

FEDERAL UNIVERSITY OYE-EKITI

1ST INAUGURAL LECTURE

Titled

**THE PLACE OF PLANT OIL DERIVED PRODUCTS AS
SUSTAINABLE REPLACEMENT FOR PETROCHEMICAL
PRODUCTS IN INDUSTRIES**

Delivered by

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The Vice-Chancellor,
Deputy Vice-Chancellor,
The Acting Registrar and other Principal Officers,
Deans of Faculties,
Heads of Departments,
Distinguished Ladies and Gentlemen.

Preamble

I feel extremely humbled by the privilege and opportunity of delivering this inaugural lecture. The uniqueness of my responsibility today is that by sheer Providence, I am delivering the first inaugural lecture of this eight years old University. I therefore heartily welcome all who have come to share with me this joy as I deliver and dedicate this inaugural lecture titled “The Place of Plant Oil Derived Products as Sustainable Replacement for Petrochemical Products in Industries” to the glory of God.

Mr Vice-Chancellor sir, with all sense of academic humility, I seek your indulgence to make a brief historical excursion into my past to illuminate the present. I gained admission into the Federal Polytechnic, Ado-Ekiti in 1988 to study Science Technology. I must say that we had many great Lecturers taking us various courses, but our Chemistry Lecturer in particular was very inspiring in the way he taught us. This particular Chemistry Lecturer was always thrilled by my outstanding performances in Mathematics and Chemistry courses. He therefore took interest in encouraging me and was always commending my efforts, brilliance and my excellent moral behaviour. I completed the Ordinary National Diploma (OND) in Science Technology with an Upper Credit, but rather than encouraging me to go for the compulsory one year industrial attachment before coming back for my Higher National Diploma, this Lecturer took it upon himself to purchase Direct Entry Jamb form, processed it and eventually brought my admission letter to study Industrial Chemistry at the Federal University of Technology, Akure to my parents while we lived in Ilawe - Ekiti. Even though, I

was better in Mathematics, I believed he chose Chemistry for me because he was not only convinced of my ability to excel in the course, but also for his dogged believe that Chemistry is everything. So in my success story, this Lecturer is the one that made a courageous decision. My late father who was a strict disciplinarian (my many uncles present at this gathering would attest to that fact) was immediately convinced of the genuineness of his motives. Others see your deeds, God sees your motives. Motives though invisible are the true test of character. It is motive that gives character to the actions of men. You cannot connect the dots of life looking forward, you can only connect them looking backward and now when I connect my dots backward, I can see that this man and I are Partners by fate. We much later became friends by choice. This man is Prof Emmanuel T. Akintayo. He mentored me all along. Academically, he has been a leader that helped my brilliance to shine and never allowed them to be hidden in his shadow. And, that is how by the grace of God, I took to Chemistry and I stand before this great audience today as a Professor of Industrial Chemistry

Introduction

If or suppose a well informed non-scientist is asked to mention some important scientific advances of the last couple of centuries you would find the reply including such topics as the invention of radio, colour television, laser and computers. When a scientist is asked the same question, the reply will probably include a mention of Maxwell's theory of electromagnetic radiation, the quantum theory, its extension into quantum mechanics and the theory of relativity. Why this remarkable difference in the two sets of answers? It is because there is a serious discrepancy between the public's and scientist's idea of science. Oftentimes, the non-scientists list advances in technology for advances in science (Williams, 1990). Science is studied with the main objective of discovering the earth. Science may be defined as an intellectual activity carried out to discover information about our natural world and to discover the ways the information can be organized into meaningful patterns to discern the order that exist between and among the facts (Gottlieb, 1997).

Chemistry is the study of matter, its properties, how and why substances combine or separate to form other substances and how substances interact with energy. Many people see chemists as scientists in white laboratory coat mixing strange liquids in the laboratory but the truth is that we are all chemists. Chemistry happens in the world around you, not just in a laboratory. Every time you cook or clean, it is chemistry in action. You use chemistry to decide which cleaner is best for your dishes, laundry or your body. Chemical reactions occur when you breathe, eat or read. What is in this world that is not Chemistry? For example;

- plants apply a chemical reaction called photosynthesis to convert carbondioxide and water into food (glucose) and oxygen. This is how plants produce food for themselves, animals and man.
- thousands of chemical reactions take place during digestion.

