world average, at the time, being 4.8%. It is pertinent to note that associated gas is more than 90% methane and flaring releases carbon dioxide and other gases notably sulphur oxides, nitrogen oxides which pollute the environment and are inimical to health.Nigeria's export is dominated by crude oil, 79.1% in 2017, and it accounts for over 90% of her foreign exchange receipts. Development of the downstream sector of the petroleum industry

is very rudimentary and is reflected in its low contribution to the country's GDP as can be seen in Table 1.

| Sector                               | %     | Year |
|--------------------------------------|-------|------|
| Crude Petroleum and Natural gas      | 9.11  | 2017 |
| Plastics and Rubber Products         | 0.31  | 2018 |
| Oil Refining                         | 0.18  | 2018 |
| Chemical and Pharmaceutical Products | 0.22  | 2018 |
| Agriculture                          | 21.21 | 2016 |
|                                      | 18.0  | 2017 |
| Metal Ores                           | 0.01  | 2018 |

Table 1: Contributions to GDP by Selected Sectors

Source: National Bureau of Statistics, Nigeria, 2015.

Substantial amounts of the chemicals used for production in Nigeria are imported. In 2017, Nigeria's import trade by sector was dominated by the imports of 'mineral' products accounting for 33.6% of total value of imports. Products of the chemical and allied industries (9.1%), base metals and articles of base metals (6.1%). In monetary terms, imports of fuels and lubricants (N743.1 billion or 32.5%); industrial supplies (N 554.1 billion or 24.2%); PMS (N507.9 billion) (National Bureau of Statistics, 2015). The contribution of Agriculture to GDP is a sad reflection of low value-chain agro-based industrialization in Nigeria. Even for primary commodity, the case of palm oil export for the period 1964 – 2018 for Nigeria juxtaposed with that of Malaysia shows a progressive decline for the former and an astronomical progression for the latter as can be seen in Table 2.

| Year         | Nigeria    | Malaysia   |
|--------------|------------|------------|
| 1064         | 150        | 1.4.1      |
| 1964<br>1965 | 152<br>146 | 141<br>181 |
| 1974         | 31         | 1160       |
| 1997         | 20         | 7421       |
| 2000         | 9          | 10,579     |
| 2007         | 19         | 15040      |
| 2018         | 18         | 17,600     |

 Table 2: Palm Oil Export by Year for Nigeria and Malaysia

 Export (1000mt)

Source: United States Department of Agriculture

There is sense in which it can be argued that a robust chemical industry promotes productive economic activities of sectors to which it is linked and by extension the overall economic wellbeing of citizens, as can be seen in Table 3.

| Population<br>(Million) | GDP/Capita (USD)                    | Unemployment (%)  |
|-------------------------|-------------------------------------|---|
| 5.68                    | 59,797.8                            |   |
| 32.36                   | 10,401.7                            | (3.4)   |
| 51.78                   | 31,489.1                            |   |
| 206.14                  | 2,097.1                             |   |
|                         | (Million)<br>5.68<br>32.36<br>51.78 | (Million)         5.68         59,797.8           32.36         10,401.7           51.78         31,489.1 |

 Table 3:Population and GDP Per Capita for Selected Countries (2020)

Source: The World Bank, 2020.

It is instructive that Singapore with no natural resource endowment as mentioned in Section 3.1 has very high GDP per Capita, a reflection of virile productive activities in the Chemical Industry and in the manufacturing sector of the economy.Similarly, Malaysia has demonstrable capacity in conversion of natural resource endowments into products and intermediates of economic value via a virile Chemical Industry

and manufacturing. This is applicable to South Korea as well. In contradistinction, Nigeria's resource endowments are dormant, yet to find expression for national economic development. The Petroleum Industry bill which is intended to liberalize the petroleum industry in Nigeria has been oscillating between the National Assembly and the Nigerian President with no light from it, ostensibly because of oil politics. Thus, the Nigerian economy is deprived of the manifold benefits that could accrue from a robust petrochemical industry in promotion of multi-sector activities covering agriculture - fertilizers and irrigation; building industry electrical insulation, pipes and conduits, ceiling tiles, paints, bathroom facilities; household goods - mattresses, kitchen appliances, carpets; apparel – textiles, shoes, detergents; automotive industry – upholstery, tyres, synthetic rubbers, battery casing; pharmaceuticals- packaging, surgical appliances, cosmetics, etc.

It is evident that Nigeria's Chemical Industry is not developed and positioned to uplift productive economic activities. The country has not transcended the rhetoric of economic diversification by ignoring value-chain industrialization that should find expression in development of its abundant resource endowments.Rather the country is fixated in sales of crude oil in which she has no demonstrable capacity in the technology of the upstream operations, onshore and off-shore.

Mr. Chairman the maxim, **'necessity is the mother of invention'** has seen the deployment of basic principles of Chemistry to meet critical societal needs in what can be tersely described as Chemistry in Action.

# **3.5 CHEMISTRY IN ACTION: RESEARCH FOR DEVELOPMENT**

Research for development is the linchpin of every industrial enterprise and holds true for the Chemical Industry, providing innovative solutions to problems of society. There are a variety of utilitarian products in place through the instrumentality of Chemistry, in chemical reactions and chemical technologies (McMurry et al., 2010).

## 3.5.1 Anesthetics

Prior to 1846, dental surgery was carried out with patient fully conscious and at great pains. But in 1846, William Morton demonstrated ether-induced anesthesia for dental surgery. This was followed by the use of chloroform, popularized by Queen Victoria of England who, in 1853, gave birth to a child while anesthetized by chloroform.

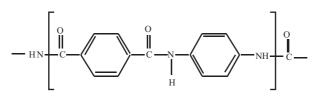
#### 3.5.2 Anti-coagulant

Aspirin – acetyl salicylic acid, possesses anti-coagulant properties, and in low doses can help prevent heart attack and minimize the damage caused by strokes. Its genesis is traceable to a combination of serendipity and scientific method by the isolation of salicin, a bitter-tasting yellow extract from willow bark. The latter, though effective, had an unpleasant taste and often caused stomach irritation and indigestion. A French Chemist, Charles Gerhardt, in 1853 was the first to synthesize the derivative, acetyl salicylic acid, the form in which it is currently marketed.

## 3.5.3 Bullet-Proof Vest

The bullet-proof vest is a common wear that protects police operatives, soldiers, fire fighters, bicycle riders and many others engaged in hazardous activities. The vest is filled with fibres made of 'kevlar', an aramide synthesized from terephthalic acid and 1,4diamino benzene i.e.,

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Stephaine L. Kivolek, a Chemist at Dupont developed the polymer which is five times stronger than steel, almost half as dense as fiberglass, highly resistant to damage by chemicals, dimensionally-stable, very difficult to cut or break, a poor electrical conductor and is flame-resistant. If ignited, it selfextinguishes. Kevlar derives its strength from the way the molecules are arranged and held together by hydrogen bonds into a network polymer.

# 3.5.4 Oxygen Mask

As a routine in airlines, passengers are taken through a protocol of safety procedures in case of emergencies. A notable one is in the event of loss of pressure in the air cabin, and the use of oxygen masks. The oxygen is generated in the circumstance by the simple reaction of sodium chlorate when heated i.e.,

$$2NaClO_3 \rightarrow 2NaCl + 3O_2 \uparrow$$

## 3.5.5 Infant Jaundice

Infant jaundice is a condition in which the skin and the whites of the eyes appear yellow because of high levels of the bile pigment, bilirubin in the blood. Bilirubin is a breakdown product of the oxygen-carrying blood protein, hemoglobin. Accumulation of bilirubin in the body can cause brain damage and death. The immature liver of the baby cannot remove the bilirubin. An observant nurse in England noticed that when jaundiced babies were exposed to sunlight, the jaundice faded. Research based on her observation showed that the UV light changed the bilirubin

into another substance that can be excreted by the baby. This marked the beginning of the use of UV light for treatment of jaundiced newborns.

# 3.5.6 Air Bag

Modern cars are equipped with air bags which can inflate very rapidly in approximately 40 milliseconds i.e., in less than 0.05 seconds then deflate to provide a steady deceleration cushioning the occupants from impact. The inflation of the bag is made possible by the reaction of sodium azide i.e.,

$$2\mathrm{NaN}_{3}(\mathrm{s}) \rightarrow 2\mathrm{Na}(\mathrm{s}) + 3\mathrm{N}_{2}(\mathrm{g}) \uparrow$$

When detonated by the mechanical energy produced by an electric current, sodium azide decomposes to liberate nitrogen gas which inflates the air bag.

## 3.5.7 Breathalyzer

Beyond certain threshold (0.05-0.15%), alcohol in blood can lead to loss of co-ordination, and driving under such circumstance can be dangerous. A suspect is required to exhale into a solution, a yellow-orange acidic solution of dichromate ion. The alcohol reduces the chromium in the dichromate ion from +6 to +3 oxidation states, the latter being green in colour. The intensity of the green colour is measured, and is proportional to the amount of ethanol that was oxidized i.e.,

$$3CH_{3}CH_{2}OH + 2CrO_{7}^{2} + 16H^{+} \rightarrow 3CH_{3}COOH + 4Cr^{3+} + 11H_{2}O$$
  
Oxidized reduced  
(green)

## 3.5.8 Defense Mechanism

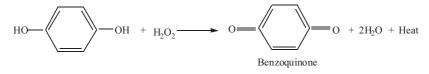
The Chemistry in natural defense mechanism is demonstrated by the Bombardier Beetle.

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Plate 1: Bombardier Beetle Source: Google image

This insect defends itself by spraying boiling hot (*ca*  $100^{\circ}$ C) benzoquinone (a ketone) at a predator. The benzoquinone is produced in a fraction of a second by a redox reaction between dihydroxybenzene and hydrogen peroxide dispensed from two different compartments in the body of the insect. The reaction is exothermic providing the vaporization of benzoquinone i.e.,



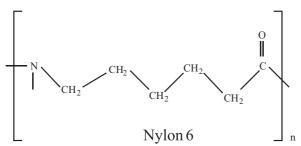
## 4.0 MYRESEARCH CONTRIBUTIONS

The Vice-Chancellor Sir, over the years I have been active in two broad areas of research. First, the physical, chemical and thermal properties of industrial polymers. Second, on raw materials

research and development. These areas are consistent with my training in industrial chemistry with specialization in polymer science. Studies on physico-chemical and thermal properties have been on high tonnage synthetic industrial polymers, nylon6 and polyvinylchloride and on natural polymers namely cellulose fibres and starch. In both cases the interest has been to establish conditions under which their physico-chemical, thermal and mechanical properties can be improved upon for greater and more effective utilization as industrial materials.