When you put food in your mouth, an enzyme in your saliva called amylase starts to break down sugars and carbohydrates into simpler forms that your body can absorb. Furthermore, hydrochloric acid in your stomach provides the enabling environment for enzyme pepsin to break protein down, while enzyme lipase cleaves fats so they can be absorbed into your bloodstream through the walls of intestine.

- cutting onions burst its cells and amino acid sulfoxides form sulfuric acid which react with enzymes to produce propanethial S-oxide (C_3H_6OS) a volatile sulphur compound gas that wafts into your eyes as you cut onions. The gas reacts with water in your tears to form sulphuric acid. The sulphuric acid burns, stimulating your eyes to releasing more tears to wash away the irritant.

I have given these few examples to let you know that you are also a chemist.

Recently, there has been an increasing demand for the applications of natural products to address problems in the environment; in waste disposal and in the depletion of non-renewable resources. Renewable resources can provide an interesting sustainable platform to substitute partially and to some extent totally, petroleum based products through the designing of biobased products that can compete or even surpass the existing petrochemical based materials on cost performance basis with a positive environmental impact (Belgacem and Gandini 2008; William and Hillmeyer, 2008; Gallezot, 2012)

The current move of the chemical industry to substitute a growing part of fossil feed stocks with renewable carbon is not only driven by a fear of dwindling fossil resources or global warming, but also by other forces at play. In some cases, the knowledge and technology to process one type of biomass is already available. In other cases, the products may be based on substances with no petrochemical equivalent for example, lactic acid or furfural. Lastly, there is a

general demand for renewable or green products from consumers, exemplified by the plant bottle from coca-cola company. The utilization of renewable raw materials meets the 7th principle of 12th principle of Green Chemistry that contributes to sustainability in chemistry (Anastas and Eghbali 2010). Before the general availability of fossil oil and its fractions, oils and fats of vegetable and animal origin were widely used as illuminant and as lubricants. Eventually the oils and fats used for these purposes were replaced by products derived from fossil oil and its fractions. Lamps now use kerosene, gas or electricity. Lubricants are now based on mineral oils enhanced with a range of additives. However, today there is current drive towards returning to vegetable oils and fats as alternatives to mineral oil-based products. This leads us to the topic of this inaugural lecture “The place of plant oil derived products as sustainable replacement for petrochemical products in industries”

Crude oil

Crude oil is a dark viscous liquid which consists of a highly complex mixture, its main constituents being hydrocarbon (Galadima and Abdulahi, 2014). On a structural basis, hydrocarbon can be divided into 2 main classes viz: (a) Aliphatic (straight chain, branched, open or closed) and (b) Aromatic (cyclic or ringed). Generally, petroleum (crude oil) differs in composition from field to field. For example, Nigerian petroleum is low in sulphur which makes it less polluting. The preparation of useful products from crude oil or petroleum is known as refining where petroleum is processed with heating in a furnace to about 400^oC and then rapidly pumped into fractionating tower to yield different fractions as depicted in Table 1.0 below;

Table 1.0 :- Petroleum fractions at different temperatures and their uses (Galadima and Abdulahi, 2014)

Boiling Point (°C)	Product	Approximate composition range	Uses
Below 20	Gaseous compounds: natural gas, methane, ethane propane, butane	C1 – C4	Fuel, raw material for chemical industries.
20 – 90	Light petroleum	C5 – C7	Solvents
90 – 120	Ligroin (High BP Petroleum ether)	C7 – C8	Solvents
100 – 120	Petrol (Gasoline)	C5 – C10	Fuel for automobile
200 – 300	Paraffin (kerosene)	C12 – C18	Fuel for automobiles, lamp, stove and jet aircraft
300 – 400	Diesel oil	C15 – C25	Fuel (Locomotives)
300 – 400	Lubricating oil	C20 – C24	Lubricants, waxes, vaseline
Above 400	Paraffin wax	C21 – C30	Various uses (candles)
Solid residue	Asphalt (Bitumen)	C40 & above	For road construction and for making roofing

Petrochemicals and products

Petrochemicals are organic compounds (hydrocarbons) or chemicals gotten from petroleum. Petrochemical products are useful in agricultural industries, food industries, pharmaceutical industries, technological industries, and others too numerous to mention. Some of these products and their uses are outlined below:

Table 2.0 :- Petrochemical products and their uses.

Product	End Use (Application)
1. Polypropylene (PP)	a. Injection Molded products for example, battery cases, fan blades, syringes b. Crates:- storage for bottled beverages for example, soft drink, beer

c.	Woven sacks:- sacks for packaging foodstuff for example, rice, millet, animal feeds
2. Alkyl Benzene (AB)	Detergent (liquid & powdered)
3. Benzene	Reagent (solvent)
4. Solvents	Degreasers, metal cleaners, insecticides, odourless paints, dry cleaning agents
5. Heavy Alkylate	Crude oil additives, thermal fluids, transformer oil, etc.
6. Sodium hydroxide	Domestic soap and detergent, enamel ware, bottle washing, glass making, water treatment and vegetable oil refining etc.
7. Polyvinyl chloride (PVC)	a. Extrusive pipes for example, conduits bottles, wires and cable insulation b. Injection molding footwear, household containers, pipe fittings, etc.
8. Low density polythene	a. Extension packaging film for example, polybags, broad wraps, films for textile, craft wraps, etc. b. Non-packaging sheets c. Injection molding: for example, buckets, plates, cups, pen, etc. d. Blow molded products for example, bottles for drugs and cosmetics, squeezable bottles
9. High Density Polythene	a. Extension for example, merchandise bag. b. Infection molded products soft drink crates, household utensils c. Blow molded products for example, industrial drums, jerry cans and other container
10. Carbon Black (CB)	a. Rubber industry for example, tyres, foot wears, gaskets, etc b. Pigments for example, paints, ink, etc. c. thers:- for example, carbon papers electrodes

As enumerated above, the petrochemical products, made entirely out of crude oil and natural gas include a catalogue of useful materials: cloth with the sheen of silk or the fuzziness of wool, cables stronger

than steel: synthetics with the elasticity of rubber, the flexibility of leather, the lightness of paper or the workableness of wood, detergent that wash as well as soap without curdling in hard water, chemicals that can kill dandelions but not grass; repel mosquitoes, but not people; chemicals that can reduce blood pressure or cure tuberculosis, etc

The products from petrochemicals are wonderful and increasingly Chemists succeed in synthesizing new, useful, highly competitive substances. However, most of these substances are cast aside because of their biological hazards: food dyes and fire retardants for children; sleepwear are banned because they may cause cancer; a new industry to produce plastic soda bottles built at a very expensive cost is asked to stop work as the Food and Drug Administration discovers that a chemical which may leach out of the bottle causes tumor in mice; pesticides are taken off market because they kill fish and wildlife; Firemen would like to ban plastic building materials because they produce toxic fumes when they burn. The petrochemical products though largely successful are now caught by forces that threaten its viability and there is a huge cry for biobased chemicals to replace petrochemicals (Barry, 1977).

Why the move towards bio-based chemicals

The transition to biobased chemicals from petrochemicals has multiple drivers:

- The need to develop an environmentally, economically and socially sustainable global economy.
- The anticipation that oil and gas will reach peak production and thereafter decline in not too distant future, leading to increase in prices of petrochemical and derivable products.
- The desire of many countries to reduce dependency on petrochemical products and the need for these countries to diversify their industrial raw material base in a manner that is

consistent with their natural resources abundance.

- The global issues of climate change and the need to reduce atmospheric green house gases emission.
- The need to stimulate regional and rural development (EuropaBio and ESAB 2011, Langeveld et al 2010)

Potential Chemicals from Biorefinery Platforms

Syngas platform

Synthetic gas (syngas) is a mixture of mainly carbon monoxide and hydrogen. It is produced by subjecting biomass to extreme heat (over 430°C in pressure of air), a process called gasification. Syngas can be converted to lower alcohols or fermented to give methanol, ethanol, ammonia and other potential chemical building blocks (Ineosbio, 2011)

C₆/C₅ Sugar platform

Mixed six and five carbon platforms produced from hydrolysis of hemicelluloses or six carbon platforms from hydrolysis of starches or cellulose may:

- undergo fermentation to produce chemicals like succinic acid, itaconic acids, adipic acid, glutamic and aspartic acids
- undergo chemical fermentation like selective dehydration, hydrogenation and oxidation reactions to give useful products like furfural, glucuronic acid, levulinic acid and sorbitol which is used as food ingredient and in personal care product (for example, toothpaste) (ERRMA 2011)