#### 4.1 NYLON 6

On nylon 6, I have examined the anisotropy of the dynamic modulus at low frequency in drawn films of the polymer in directions parallel and perpendicular to the draw direction. The anisotropy was of interest because when a polymer is oriented such as by drawing, its macroscopic properties exhibit directional dependence. Previous studies on the directional variation of Young's modulus of polyamides were limited to nylon 66 films. In this study, nylon 6 films were used. Nylon 6 is a step-growth polymer having an hexano-6-lactam repeat unit i.e.,



Nylon 6 is one of the most widely used of all commercial nylons, semi –crystalline and highly valued for its strength, elasticity and durability. As an engineering material, it finds application as gears, bearings, bushes and valve seats. As films, it is used widely in the food industry primarily for packaging. And as fibres, it has a range

of applications which include knitted clothing, parachutes, tooth brush, cordage, etc. Experimentation involved the use of Rheovibron viscoelastometer for measurement of storage modulus, E' and the dynamic loss tangent tan  $\delta$  at specific frequencies (3.5, 11, 35 and 110 hz) of strain input. Samples were prepared by a particular technique to obtain a range of differently oriented samples whose degrees of orientation were determined from their birefringence. The mechanical properties of films are improved when they are drawn. Drawing allows the intermolecular forces to maximize the ordered cohesive aggregates of polymer chains and causes them to become oriented along the direction of applied stress. In this study nylon 6 samples were drawn at different draw ratios, 2:1, 2.5:1 and 3:1 as shown in Fig 1.

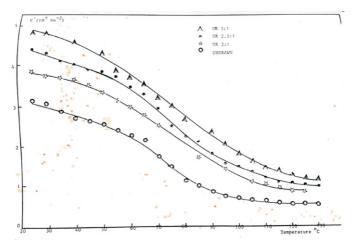


Figure 1: Storage modulus versus temperature as a function of Draw Ratio

Furthermore, I have examined the effects of annealing on nylon 6 films using steam. Annealing as a heat treatment process removes strains and stresses built in a material during formation and fabricating operations. For a polymer, annealing increases its

density and improves heat resistance and dimensional stability when exposed to elevated temperatures.

| Sample<br>Condition | Annealing temperature<br>(°C) | density<br>(g/cm <sup>3</sup> ) | Crystallinity<br>(%) |  |
|---------------------|-------------------------------|---------------------------------|----------------------|--|
| Fixed length        | 110                           | 1.143                           | 35.59                |  |
|                     | 120                           | 1.147                           | 38.77                |  |
|                     | 130                           | 1.152                           | 42.71                |  |
| Relaxed state       | 110                           | 1.1405                          | 33.59                |  |
|                     | 120                           | 1.140                           | 33.19                |  |
|                     | 130                           | 1.143                           | 35.59                |  |

Table 4: Data for steam-setting nylon 6 at fixed length and in the relaxed state

Source: Bamkole C.O.M.Sc. Thesis, University of Manchester, (1981).

From birefringence and viscoelastic property measurements, I have established that drawing nylon 6 film in the uniaxial direction aligns the molecules in the direction of draw resulting in dependence of birefringence and modulus of the polymer on the degree of orientation (Bamkole, 1981). Birefrigence increased for samples held at constant length at different steam-setting temperatures, increasing gradually up to 100°C but markedly at higher temperatures (Bamkole-Eromosele, 1991). The dynamic storage moduli along the stretch direction E', for samples of draw ratio 3:1, steam-set at 110°C were higher than the corresponding moduli in the perpendicular direction, E'<sub>90</sub>. This was the case for the un-annealed drawn samples. But for sample steam-set at 120°C, the E' was less than  $E'_{90}$  that is, higher moduli in the perpendicular direction of stretch. The effect of annealing nylon 6 films using steam was dependent on whether the sample was held at constant length or in a relaxed state. Although the density and crystallinity of steam-set films increased with annealing temperature, whether at constant length or in a relaxed state, the increase was more pronounced for the steam-set film at constant length.

# 4.2 STABILIZATION OF POLYVINYL CHLORIDE

Studies on polyvinylchloride (PVC) was against the backdrop of its instability at elevated temperatures liberating hydrochloric acid and yielding polyene whose properties differ markedly from those of the original polymer.i.e.,

```
\sim CH_2 - CHCl - CH_2 - CHCl \sim \rightarrow \sim CH = CH - CH = CH \sim Polyene
```

The low thermal stability of PVC is one of the inherent problems associated with the manufacture and use of the polymer. The thermal degradation of PVC is generally considered to be initiated at unstable structural irregularities, particularly tertiary and allylic chlorides within the polymer. But there is the overwhelming evidence that initiation of degradation in PVC takes place also at regular repeat units leading to random elimination of HCl from such units (Okieimen and Eromosele, 1999). The poor thermal stability of PVC requires the use of stabilizers for processing of the polymer which act to replace labile chlorine atoms, or modify the chain reactions thereby inhibiting elimination of HCl. Such stabilizers include metal salts of organic acids, organo-metallic compounds and inhibitors of radical chain reactions.

Heavy metal soaps of fatty acids have been demonstrated to exert some stabilizing effect on PVC against thermal and thermooxidative degradation. In this regard, we have examined the effects of heavy metal soap derivatives of seed oils of *Khaya senegalensis*, *Ximenia americana*, *Balanites aegyptiaca* and *Hura crepitans* on thermal stability of PVC. Furthermore, we examined the stability of the polymer using metal soaps of

epoxidized seed oil. Because seed oils have unique physicochemical characteristics associated with their fatty acid profiles, the effects of the latter on stabilization of PVC by metal soaps were also evaluated. For Khaya seed oil, a polysaturate and iodine value,  $68 I_2/100g$  (Table 5)

Characteristics Value Specific gravity at 30°C 0.962 Free fatty acid as oleic acid (wt.-%) 7.64 Acid value (mgKOH/g) 24.0Peroxide value (meq/kg) 26.0Iodine value (g  $I_2/100g$ ) 68.0 Saponification value (mgKOH/g) 186 Fatty acid composition (wt.-%): Caprylic acid 3.82 Myristic acid 1.64 Palmitic acid 19.05 Stearic acid 10.42 Oleic acid 54.34 Arachidic acid 2.04 Lignoceric 0.90 Vernolic acid 5.44 Behenic acid 3.26

Table 5: Physico-chemical Characteristics and Fatty acid Profile of Khaya Seed Oil

Source: Okieimen & Eromosele, 1999.

the stabilizing effects of the metal soaps namely, calcium, cadmium, lead and zinc on the thermal degradation of PVC were assessed at 180 and 190°C from measurements of rates of dehyrochlorination,  $R_{\rm DH}$ , time required for degradation to attain 1% dehydrochlorination,  $t_{\rm DH}$ , changes in intrinsic viscosity,  $[\eta]/[\eta_o]$  and levels of unsaturation of the degraded samples(Table 6).

| Additive     | T (°C) | t <sub>DH</sub> (min) | $R_{DH} x 10^2 (\% min^{-1})$ |
|--------------|--------|-----------------------|-------------------------------|
| None         | 180    | 53 (84)               | 2.00 (2.00)                   |
| None         | 190    | 35 (44)               | 2.86 (4.41)                   |
| Barium soap  | 180    | 100                   | 1.79                          |
| Burrum soup  | 190    | 60; 70 <sup>b</sup>   | 2.09; 1.92 <sup>b</sup>       |
| Cadmium soap | 180    | 120                   | 1.27                          |
| 1            | 190    | 70; 88 <sup>b</sup>   | 1.65; 1.68 <sup>b</sup>       |
| Lead soap    | 180    | 110                   | 1.27                          |
| -            | 190    | 70; 82 <sup>b</sup>   | 1.81; 1.74                    |
| Zinc soap    | 180    | 101                   | 143                           |
| -            | 190    | 60; 78 <sup>b</sup>   | 2.00; 1.77                    |

Table 6: Kinetic data $^{*}$  for dehydrochlorination of PVC in the presence of 3wt.-% of metal soaps of khaya seed oil

Source: Okieimen and Eromosele, (1999).

- a) values in the presence of 10 wt.-% epoxidized khaya seed oil (with 10 mol-% epoxide content) in parentheses.
- b) values in the presence of metal soaps of epoxidized khaya seed oil ( with 10 mol.-% epoxide content.

From these studies, we have established that metal soaps of Khaya seed oil are effective for stabilizing PVC against oxidative and non-oxidative thermal degradation in the order: metal soaps of epoxidized oil > metal soaps of un-epoxidized oil > seed oil. For the metal soaps, barium and cadmium were more effective than the zinc and lead derivatives for stabilization of PVC as deduced from the intrinsic viscosity parameter ( $[\eta]/[\eta_o]$ ) of samples degraded at 190°C under thermo-oxidative conditions (Figure 2).