Organic solution platform

A green biorefinery (Kamm et al., 2006) process fresh wet biomass like grass or immature cereals by screw press to obtain two separate intermediates: a nutrient rich juice “ organic solution” and a fibre - rich lignocellulosic press cake. The organic solution portion contains valuable components like carbohydrate, proteins, organic acids, hormones, etc

Lignin platform

Lignin nature structure makes it a good chemical feedstock for the production of supramolecular materials and aromatic chemicals (Hatakeyama and Hatakeyema, 2010, Holladay et al., 2007). Some potential chemical products from lignin are illustrated in Figure 1

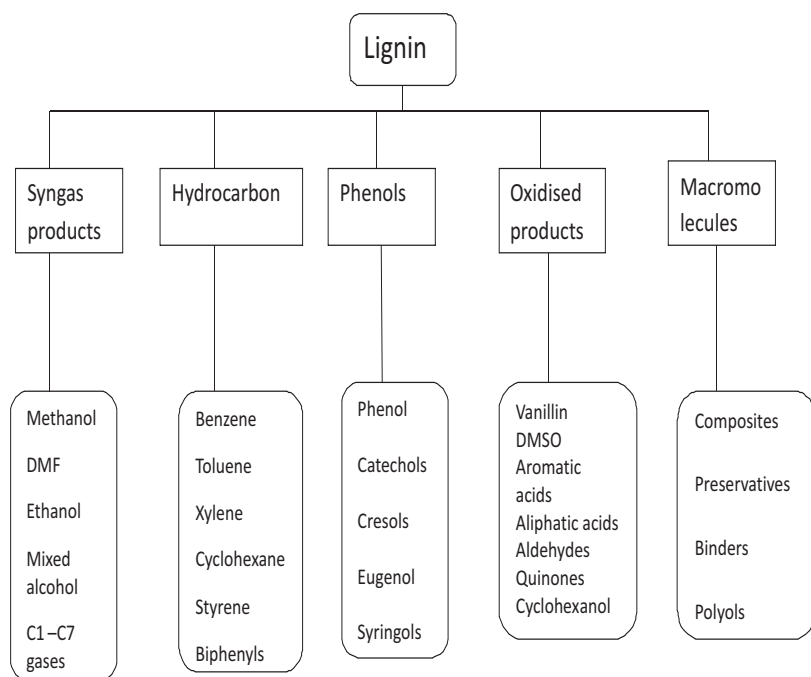


Figure 1.0:- Chemical products from lignin

Plant oils as platform chemicals for replacing petrochemicals

Vegetable oils are considered to be one of the cheapest and most abundant biological sources and their use as platform chemicals to replace petrochemicals has numerous advantages (Guadini 2008; Biermann et al., 2000). Chemists have much to contribute to meet this shift. Classical and well established oleochemical transformations occur preferentially at the ester functionality of the native triglyceride(Baumann et al., 1988; Anneken et al., 2006) to yield free fatty acid and glycerol. The fatty acids may be transformed by reactions at the carboxyl group to soaps, esters, amides or amines. Hydrogenation of the fatty acids or their methyl esters give fatty alcohols. But the fatty acids of plant seed oils show remarkable variety depending on location and weather(Gunstone et al., 2007) and it would be important to clearly understand the composition of a particular oil in order to take full advantage of its utilization to produce bio-based chemicals.

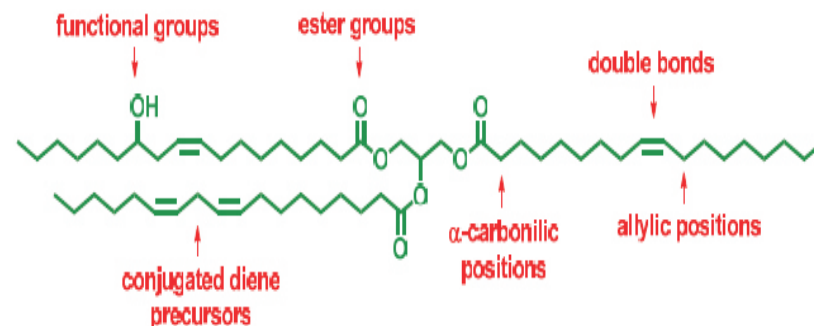


Figure 2.0:- Reactive positions on the triglyceride chains of vegetable oils

Vice - Chancellor Sir, since Nigeria as a country requires development strategies that are consistent with her natural resources endowment, the main focus of my research around producing industrial materials from plant oils have been guided by research activities that may be classified into the following:

- Composition , analysis and chemical transformation of plant oils to plant chemicals.
- Vegetable oil based polymeric materials.
- Polymers and polymer composites from triglycerides oils.