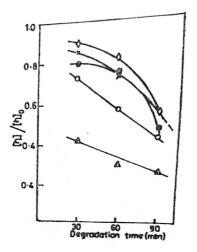


Figure 2: Variations of relative viscosity with degradation time for the thermooxidative

Degradation of PVC at 190°C in the presence of 3 wt-% metal soaps of KSO;

(•) barium soap, (\$) cadmium soap, (x), lead soap and (o) zinc soap; ( $\Delta$ ) without additive

These were corroborated from estimates of the number of double bonds in the polymer sample degraded in air and from the infrared measurements of PVC films (Okieimen and Eromosele, 2000). Thermogravimetric studies of the metal soaps showed stability up to 200°C, the temperature range for studies on the kinetics of PVC degradation and showed a weight loss of not higher than 1.5% for cadmium soap. From the weight loss in PVC degradation, it was established that hydrochloric acid was the only volatile product between 170 and 200°C with rate of dehydrochlorination at the latter temperature of the order of 10<sup>-2</sup>%min<sup>-1</sup> which was consistent with values obtained from kinetic studies Okieimen and Eromosele, 1999). The temperature at which maximum rates of degradation occurred, t<sub>dmax</sub>from thermogravimetry was higher for cadmium (328.5°C) than barium (322.3°C). A combination of barium and cadmium soaps at 10:90 ratio showed higher stabilization of PVC with  $t_{dmax}$  value of 329.5°C(Table 7)

Table 7 : Evaluation of relative thermal stability of PVC stabilized with metal soaps of khaya seed oil at temperature at which various extents of degradation were attained

|                               | Temper            | ature at w | hich deg | gradation | were attain | ned (°C) |
|-------------------------------|-------------------|------------|----------|-----------|-------------|----------|
| Additive<br>(°C)              | t <sub>dmax</sub> | 1%         | 5%       | 10%       | 30%         | 50%      |
| None                          | 302.5             | 256.8      | 281.8    | 291.2     | 307.9       | 336.0    |
| Barium soap                   | 322.3             | 260.0      | 295.4    | 310.0     | 331.2       | 345.6    |
| Cadmium soap                  | 328.5             | 262.1      | 297.5    | 312.1     | 332.5       | 349.2    |
| Barium/Cadmium                |                   |            |          |           |             |          |
| Soap mixture<br>10 wt% Cadmiu | m 324.4           | 268.3      | 304.7    | 332.5     | 345.8       | 357.0    |
| 50 wt% Cadmius                | m 328.4           | 274.6      | 301.6    | 349.2     | 346.6       | 351.4    |
| 90 wt% Cadmiu                 | m 329.5           | 276.6      | 303.7    | 314.1     | 338.1       | 352.5    |

Source: Okieimen & Eromosele, 2000

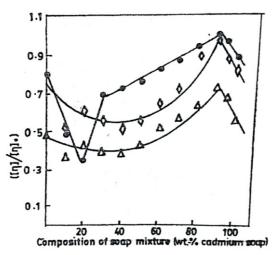


Figure 3: Variations of relative intrinsic viscosity with composition of 3 wt-% soap Mixture for the thermo-oxidative degradation of PVC at 190°C in the presence of mixtures of barium and cadmium soaps of KSO; degradation time: ( $\bigcirc$ ) 30 min, ( $\diamond$ ) 60 min, ( $\Delta$ ) 90 min.

The observed higher stabilizing effect of metal soaps of epoxidized khaya oil on PVC compared to the un-epoxidized oil was adduced mechanistically to combined effects of the epoxy group, as HCl scavenger, and the metal soap, acting to substitute labile chlorine atom in the polymer (Sogbaike et al., 2005).

The reactions that may accompany thermal dehydrochlorination of PVC include chain scission and cross linking of the polymer. The former leads to reduction in intrinsic viscosity, and the latter to higher value. From our studies, based on  $[\eta]/[\eta_0]$  and S derived from the relation,  $[\eta]/[\eta_0] = (1+S)^a$  chain scission is the predominant reaction which accompany dehydrochlorination of PVC under our experimental conditions where S is the average number of random

chain scission per original polymer molecule, and a is the empirical constant in the Mark-Houwink viscosity –average molecular weight equation (Table 8).

| Additive            | Degradation | Huggins                    | S    | Relative              |
|---------------------|-------------|----------------------------|------|-----------------------|
|                     | Period      | Constant (k <sub>H</sub> ) |      | Iodine Value          |
|                     | (min)       | (                          |      | (IV/IV <sub>o</sub> ) |
| None                | 30          | 36.89                      | 0.56 | 15.51                 |
|                     | 60          | 63.92                      | 0.85 | 18.87                 |
| KSO                 | 30          | 23.63                      | 0.36 | 10.43                 |
|                     | 60          | 49.38                      | 0.62 | 10.48                 |
| EKSO                | 30          | 9.63                       | 0.12 |                       |
|                     | 60          | 23.96                      | 0.34 | _                     |
| Metal Soaps of KSO  |             |                            |      |                       |
| Barium Soaps        | 30          | 8.44                       | 0.12 | 11.51                 |
| Ĩ                   | 60          | 10.73                      | 0.15 | 12.64                 |
| Cadmium soaps       | 30          | 7.12                       | 0.06 | 8.89                  |
| -                   | 60          | 10.19                      | 0.11 | 10.07                 |
| Lead soaps          | 30          | 5.93                       | 0.09 | 7.28                  |
| -                   | 60          | 12.69                      | 0.17 | -                     |
| Zinc soaps          | 30          | 6.91                       | 0.17 | 10.61                 |
|                     | 60          | 21.30                      | 0.33 | -                     |
| Metal Soaps of EKSO |             |                            |      |                       |
| Barium Soaps        | 30          | 7.21                       | 0.09 | 10.48                 |
|                     | 60          | 14.14                      | 0.21 | -                     |
| Cadmium soaps       | 30          | 4.41                       | 0.01 | 7.20                  |
|                     | 60          | 7.94                       | 0.05 | -                     |
| Lead soaps          | 30          | 5.90                       | 0.09 | 6.61                  |
| -                   | 60          | 8.89                       | 0.11 | _                     |
| Zinc soaps          | 30          | 8.24                       | 0.09 | 9.41                  |
| -                   | 60          | 9.06                       | 0.14 | _                     |

**Table 8 :** Thermo-oxidative degradation of PVC at 190 °C in the presence of derivatives of KSO (intrinsic viscosity and levels of unsaturation in the degraded polymer samples)

Source: Sogbaike, Okieimen and Eromosele (2005)

 $[\eta_0]$  = intrinsic viscosity of undegraded PVC = 1.15. IV\_0= iodine value of undegraded PVC=9.80 [24]

The effect of the intrinsic properties of oil in stabilization of PVC by their metal soap derivatives was examined by using Ximenia americana and Balanites aegyptiaca seed oils, the former unsaturated (Iodine value,  $158I_2/100g$ ) and the latter saturated ( Iodine value, 102.6 I<sub>2</sub>/100g). Under nitrogen atmosphere, PVC was stabilized by the oils in the temperature range, 170 -190°C. This was attributed to trapping of HCl in addition reaction across the double bonds of fatty acids and consequent retardation of acid -catalysed degradation of the polymer. Ximenia oil was more effective than Balanites for stabilization of PVC consistent with higher unsaturation of the oil (Folarin et al., 2011). Furthermore, from thermogravimetric analysis, Ximenia oil was more stable than Balanites oil. But the metal soap derivatives of Balanites showed higher stability than the corresponding ones of Ximenia in the temperature range, 170 -220°C. This was consistent with results of kinetic studies which showed that the metal soaps of Balanites were more effective stabilizers of PVC under oxidative and non-oxidatitive conditions. For this case, however, the dominant mode of stabilization is by substitution of labile chlorine atom in the polymer by carboxylate group of the metal soap.

|               |                     | ]                    | Femperature ( <sup>c</sup> | C)           |            |       |
|---------------|---------------------|----------------------|----------------------------|--------------|------------|-------|
| Metal Soap    | 170                 | 180                  | 190                        | 200          | 210        | 220   |
|               |                     |                      |                            |              |            |       |
| Zn-XSO        | 94.55               | 94.31                | 94.08                      | 93.85        | 93.60      | 93.31 |
| Cd-XSO        | 96.54               | 96.17                | 95.83                      | 95.52        | 95.17      | 95.00 |
| Pb-XSO        | 97.27               | 96.09                | 95.59                      | 95.37        | 95.28      | 95.22 |
| Ba-XSO        | 97.74               | 97.62                | 97.51                      | 97.44        | 97.38      | 97.31 |
| Ca-XSO        | 97.66               | 97.46                | 97.25                      | 97.05        | 96.85      | 96.67 |
|               |                     |                      |                            |              |            |       |
| Zn-BSO        | 96.82               | 96.37                | 96.00                      | 95.58        | 95.20      | 94.77 |
| Cd-BSO        | 97.84               | 97.63                | 97.43                      | 97.23        | 96.93      | 96.25 |
| Pb-BSO        | 98.41               | 97.92                | 97.78                      | 97.68        | 97.55      | 97.40 |
| Ba-BSO        | 99.22               | 99.13                | 99.00                      | 98.86        | 98.68      | 98.45 |
| Ca-BSO        | 98.85               | 98.74                | 98.61                      | 98.49        | 98.37      | 98.25 |
| Source: Folar | rin, <i>Ph.D.</i> 7 | <i>Thesis</i> , Univ | ersity of Agric            | ulture, Abeo | kuta (2008 | ).    |
|               |                     |                      | ersity of Agric            |              |            | ).    |

Table 9: Residual weights (%) of metal soaps at the initial stage of decomposition (170-220°C)

Vice-Chancellor Sir, these studies demonstrate value-addition to seed oils, many of which grow in the wild, in their conversion to heavy metal soap derivatives and utilization as thermal stabilizers of polyvinylchloride. We have demonstrated that the time required to attain 1% degradation of PVC under non-oxidative conditions in nitrogen at 180°C was increased by 126% in the presence of cadmium soap i.e., a reduction in rate of dehydrochlorination of 37% (Okieimen and Eromosele, 1999).

Thermo-oxidative degradation of PVC was conducted in the presence of mixture of barium and cadmium soaps of khaya seed oil. The effect of the mixture was non-additive showing antagonistic behaviour for composition with up to 70wt-% cadmium soap and a synergistic effect at higher cadmium content (Okieimen and Eromosele, 1999) as evident in values of intrinsic viscosity which decreased initially and increased at the latter mixture composition. The stabilization involves unequal activities of the soaps albeit operating by the same mechanism with a reaction sequence which involves: a) facile reaction of the more reactive component of the mixture (cadmium soap) with labile chlorine atoms in PVC leading to their replacement with more heat-stable carboxylate group, b) the conversion of the cadmium chloride formed from the latter reaction to the soap by reaction with barium soap and c) scavenging of HCl formed during dehydrochlorination.

## 4.3 STUDIES ON SEED OILS

Oleo-chemicals derivable from palm oil and palm kernel oil have been shown in Section 3.2 as foundational to agro-based industrialization processes in Malaysia. Therefore, the potentials of agro-driven industrialization based on abundant seed oils in Nigeria cannot be overstated. Thus, as an exploratory work, we have established the physico-chemical characteristics of a number of seed oils, edible and non-edible, some of which grow in the wild in the northern part of Nigeria (Tables 10 and 11).Some of them have been characterized in their fatty acid profiles (Eromosele and Eromosele, 1993; Eromosele et al., 1994; and 1998). Specifically, the fatty acid composition of *Haematostaphis barteri* and *Ximenia Americana* have been determined (Table 12)

| Seed                       | OIL    | SV    | PV     | IV          | AV      | Status/Class      |
|----------------------------|--------|-------|--------|-------------|---------|-------------------|
|                            | %(w/w) | mgKOH | mEq/kg | $gI_2/100g$ | mgKOH/g | of Oil            |
| Hematostaphis<br>berteri   | 54.5   | 213   | 27.5   | 125.7       | 0.11    | Edible/SD         |
| Deterium<br>microcarpum    | 7.4    | -     | 150    | 58.9        | 0.2     | -/ND              |
| Balanites<br>aegyptiaca    | 38.2   | 165.5 | 22.5   | 76.2        | 0.11    | Edible/ND         |
| Ximenia<br>americana       | 49.9   | 182.3 | 29.4   | 149.8       | 0.14    | Edible/SD         |
| Lophira<br>lanceolata      | 40     | 219.0 | 95     | 65          | 0.03    | Non-<br>Edible/ND |
| Blighia sapida             | 26.0   | 261.0 | 135    | 87.6        | 0.34    | -/ND              |
| Sterculia<br>setigera      | 33.0   | 212.8 | 35     | 67.3        | 0.50    | Edible/ND         |
| Sclereocarya<br>birrea     | 42.0   | 199.3 | 25     | 69          | 025     | Edible/ND         |
| Khaya<br>senegalensis      | 52.5   | 186.0 | 26     | 68          | -       | Non-<br>Edible/ND |
| Canerium<br>schweinfurthii | -      | 213.0 | 40     | 87          | 0.34    | Edible/ND         |
| Bridelia<br>ferruginea     | 54.7   | 32.3  | <1     | 149         | 23.4    | -/SD              |
| Crysophilium<br>abidun     | 2.9    | 44.9  | <1     | 157.5       | 26.9    | -/SD              |

Table 10: Physico-chemical characteristics of seed oils

SD, Semi-drying; ND, Non-drying.

Source: Eromosele & Eromosele (1993); Eromosele et al., (1994, 1998).

| Seed<br>variety | Oil<br>%(w/w) | IV<br>gI <sub>2</sub> /100g | PV<br>mEq/kg | SV<br>mgKOH | AV<br>mgKOH/g | % ffa<br>(as Oleic<br>acid) | Class of<br>Oil |
|-----------------|---------------|-----------------------------|--------------|-------------|---------------|-----------------------------|-----------------|
| Petters         | 13.9          | 139.4                       | 0.0          | -           | 20.4          | 10.2                        | SD              |
| Ibadan          |               |                             |              |             |               |                             |                 |
| Hindi -         | 25.8          | 47.0                        | 0.0          | 102.7       | 21.6          | 10.8                        | ND              |
| Sinnar          |               |                             |              |             |               |                             |                 |
| Petters-        | 12.2          | 21.6                        | 0.0          | 41.0        | 55.7          | 27.8                        | ND              |
| Kazaure         |               |                             |              |             |               |                             |                 |
| Alphonse        | 21.6          | 41.9                        | 0.0          | 164.4       | 5.6           | 2.8                         | ND              |
| Binta           | 22.1          | 40.6                        | 0.0          | 257.8       | 4.6           | 2.3                         | ND              |
| Sugar           |               |                             |              |             |               |                             |                 |
| Dabsha          | 16.1          | 49.5                        | 0.0          | 157.4       | 2.2           | 1.1                         | ND              |

Table 11: Characteristics of the oils of some varieties of Mangifera indica

Extractant: n-hexane; Class of Oils: SD = semi-drying; ND = Non -drying.

Source: Eromosele et al., 1998.

| Table 12: Fatty acid compositions | of <i>H</i> . | barteri | and X. | americana |
|-----------------------------------|---------------|---------|--------|-----------|
|-----------------------------------|---------------|---------|--------|-----------|

| Fatty acid                                | H. barteri (%)              | X. americana (%) |
|---|-----------------------------|------------------|
| Caprylic                                  | ND                          | 0.55             |
| Myristic                                  | 4.23                        | ND               |
| Palmitic                                  | 1.35                        | 3.31             |
| Stearic                                   | 15.40                       | 3.47             |
| Oleic                                     | 69.35                       | 72.09            |
| Linoleic                                  | ND                          | 1.34             |
| Linolenic                                 | ND                          | 10 31            |
| Eicosadienoic                             | 6.92                        | ND               |
| Eicosatrienoic                            | ND                          | 3.39             |
| Arachidonic                               | ND                          | 0.60             |
| Erucic                                    | 2.74                        | 3.46             |
| Nervonic                                  | ND                          | 1.23             |
| Total unsaturation<br>Soucre: Eromosele & | 79.01%<br>& Eromosele (2002 | 92.42%           |

These analyses were important for evaluation of suitability of the oils for a variety of applications, notably as base materials for paint and for their nutritional status. For example, the presence of essential fatty acids namely, linoleic (1.34%), linolenic (10.31%) and arachidonic (0.60%) confers on the oil considerable nutritional value. In particular, linoleic acid is important for its metabolic role in the synthesis of prostagladins. As alkyd resin derivative, Ximenia oil has been demonstrated to be an effective base material for formulation of oil paint (Oladipo et al., 2013) underscored by its linolenic acid content and total unsaturation of 79% which is comparable to the value for linseed oil (75 -90%).Unsaturation is a key property of the oil for suitability as base material for alkvd resin for paint. This property enables the alkyd in paint to undergo oxidative crosslink when exposed to air to form dry, tough, transparent and infusible coatings. We have also demonstrated the suitability of Hura crepitans seed oil for paint formulation via its alkyd resins (Eromosele et al., 2014). The fatty acid composition of the oil (Table 13) showed a predominance of oleic acid at 63.2% with total un-saturation of 66.5% consistent with its iodine value of 177.6 L/100g. Alkyd resins were prepared from the oil at 40, 50 and 60% oil lengths, and the kinetics of the reaction monitored via acid values of samples at regular intervals. The corresponding second-order rate constants at the oil lengths for the alkyd resin synthesis were  $5.67 \times 10^{-4}$ , 5.38 $x 10^{-4}$  and 4.67 x  $10^{-4}$  g(mgKOH)<sup>-1</sup>min<sup>-1</sup>. The alkyd resins were fairly resistant to water, brine but showed remarkable resistance to alkali. For paints formulated from the alkyds, the drying times decreased with increase in oil length. H. crepitans seed oil was epoxidized and alkyd resins synthesized from it. The paint based on the epoxidized resin showed a remarkable improvement in drving properties compared to the un-epoxidized resin(Afuwape, 2014).

Methylol urea is a material that has shown good properties for paint production due to its high cure rate, good adhesion and low cost, albeit, it has the drawback by its brittleness, poor moisture resistance and emission of formaldehyde gas. We have blended *H. crepitans* seed oil with methylol urea at different ratios in the range, 5-30% of the oil and characterized the resultant film in its physico-chemical and mechanical properties. The blend at 10 and 15% oil gave higher values of tensile strength i.e., 5.65 and 5.09 Nm<sup>-2</sup> respectively. Thus, modification of the oil by blending with methylol urea has, demonstrably, the potential to give polymer blends with improved properties as binders for emulsion paints.

| Fatty acid        | %     |  |
|-------------------|-------|--|
| Palmitic acid     | 4.40  |  |
| Stearic acid      | 4.59  |  |
| Total saturated   | 8.99  |  |
| Oleic acid        | 63.19 |  |
| Linoleic acid     | 2.01  |  |
| Eicosenoic acid   | 1.27  |  |
| Total unsaturated | 66.48 |  |
| Others            | 29.11 |  |
|                   |       |  |

Table 13: Fatty acid composition of Hura crepitans seed oil

Source: Awosanya, M. Sc. Dissertation, University of Agriculture, Abeokuta, 2011

Because vegetable oils have become increasingly important as industrial raw materials for a variety of applications which include high pressure lubricants, we have examined the viscosity properties of a number of seed oils at varying temperature conditions (Table 14).

| kinematic viscosity (cst) |       |       |       |       |         |
|---------------------------|-------|-------|-------|-------|---------|
| Seed oil                  | 30    | 40    | 50    | 60    | 70 (°C) |
| B. aegytiaca              | 59.8  | 46.8  | 42.2  | 34.0  | 24.3    |
| L. lanceolata             | 153.3 | 109.1 | 79.8  | 59.9  | 48.1    |
| S. setigera               | 218.2 | 155.6 | 111.6 | 83.1  | 52.8    |
| K.senegalensis            | 266.8 | 186.0 | 131.3 | 96.1  | 75.0    |
| X. americana              | 938.2 | 624.2 | 450.8 | 331.8 | 262.7   |
| S. birrea                 | 184.5 | 142.6 | 103.0 | 76.3  | 46 1    |

Table 14: Effect of temperature on the kinematic viscosity of seed oils

Source: Eromosele and Paschal (2003)

As expected, the viscosities of the oils showed negative dependence on temperature over the range,  $30 -70^{\circ}$ C. The remarkably high viscosity values even at high temperatures for *X*. *americana* seed oil are note worthy for its potential as base material for lubricants. The oil is being used as skin cosmetic; for prevention of stretch marks in pregnant women and as hair conditioner in southwest Angola.