COMPOSITION, ANALYSIS AND CHEMICAL TRANSFORMATION OF PLANT OILS TO PLATFORM CHEMICALS

The word “oil” is used for triglycerides that are liquid at ordinary temperatures. They are water-insoluble products of plants. A triglyceride is an ester product obtained from one molecule of glycerol and three molecules of fatty acids as represented in Figure 3

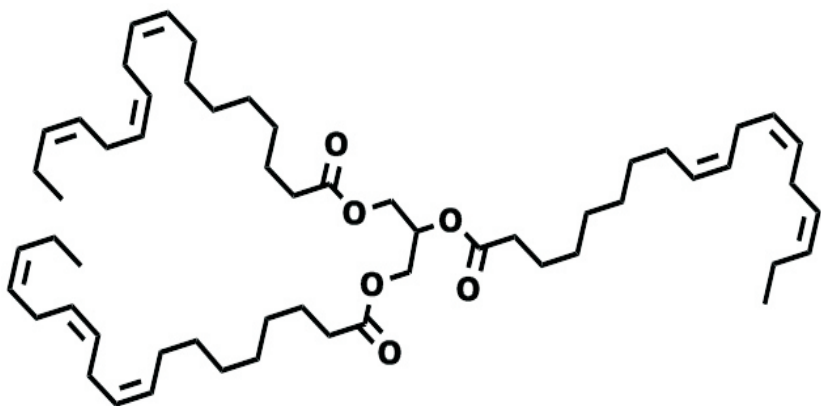


Figure 3.0: BASIC TRIGLYCERIDE STRUCTURE

The fatty acids contribute 94-96% of the total weight of one molecule of triglyceride (Gunner et al., 2001). The composition of the fatty acids contained in the oil (that is, fatty acid spectrum) determines the further use of the oil. Many techniques like gas chromatography (Parcerisa et al., 1993), high performance liquid chromatography (Itabashi et al., 1993,) and super critical fluid chromatography (Lee et al., 1991) have been used to establish the fatty acid composition of oils. However we have been able to show that Carbon-13 nuclear magnetic resonance (NMR) technique is a more adequate method for defining the composition of oils (Akintayo et al., 2004a, Akintayo et al., 2004b). The superiority of the Carbon -13 NMR technique derives from the fact that the NMR gives a spectrum where each nucleus is represented by a peak at a particular frequency and the area under a peak arising from each Carbon 13 nucleus is proportional to the number of nuclei in that environment under certain experimental conditions. Akintayo et al. 2004a reported that gated decoupled ¹³C NMR employed to determine the acyl composition and acyl positional distribution on the glycerol backbone of the triacylglycerol of *Jatropha curcas* oil revealed the presence of saturated, oleic and linoleic acids. Integrals obtained from the allylic carbons when used for semi quantitative analysis of oil gave the percentage of total saturated , oleic and linoleic acids in the oil as 27, 41 and 32 respectively. In the same vein high resolution Carbon -13 NMR of *Adenopus breviflorus* oil (Akintayo et al., 2004b) revealed the percentage composition of the oil as saturated 25%, oleic 14% and linoleic 60%. The spectra further revealed that while the saturated fatty acids were distributed between 1,3(α) and 2(β) glyceridic positions, oleic acid was attached only at the α glyceridic position while linoleic was attached at the β glyceridic position. Adubiaro et al. (2013) also used ¹³C and ¹H NMR spectroscopic analysis to compare the fatty acid composition of *Adasonia digitata*, *Albizia lebbek* and *Daniellia oliveri*. Results showed that the peaks at 0.7ppm and 0.9ppm which correspond to the terminal methyl groups in the fatty acid were more intense and bigger in the *Daniellia oliveri* implying that it is more saturated than *Adasonia digitata* and *Albizia lebbek*. In the same vein, Olatunya et al. (2015) carried out qualitative

and quantitative analyses of the fatty acid composition of *Parkia biglobbosa* oil using ^1H NMR and ^{13}C NMR respectively. The results confirmed the spectroscopic methods are as accurate as gas chromatographic methods for fatty acid compositional analysis. A busy laboratory may therefore find the spectroscopic methods more suitable for fatty acid analysis because they are less time consuming and not as laborious as the conventional gas chromatographic methods.