Furthermore, we have added value to *H. crepitans* and sesame seed oils through the instrumentality of nanoscience and technology, a new branch of science concerned with creating nanoparticles and deploying them for a variety of applications in the food, pharmaceutical industries, etc. In the pharmaceutical industry, nano emulsions are suitable for efficient drug delivery of active ingredients through the skin. In our studies, we prepared colloids, i.e., oil-in-water (O/W) nano emulsion from *H. crepitans* and Sesame oils for delivery of Ciprofloxacin, a synthetic antibiotic. The formulation included surfactants namely, polyethylene

sorbitanmonoleate and polyethylene sorbitanmonolaurate and a co-surfactant, polyethylene glycol 400. Ciprofloxacin was incorporated into the oil phase of the stable nano emulsion formulation prior to emulsification. Both the drug-free and drug-loaded nano emulsion formulations were subjected to potency test in the organic phase of the emulsion on E. coli by measuring zones of inhibition. *H. crepitans* seed oil formulation was effective for trans-dermal drug delivery in terms of stability while the sesame oil counterpart showed a more effective penetration, ascribed to the smaller globule size of the dispersed phase (Bamisaye et al., 2020).

Mr. Chairman the import of this expose is to emphasize the need for value-addition to seed oils which abound in our localities, domesticated and in the wild, for overall promotion of the Chemical Industry in Nigeria.

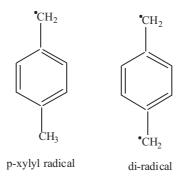
# 4.4 CELLULOSIC GRAFT COPOLYMERS

Cellulose is a biopolymer and the most abundant organic polymer on Earth, consisting of several hundred to several thousand anhydroglucose units condensed and linked together linearly by means of 1,4-β-glucosidic bonds. Cellulose was discovered in 1838 by a French Chemist, Anselme Payne who isolated it from plant matter and determined its chemical formula.(Wikipedia).Cellulose is widely used as fibres, textiles, etc having a combination of properties namely, low cost, fine cross-section, high strength and durability, high thermal stability, good mechanical properties, ability to absorb moisture, easy dyeability and wearing comfort. Moreover, its increasing importance as an industrial raw material resides in its biodegradability and in being a renewable resource, promoting sustainable development (Hebeish and Guthrie, 1981). However, cellulose has some intrinsic drawbacks and these include poor solubility in many solvents, poor crease resistance, lack of thermoplasticity required for heat-setting and shaping of

garments; poor dimensional stability during laundering and ironing.

Over the years we have studied the chemical modification of cellulose through grafting of synthetic polymers onto fibres or pulp with the objective to impact the intrinsic properties of the former on the latter. In this regard, we have established the conditions under which synthetic polymers of the olefinic type can be effectively and optimally grafted onto cellulose, and the kinetics and mechanism of the processes. Specifically, the graft copolymerization of acrylic acid on methylcellulose by ceric ionp-xylene redox pair in aqueous medium under homogenous conditions showed the following features (Eromosele et al, 2002):

• Two kinetically-controlled reactions initiated by p-xylyl radical and di-radical species generated at 10mins pre-oxidation time.



• The concentration dependence, in graft yield, on p-xylene showed an optimum and a minimum followed by an enhanced graft yield which were associated with the activities of p-xylyl and di-radical initiating species (Figure 4).

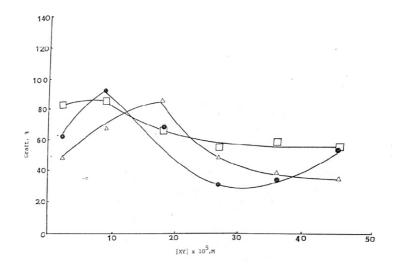


Figure 4: Effect of p-xylene on graft yield at different pre-oxidation times.  $[H^+] = 0.52M$ ;  $[Ce(IV)] = 33.3 \times 10^{-3}M$ ; [AA] = 0.46M; MC = 0.1g; [AcOH] = 1.17M.

Pre-oxidation time:  $10 \min(\bigcirc)$ ;  $30 \min(\Delta)$ ;  $60 \min(\Box)$ . Time = 3 h; Temperature =  $30^{\circ}$ C.

- In the temperature range, 30 -50°C, the graft yields showed negative dependence with initial rate of graft at 50°C being 37% of the value at 30°C.
- At higher pre-oxidation time of 30 and 60 min, the graft yield profile was normal i.e., exhibiting no minima. This indicated the presence of only the p-xylyl radical species for the initiation process.

These features were observed also when ceric ion was replaced with permanganate as an oxidant under the same conditions(Figure 5) (Eromosele and Nwokata, 2003).

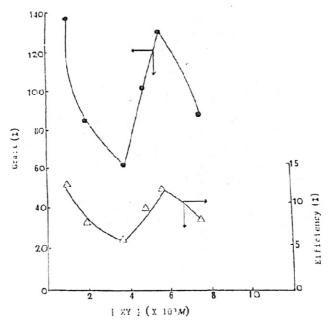


Figure 5: Effects of p-xylene concentration on graft yield and efficiency of graft.  $[H^+] = 0.52M$ ; [AcOH] = 1.17M; [AA] = 0.46M;  $[KMnO_4] = 33.3 \times 10^{-3}$ ; MC = 0.1g:

Pre-oxidation time = 10 min; Time = 3h; temperature =  $30^{\circ}$ C.

However, ceric ion in combination with p-xylene was more effective for graft copolymerization of acrylic acid onto methylcellulose than the analogous permanganate – p-xylene redox pair under identical reaction conditions. Additional features for the latter redox pair include:

• The efficiency of the reaction in conversion of monomer to graft polymer was not higher than 12.9% at p-xylene concentration of 0.93 x 10<sup>-3</sup>M. The low efficiency of graft was attributed to a preponderance of a competitive homopolymerization of acrylic acid under homogenous condition.

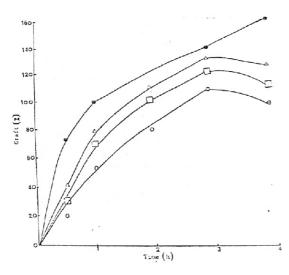


Figure 6: Effect of temperature on graft yield. [H<sup>+</sup>] = 0.52M; [AcOH] = 1.17M; [AA] = 0.46M; [KMnO<sub>4</sub>] = 33.3 x 10<sup>-3</sup>M; [XY] = 3.37 x 10<sup>-3</sup>M; MC = 0.1g;
Pre-oxidation time = 10 min; temperature: (●) 30°C; (△) 40°C; (□) 50°C; (o)
60°C

Interesting features were found when acrylic acid was grafted onto cellulosic pulp by potassium permanganate in the presence of toluene derivatives – p-bromo toluene, o-amino toluene and mamino toluene.

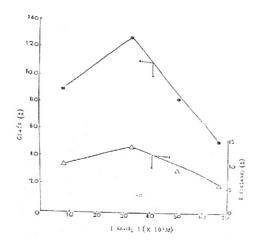


Figure 7: Effect of [KMnO<sub>4</sub>] on graft yield and efficiency of graft. [H<sup>+</sup>] = 0.52M;

 $[AcOH] = 1.17M; [AA] = 0.46M; [XY] = 5.60 \times 10^{-3}M; MC = 0.1g;$ Pre-oxidation time = 10 min; time = 3 h; temperature = 30°C.

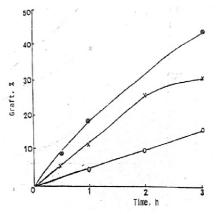


Figure 8: Effect of toluene derivatives on graft yield.  $[H^+] = 0.62M$ ; [AcOH] = 1.1M;

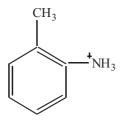
 $[Toluenes] = 1.8 \times 10^{-4}M; [KMnO_4] = 33.3 \times 10^{-3}M; [AA] = 0.46M;$ Pulp =

0.1g; temperature = 30°C; Pre-oxidation time = 10 min. Toluenes: oamino

Toluene (x); m-amino toluene ( $\bigcirc$ ); p-bromo toluene (o).

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The substituents on the toluene exerted profound effects on the graft reactions and yields, the order of reactivity being m-amino toluene > o-amino toluene > p-bromo toluene consistent with the electron-withdrawing capabilities of the substituents and disparate effects of the ortho and meta positions on the amino function. Thus, the meta derivative was a factor of 1.6 more active than the ortho analogue for graft reaction (Eromosele et al., 2004). The effect of o-amino toluene on the graft reaction at varying sulphuric acic concentrations, 0 - 1.55 M, exhibited maxima and minima profile which suggested that there existed a quaternary ammonium derivative, not readily oxidized by permanganate resulting in low graft yield i.e.,



The increase in graft yield after a minimum was ascribed to increasing levels of the more readilyoxidized*o*-amino toluene at higher concentrations of the latter.

Grafting of methacrylonitrile on caesarweed fibres and on its sodium derivative initiated by ceric ion-isopropanol redox system showed interesting features (Table 15) (Eromosele et al., 2006) notably,

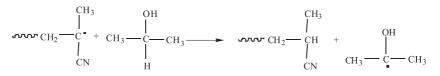
|                   |                | Caeserweed | l                                    |                     | Na                |
|-------------------|----------------|------------|--------------------------------------|---------------------|-------------------|
|                   |                |            |                                      |                     | <b>Caeserweed</b> |
| [ISP] x           | $\mathbf{P_g}$ | Efficiency | $\mathbf{M}_{\mathbf{v}} \mathbf{x}$ | $F_{g} \ge 10^{-2}$ | Pg                |
| 10 <sup>2</sup> M | %              | %          | 10 <sup>-3</sup>                     | $N_g/10^4$          | (%)               |
|                   |                |            |                                      | AGU                 |                   |
| 0                 | 57.7           | 5.8        | 0.30                                 | 5.72                | 62                |
| 5.6               | 110.9          | 11.1       | -                                    | -                   | 66                |
| 16.7              | 59.6           | 5.9        | 0.94                                 | 1.32                | 67                |
| 27.8              | 55.1           | 5.5        | 0.47                                 | 2.62                | 36.2              |
| 44.4              | 64.6           | 6.5        | 0.42                                 | 2.81                | -                 |
| 55.6              | 75.3           | 7.5        | 0.41                                 | 2.56                | 45.6              |

Table 15: Effect of Isopropanol Concentration on Grafting of Methacrylonitrile on Caeserweed and Sodium Fibres in Aqueous Media by Ceric Ions.

 $[H^+] = 0.62M$ ; [AcOH] = 1.1M; fibre = 0.1g;  $[Ce^{+4}] = 3.3 \times 10^{-3}M$ ; [MA] = 0.49M; POT =10min; time = 3h; temperature = 30°C

Source: Eromosele et al., (2006)

- The graft reaction was characterized by a high grafting frequency,  $F_g$  of up to 2.81 x  $10^2 N_g/10^4 AGU$ , and a low molecular weight of the grafted polymer which was not higher than 0.94 x  $10^3$ .  $N_g$  is the number of moles of grafted polymer.
- The molecular weight of the grafted polymer was negatively dependent on the concentration of isopropanol (Figure 9), and suggested involvement of the latter in transfer reactions with growing graft polymer chains i.e.,



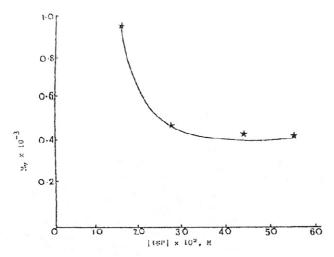


Figure 9: Effects of ISP concentration on  $M_v$  for grafting of MA to caesarweed fibres. [MA] = 0.49M; [Ce<sup>+4</sup>] = 33.3 x 10<sup>-3</sup>M; temperature = 30°C.

- A ten-fold increase in graft yield i.e., from 20.7 -216.3%, resulted in an 88% reduction in solubility of the graft copolymer in 72% sulphuric acid (Figure 10).
- The formation of sodium caesarweed fibres gave lower yields of graft copolymer (Table15),traceable to reduction in the number of oxidizable hydrogen of the anhydroglucose units a primal facie evidence of the mechanism of graft initiation by redox systems, generally believed to occur by abstraction of hydrogen from the substrate.
- The rate constant, k of the graft reaction at varying temperatures in the range,  $30 50^{\circ}$ C, was obtained from the conversion plot of the reciprocal of monomer concentration,  $[MA]^{-1}$  versus time. From the Arrhenius expression,  $k = Ae^{-E_{RT}}$ , the activation energy for the graft reaction was 10.5kcalmol<sup>-1</sup> which was consistent with the observed low graft yield and low molecular weight of the grafted polymer.

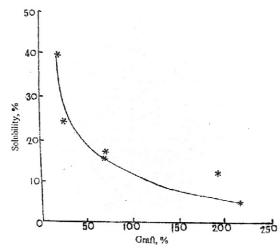


Figure 10: Solubility of ceaserweed-polymethacrylonitrile graft polymer in 72 % sulphuric acid.

Allylation of cellulose fibres was undertaken prior to grafting of monomer onto it for elucidation of the mechanism of the process. Specifically, graft copolymerization of acrylonitrile onto allylated caesarweed fibres by ceric ion / 2-mercapto ethanol and by potassium permanganate/ N, N'-dimethylacetamide redox pairs (Eromosele et al., 2008a; 2008b) gave the following features:

• There was considerable reduction in graft yield for the allyl fibre compared to the unmodified fibre by up to a factor of 2 and was attributed to resonance stabilization of initiated macro radicals of the modified fibre.

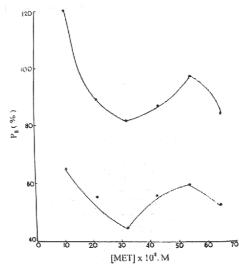


Figure 11: Effect MET concentration on graft yield for grafting of AN to caesarweed

Fibres and allyl derivative.[AcOH] = 0.56M; [Ce<sup>+4</sup>] =  $33.3 \times 10^{-3}$ M; [AN] = 0.31M; [H<sup>+</sup>] = 0.52M; Fibre = 0.1g; POT = 10 min; time = 3 h; temperature =  $30^{\circ}$ C; (A) unmodified; (B) allyl derivative

- The graft yield profiles for both fibres showed characteristic minimum graft yield at certain concentrations of 2-mercapto ethanol and suggested the presence of two initiating species, a thioglycol radical and 2-mercapto ethoxyl radical (Figure 11)
- Infra red spectroscopy showed radical coupling reaction between the thioglycol radical and allylic macro radical of the allyl fibre with consequent reduction in the frequency of graft.
- A five-fold increase in the concentration of 2-mercapto ethanol was accompanied by reduction in the frequency of graft from 75.6 to  $0.79 \text{Ng}/10^4 \text{AGU}$  and a concomitant increase by two orders of magnitude, in the average molecular weight of grafted polymer with values of up to  $11.78 \times 10^5$  (Table 16).

| [MET]<br>(M) | P <sub>g</sub> F <sub>g</sub><br>(%) | $P_g/P_{g0}$ | $M_v \ge 10^{-5}$ | $M_{v}\!/M_{v0}$ | (Ng/10 <sup>4</sup> AGU) |
|--------------|--------------------------------------|--------------|-------------------|------------------|--------------------------|
| 0            | 74.9                                 | -            | 2.73              | -                | 4.37                     |
| 10.7         | 65.5                                 | 0.87         | 0.14              | 0.05             | 75.6                     |
| 21.3         | 55.8                                 | 0.74         | 0.23              | 0.08             | 39.2                     |
| 32.0         | 44.5                                 | 0.59         | 1.01              | 0.36             | 7.12                     |
| 42.7         | 55.9                                 | 0.75         | 1.90              | 0.69             | 4.76                     |
| 53.3         | 59.3                                 | 0.79         | 11.78             | 4.31             | 0.79                     |

Table 16: Effect of 2-Mercaptoethanol on Graft Yield, Molecular Weight and Frequency of Graft on Allylfibre.

 $[AcOH] = 0.56M; [Ce^{+4}] = 33 \times 10^{-3}M; [AN] = 0.31M; [H^+] 0.52M; Fibre = 0.1g; POT = 10 min; time = 3 h: temperature = 30°C$ 

Source: Eromosele et al., (2008).

As an extension of these studies, we have examined features of graft reactions using starch, an important raw material for a number of industrial processes and applications. The global starch market is projected to reach 156.3 million metric tons underscored by numerous applications in the food and non-food industries. Starch is an excellent pharmaceutical excipient given its non-toxic properties. Other notable applications include starch-based biodegradable polymers, starch derivatives in detergents, as flocculants, and as thickeners for textiles. Important industrial applications are known when starch is modified through graft copolymerization of vinyl monomers. For example, starch-gpolyacrylamide and starch-g- polyacrylic acid copolymers are of great interest for enhanced oil recovery operations. For the latter copolymer, its application as sizing agent for improved physical properties of textile fabrics has been demonstrated. Furthermore, the presence of hydrophilic polyacrylic acid has been reported to impart water sorbency and ion exchange properties on the graft copolymer. Against this background, we have grafted acrylic acid

onto cocoyam starch initiated by ceric ion in the presence N, N'dimethyl acetamide, and established the following features (Eromosele et al., 2008c):

- The reaction was characterized by high graft yields of up to 676%.
- Low concentrations of N,N'-dimethylacetamide were favourable to graft yields(Table 17)

Table 17: Effect of DMAc on graft yield

Source: Eromosele et al., (2008c).

 $[H+] = 0.54M; [Ce^{+4}] = 8.33 \times 10^{-3}M; [AA] = 0.46M; starch = 0.1g; [ACOH] = 0.5M; temperature = 30^{\circ}C; time = 3h.$ 

- Ceric ion was non-terminating of the graft reaction and a 10-fold increase in its concentration of 4.16 x 10<sup>-3</sup>M, resulted in high efficiency of graft (50.2%) in monomer conversion to grafted polymer.
- Long reaction time, greater than 30min, was unfavourable to the graft reaction, and the latter showed negative dependence on temperature in the range, 30 -50°C. At 30min reaction time, the graft yield at 50°C was not more than 70% of the value at 30°C.
- Enhanced homopolymer formation and low efficiency of graft were observed at monomer concentration higher than 0.69 M.

# 4.5 FOOD CHEMISTRY

Vice-Chancellor Sir, in the realm of raw materials research and development, plant proteins have become increasingly important in formulation of food products by food industry, ostensibly because of their relatively low cost as compared with animal proteins, and also for reasons of their preference by some people. African yam bean, Sphenostylis stenocarpa, is one of the largely under-utilized legumes found in various parts of Africa with tubers and grain seeds which are nutritious, having a percentage ratio of essential to non-essential amino acids in the range 45 - 47% which is above 36% considered adequate for an ideal protein (Arogundade et al., 2009). In a number of studies, we have established appropriate conditions for effective isolation of S. stenocarpa proteins. Specifically, water extractable S. stenocarpa protein aggregates more with addition of either Ca<sup>2+</sup> or Mg<sup>2+</sup> than at isoelectric point. In alkaline extractants (except at pH 10), aggregation tendency of the protein was in the order, isoelectric point>Ca<sup>2+</sup>>Mg<sup>2+</sup>

| Amino acid    | IPalk          | IPsalt         | CaPsalt        | CaPalk         | Mean |
|---------------|----------------|----------------|----------------|----------------|------|
| Essential     |                |                |                |                |      |
|               |                |                |                |                |      |
| t anne        |                |                |                |                |      |
| Lysine        | Los M          | $5.6 \pm 0.0$  | $5.3 \pm 0.0$  | $4.0 \pm 0.1$  | 5.0  |
| Isoleucine    | $2.8 \pm 0.2$  | $3.4 \pm 0.0$  | $3.0 \pm 0.1$  | $3.4 \pm 0.1$  | 3.2  |
| Leucine       | $8.0\pm0.2$    | $9.1 \pm 0.1$  | $7.8 \pm 0.1$  | $9.4 \pm 0.3$  | 8.6  |
| Cystine       | $1.0 \pm 0,1$  | $1.2 \pm 0.0$  | $0.8 \pm 0.0$  | $1.3 \pm 0.1$  | 1.1  |
| Methionine    | $1.0 \pm 0.0$  | $1.4 \pm 0.1$  | $1.2 \pm 0.1$  | $1.1 \pm 0.1$  | 1.2  |
| Histidine     | $2.8 \pm 0.1$  | $2.6 \pm 0.1$  | $2.3 \pm 0.1$  | $2.8 \pm 0.3$  | 2.6  |
| Threonine     | $2.5 \pm 0.1$  | $3.3 \pm 0.0$  | $3.0 \pm 0.1$  | $2.5 \pm 0.1$  | 2.8  |
| Valine        | $4.4 \pm 0.1$  | $4.1 \pm 0.2$  | $4.2 \pm 0.1$  | $3.7 \pm 0.2$  | 4.1  |
| Tyrosine      | 3.1±0.2        | $3.5 \pm 0.1$  | $3.1 \pm 0.0$  | $3.0 \pm 0.1$  | 3.2  |
| Phenylalanine | $3.9 \pm 0.2$  | $4.1 \pm 0.1$  | $4.6 \pm 0.2$  | $3.7 \pm 0.2$  | 4.1  |
| Total         | 34.5           | 38.3           | 35.3           | 34.9           |      |
| Essential     |                |                |                |                |      |
| amino acids   |                |                |                |                |      |
|               |                |                |                |                |      |
| Non-Essential |                |                |                |                |      |
| amino acids – |                |                |                |                |      |
| NE (g/16gN)   |                |                |                |                |      |
| Arginine      | $4.5 \pm 0.2$  | $5.1 \pm 0.0$  | $5.8 \pm 0.4$  | $4.2 \pm 0.1$  | 4.9  |
| Aspartic acid | $10.4 \pm 0.1$ | $10.1 \pm 0.1$ | $9.0 \pm 0.1$  | $10.0 \pm 0.6$ | 9.9  |
| Serine        | $3.1 \pm 0.1$  | $2.7 \pm 0.2$  | $2.6 \pm 0.1$  | $2.3 \pm 0.1$  | 2.7  |
| Glutanic acid | $15.1 \pm 0.1$ | $14.1 \pm 0.3$ | $13.1 \pm 0.1$ | $12.5 \pm 0.2$ | 13.7 |
| Proline       | $2.2 \pm 0.2$  | $3.1 \pm 0.1$  | $3.3 \pm 0.1$  | $2.5 \pm 0.1$  | 2.8  |
| Glycine       | $2.9 \pm 0.2$  | $3.5 \pm 0.2$  | $3.2 \pm 0.3$  | $4.1 \pm 0.1$  | 3.4  |
| Alanine       | $4.0 \pm 0.3$  | $5.1 \pm 0.3$  | $4.5 \pm 0.1$  | $3.8 \pm 0.1$  | 4.4  |
| Total Non-    | 42.2           | 43.7           | 41.5           | 39.4           |      |
| Essential     |                |                |                |                |      |
| amino acids   |                |                |                |                |      |
| E:NE amino    | 0.82           | 0.88           | 0.85           | 0.89           |      |
| acids         |                |                |                |                |      |
| Hydrophilic   | 46.5           | 47.0           | 44.2           | 41.3           |      |
| amino acids   |                |                |                |                |      |
| Hydrophobic   | 30.2           | 35.0           | 32.6           | 33.0           |      |
| amino acids   |                |                |                |                |      |

Table 18: Amino acid composition of African yam bean(Sphenostylis stenocarpa) acid and salt protein isolates

We examined the rheological characteristics of the protein isolates against the backdrop of its usefulness in quality control, consumer acceptability, design and evaluation of food processing equipment. The flow of protein dispersions as a function of ionic strength, pH, temperature and added plasticizer exhibited pseudo-plastic behaviour having flow behaviour indices,  $(\eta)$  which were less than unity. The  $\eta$  values for salt-extracted proteins were lower than the

corresponding ones for alkaline-extracted proteins (Table 19) (Arogundade et al., 2011). Both isoelectrically precipitated protein and calcium proteinates exhibited yield stress. The apparent viscosity of *S. stenocarpa* protein isolates at room temperature ( ca 27°C) decreased significantly ( P <0.05) with increasing sheer rate, and suggested the dispersions of isolates were non- Newtonian having sheer-thinning tendencies (Table 19). Salt extracted proteins were more pseudoplastic than the alkaline extracted ones with  $\eta$  for the former (IPsalt CaPsalt) lower than the values for the alkaline protein extracts.

| Isolates ty | pe              | Apparent visco | sity at vario | us shear rate | s (s <sup>-1</sup> ) |
|-------------|-----------------|----------------|---------------|---------------|----------------------|
|             | 0.8             | 2.0            | 4.0           | 7.8 1         | 5.8                  |
| IPalk       | $400.0\pm0.0$   | $150.0\pm17.3$ | $80.0\pm8.7$  | $50.8\pm7.2$  | $25.4\pm5.8$         |
| IPsalt      | $401.7\pm2.9$   | $172.0\pm2.0$  | $90.0\pm0.0$  | $53.3\pm2.9$  | $23.8\pm0.0$         |
| CaPsalt     | $268.3\pm5.8$   | $71.3\pm2.3$   | $55.7\pm1.2$  | $32.2\pm0.6$  | $15.2\pm0.3$         |
| CaPalk      | $195.0\pm8.7$   | $88.7 \pm 1.2$ | $55.0\pm0.0$  | $32.2\pm0.6$  | $13.0\pm0.4$         |
| Source: A   | rogundade et al | l., (2011)     |               |               |                      |

Table 1 9: Apparent viscosity (Pas x  $10^{-3}$ ) of native and modified *S. stenocarpa* protein isolates at different shear rates

Acylated and dextran conjugated *S. stenocarpa* protein showed interesting features. We have examined the molecular weight distribution and rheological properties of acylated(acetylated and succinylated) and dextran conjugated proteins and established the following (Arogundade et al., 2012):

• modification by acetylation, succinylation and dextran conjugation had different effects on the protein's molecular weight distribution as deduced from their gel electrophoresis.

- Acetylated protein showed increased mobility associated with possible disruption of the protein's quaternary structure resulting in dissociation of the oligomeric protein into subunits of lower molecular weight species.
- Viscosity of modified proteins were in the order: acetylated protein > dextran conjugated protein > succinylated protein.
- For yield stress, the order was: dextran conjugated protein >succinylated protein > acetylated protein.

# 4.6 POLYURETHANE ELASTOMER FROM SEED OILS

Polyurethane is a very versatile polymer with numerous applications as materials which include foams, elastomers, thermoplastics, thermosets, adhesives, coatings, sealants and fibres. Polyurethane is the product of a reaction between a diol or polyol (ologomeric or polymeric, hydroxyl-terminated) and a diisocyanate (or polyisocyanate). These materials are obtained from petroleum sources. But environmental concerns demand increasing use of materials from bio-sources because they are biodegradable. Seed oils are biodegradable and have functional groups which lend them readily to derivatisation reactions and production of diols or polyols. In the preceding section the use of metal soap derivatives of seed oil for stabilization of PVC has been mentioned. We have also demonstrated the use of seed oil for production of polyurethane elastomers i.e., rubber. The properties of polyurethanes from seed oil derivatives depend on a number of factors which include type, composition and distribution of fatty acid residues in the constituent triglycerides. Thus, the intrinsic properties of vegetable oils, as pertaining to fatty acid constituents can have profound influence on the ultimate properties of polyurethanes based on them. In one of our studies, we established the mechanical properties of polyurethane elastomers prepared at [NCO]/[OH] ratios of 1.02 and 1.50 using three different

diisocyanates namely, hexamethylene diisocyanate (HDI), toluene diisocyanate (TDI) and 4, 4'-diphenyl methane diisocyanate (MDI) as shown in Table 20

| Polyurethane<br>Sample | Tensile<br>Strength<br>(MPa) | Elongation<br>at Break<br>(%) | Tensil e<br>Modulous<br>(MPa) |  |
|------------------------|------------------------------|-------------------------------|-------------------------------|--|
| HDPU-1.02              | $2.62\pm0.09$                | $16.75\pm0.07$                | $1.65\pm0.05$                 |  |
| TDPU- 1.02             | $2.18\pm0.13$                | $1.06\pm0.11$                 | $1.51 \pm 0.12$               |  |
| MDPU- 1.02             | $1.32\pm0.19$                | $18.39\pm0.26$                | $0.94\pm0.16$                 |  |
| HDPU-1.50              | $5.83 \pm 0.15$              | $37.56 \pm 1.09$              | $3.95 \pm 0.07$               |  |
| TDPU- 1.50             | $5.92\pm0.26$                | $2.62\pm0.35$                 | $3.46\pm0.22$                 |  |
| MDPU- 1.50             | $3.99\pm0.34$                | $48.53\pm2.06$                | $2.41\pm0.28$                 |  |

Table 20: Mechanical properties of X imenia polyurer hane elastomers at [NCO]/[OH] ratios of 1.02 and 1.50  $\,$ 

Source: Adeiza Emmanuel Samuel, Ph.D Thesis, Federal University of Agriculture, Abeokuta, 2019

The study has shown that Young's modulus and elongation at break for HDI-based polyurethanes obtained from Ximenia compare favourably with those of rubber seed oil-based elastomer. Similarly, the Young's modulus for Ximenia polyurethane elastomer was of the same order of magnitude with values for the ones obtained from petroleum-based poly(butadiene-acrylonitrile) copolymer diol and two different diisocyanate, HDI and MDI.

From the equilibrium degree of swelling (Q) in dimethylacetamide, the network parameters for polyurethane elastomer prepared at [NCO]/[OH] ratio of 1.50 were established as shown in Table 21.

| Polyurethane<br>Elastomer | Density<br>gcm <sup>-3</sup> | Swelling Degree<br>(Q) | Volume Fraction<br>Vp | Mc<br>gmol <sup>-1</sup> | $\gamma x 10^3$ |
|---------------------------|------------------------------|------------------------|-----------------------|--------------------------|-----------------|
| HDPU-1.50                 | $1.31 \pm 0.02$              | $1.08\pm0.16$          | 0.926                 | 197.87                   | 5.05            |
| TDPU-1.50                 | $1.28\pm0.20$                | $2.42\pm0.20$          | 0.413                 | 1062.55                  | 0.94            |
| MDPU-1.50                 | $1.24 \pm 0.06$              | $3.16\pm0.30$          | 0.316                 | 1816.75                  | 0.55            |
| Source: Adiza             | E. S., Ph.D The              | esis, FUNAAB 2019      |                       |                          |                 |

Table 21: Network parameters of polyurethane elastomers in dimethylacetamide

Swelling of the polyurethane in dimethylacetamide was an indication of the presence of crosslinks in the polymer, having crosslink density ( $\gamma$ ) in the order HDPU-1.50 > TDPU-1.50 > Mdpu-1.50.

From thermal studies (Table22), and based on onset degradation temperature T<sub>onset</sub> and temperature for maximum degradation  $(T_{max})$ , HDPU-1.50 showed the highest thermal stability of the three elastomers consistent with its highest crosslink density,

| Polyurethane<br>Elastomer | $T_{onset}T_{10}$<br>(°C) | % T <sub>50%</sub> T <sub>max</sub><br>(°C) | Residual V<br>(°C) | Vt.<br>(°C) | (%)   |  |
|---------------------------|---------------------------|---|--------------------|-------------|-------|--|
| TDPU-1.50                 | 250                       | 280   | 380                | 492         | 12.40 |  |
| MDPU-1.50                 | 260                       | 310   | 420                | 495         | 18.60 |  |
| HDPU-1.50                 | 265                       | 325   | 440                | 510         | 29.80 |  |

Table 22: Thermogravimetric parameters for Ximenia polyurethane elastomers

Source: Adeiza Emmanuel Samuel, Ph.D Thesis, FUNAAB 2019.

Mr. Chairman, from the foregoing, it is clear that value-added industrialization, deploying agro-raw materials which abound in Nigeria holds promise to unlocking the economic potentials of the country and for effective job creation.

# 5.0 CHEMISTRY CURRICULUM

The Vice-Chancellor Sir, there have been concerns about the quality of our university education, graduate employability and a perceived non-responsiveness of curricula to societal challenges, and in particular, failure to meet the needs of industry. But a cursory examination of chemistry curricula across countries in the world shows no fundamental differences in scope and contents for training of undergraduate students. Yet, it must be conceded that there are a number of derivative programmes, interdisciplinary in nature, which have evolved over the years in response to global challenges and needs for which the role of industry cannot be underestimated. There is evidence of industry involvement in chemistry curriculum development in the United Kingdom and Israel (Hotstein and Kesner, 2006). Such participation by industry is to ensure that enough competent chemists are available for industrial chemistry plants. By and large, a chemistry curriculum should be designed to achieve the following at the personal level (Royal Society of Chemistry):

- Inspire the students with a sense of curiosity and wonder about the fundamental nature of the world around them.
- Empower them to make decisions about their own lives and critically evaluate scientific and technological developments that impact society.
- Equip them with the knowledge and skills to pursue further study and rewarding careers in the chemical sciences and a wide range of related fields.

And at the national level, the curriculum should:

• Ensure growth and productivity as exemplified in the UK where the chemical sector contributed £14.4 billion in value to the economy every year.

• Address global challenges such as climate change, water and food security, health and energy.

Indeed to achieve all these, delivery of chemistry curriculum, in theory and practice, is an imperative for in the latter resides a full understanding and appreciation of chemistry as an empirical science. Herein is the primal issue which confronts the dispensation of chemistry curriculum in Nigeria. In the absence of uninterrupted flow of water and electricity on our university campuses, certain chemistry practical exercises have been circumscribed, to wit, virtually non-existent. Specifically, it is not feasible to conduct reflux for 24 hours continuously, manned or unmanned, let alone for any extended period as is common to do in developed countries. A vast array of experimental chemical reaction processes that should promote hands-on experience for students, undergraduate and postgraduate, has become inaccessible to them. An assessment of activities in a chemical laboratory can be made from the status of the chemical store which is a reservoir of chemical reagents of both immediate and longterm needs. The latter is important because often the exigencies of research could necessitate the need for chemical reagent(s) not initially conceived for the project. Because of paucity of funds, the chemical stores in many universities in Nigeria are stocked of reagents of immediate or recurrent need.

The pioneer Vice-Chancellor of this university, as Federal University of Technology Abeokuta, the Late Professor Chimere Ikoku , a Chemist, understood the import and desirability of a chemical store truly defined and he provided for it in the Department of Chemical Sciences. The chemicals have endured to this day, albeit the store, in not being replenished over time, is now severely depleted.

The absence of liquid nitrogen plant in many universities is a sore point which excludes low temperature experimental work in

delivery on the curriculum. Thus, synthetic experimental studies in many areas of chemistry including organo-metallic chemistry cannot be undertaken. Increasingly, it is becoming difficult to provide laboratories with light-weight equipment for hands-on experiments by students, undermining the practical content of the curriculum.

In all of this, it is evident that chemistry programme is one of, if not the most expensive programme in the university and is thus more susceptible to financial distress when there is economic downturn as it has been for Nigeria for years running. Yet, chemistry is a core requirement for many students across disciplines and reflects clearly in calculations of Full Time Equivalent (FTE), a measure of contacts with students in teaching and laboratory services. In resource allocation to programmes, it is important to recognize FTE as a critical factor.

The need for access to research facilities against the background of paucity of funds is a justification for central laboratory in a university, ostensibly to warehouse such facilities which cannot be duplicated. It seems reasonable, in the circumstance, to suggest that central laboratory should be compulsory for each university to be accredited separately as an item. This is one way to ensure commitment to its funding by university Management.

The increasing demand for admission into public universities and increases in admission quota being granted constitute a negating factor in our ability to deliver on the curriculum effectively in light of the mismatch between available facilities and number of students. For chemistry, this is particularly critical where hands-on in practical exercises are key to full appreciation of the subject. Not unmindful of the yearnings of students seeking for admission into universities, there is the need to balance admission and available learning facilities to ensure that the learning objectives of programmes are not compromised.

# 6.0 GOOD GOVERNANCE AND DEVELOPMENT

The Vice-Chancellor Sir, the foregoing sections highlight the developmental role that the Chemical Industry can play in national economies where policies of government are enabling. Symbiotic relationship between research agencies - Universities, Polytechnics, Research Institutes - and Industry is key to the promotion of the Chemical Industry for national development. This is evident in many developed countries in contrast to the clear absence of such symbiosis in underdeveloped countries such as Nigeria. The Nigerian University system is in a parlous state, a victim of poor funding and misplaced priorities of government. It is also a victim of a politico-economy that is challenged on several fronts. It is, therefore, misleading and a contradiction that tuition is free in Federal Universities, and funding by the federal government is unreflective of the aggregate funds for training of students. Lack of commensurate funding in this regard circumscribes the ability of the university to deliver on the curriculum for the benefit of students. In the circumstance, Tertiary Education Tax Fund, established as an intervention agency, now provides the bulk of the funding needs of universities. Non-commitment to funding by the federal government is evident also in the plethora of Research Institutes saddled with specific mandates to engage in research for development ultimately to add value to the multiplicity of raw materials abounding in the country.

The Vice-Chancellor Sir, the concept of development is not in the mere provision of infrastructures by government, but is understood to mean the extent to which the citizens are involved in the provision of such infrastructures, to wit, the extent to which the citizens are involved in the social, political, economic and technological activities of any given country. Therefore, 'Development is something that people do by themselves and for themselves or it does not happen' (Ake, 1996). It is evident that developed countries are the ones that have mobilized their peoples to productive activities. For Nigeria, the need for local capacity for productive activities through the promotion of endogenous technology cannot be overstated.

The politics and poor management of resourceendowments and hence, the low dividend derivable from them.underscore their perception, particularly that of the crude oil, as resource curse in Nigeria. But as an Industrial Chemist, the minerals - solid, liquid and gas - are not, truth be told, resource curse. The crux of the matter resides in our inability to transform them into developmental resources for the benefit of citizens. A major encumbrance in this regard is the dysfunctional governance system, which by our Constitution, vests ownership of these resources on the federal government that has not shown any willingness or desire to develop them. It is in this regard that I subscribe to strident demands for governance reform to allow States greater control of mineral resources with which they are endowed. This, in my humble opinion, is the overriding imperative for unlocking the latent creative energies of Nigerians for development and ultimately, for uplifting the country to a pride of place amongst the comity of nations.

I thank you for your kind attention.

# 7.0 ACKNOWLEDGEMENTS

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In closing this episode, please join me to sing this hymn:

# **Great Is Thy Faithfulness**

Great is Thy faithfulness O God my Father There is no shadow of turning with Thee Thou changest not Thy compassions they fail not As Thou hast been Thou forever will be

Great is Thy faithfulness Great is Thy faithfulness Morning by morning new mercies I see And all I have needed Thy hand hath provided Great is Thy faithfulness Lord unto me

Summer and winter and springtime and harvest, Sun, moon, and stars in their courses above. Join with all nature in manifold witness To Thy great faithfulness, mercy and love.

Great is Thy faithfulness Great is Thy faithfulness Morning by morning new mercies I see And all I have needed Thy hand hath provided Great is Thy faithfulness Lord unto me

Pardon for sin And a peace that endureth Thine own dear presence to cheer And to guide Strength for today and bright hope for tomorrow Blessings all mine, with ten thousand beside

Great is Thy faithfulness Great is Thy faithfulness Morning by morning new mercies I see And all I have needed Thy hand hath provided Great is Thy faithfulness Lord unto me

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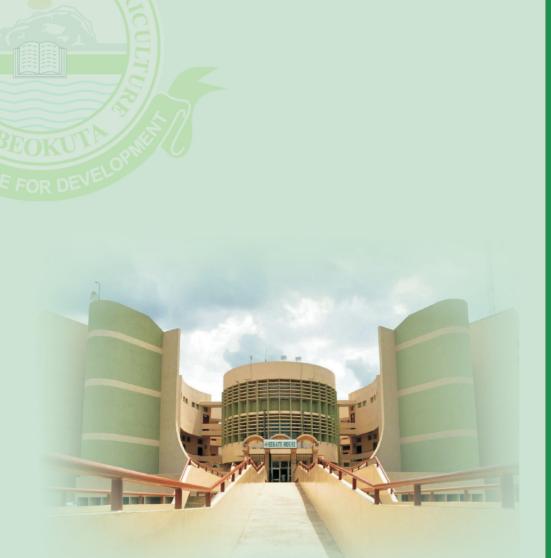
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