We also tried to improve on the compositional analysis of triacylglycerol (TAG) of plant oil as the traditional method of gas chromatography as mass spectrometry cannot detect the actual TAG composition. In this regard, Akintayo et al. (2009) applied the matrix-assisted laser desorption ionization (MALDI), time of flight (TOF) mass spectrometry (MS), a fast and easy method to determine the TAG composition of some curcubital species oils. The method provides the actual molecular distribution of the TAGs in the oils for example, bottle gourd oil contains four major TAGs, Trilinolein (LLL), palmitoyl dilinoleoyl (PLL) oleoyl dilinoleoyl (OLL) and dioleoyllinoleoyl(OOL) while snake gourd oil showed three major TAGs as tripucinin (PPP), palmitoyldilinoleoyl (PLL) and distearoylloleoyl (SSO).

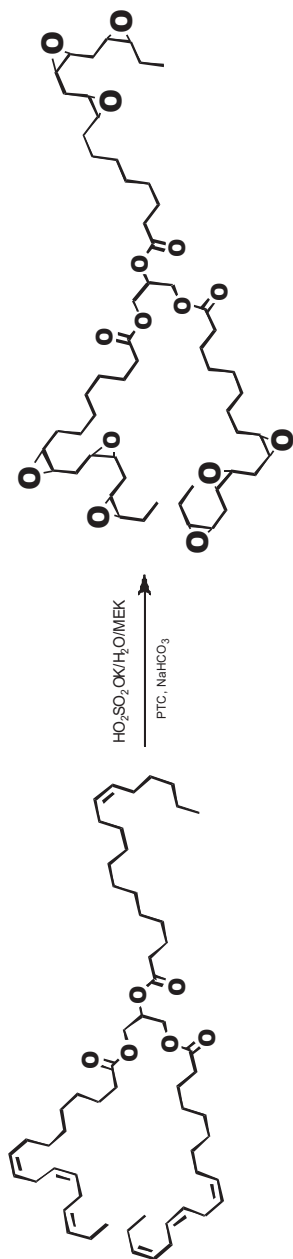
Mid-infrared spectroscopy has not been a popular choice for the study of fats and oils because some authors have observed similar infrared spectra from different vegetable oils. We however affirmed that subtle dissimilarities exist between infrared spectra of oils and these differences contain a great wealth and variety of information about the composition of the oil sample. Specifically, the bands at approximately 3008cm^{-1} , 1098cm^{-1} , 2924cm^{-1} and 2854cm^{-1} in the Fourier transform infrared (FTIR) spectra of vegetable oils could be effectively used to determine the nature of oils (Akintayo et al., 2002a). Though, amount of each fatty acid present might be difficult to ascertain from the FTIR spectra for now, at least, level of unsaturation could be predicted.

Akintayo et al. (2002b) also reported a Proton NMR technique of determining the percentage of conjugated bonds in isomerised oil. Results obtained by the ^1H NMR method agreed perfectly with that obtained by the conventional Ultra Violet spectroscopy method.

Epoxidised oils

Plant oils have continued to serve as excellent renewable source for the chemical industries. This is particularly due to the fact that vegetable oils offer a non-toxic, non polluting bio-degradable alternative with attendant manufacturing benefits for the chemical industries. In most cases however, the relatively un-reactive oils have to be functionalized to enable them serve as building blocks for various industrial products. The functionalization can be at the carboxyl group or on the alkyl chains of the oil. Presently, there is tremendous progress along the lines of the later types of reactions with their potential for considerably extending the range of compounds obtainable from oils and fats (Biermann et al., 2000). Epoxidation is one of the major types of functionalization of the oil occurring on the alkyl chain. It is the formation of an oxirane group by the reaction of peracid with olefinic or aromatic bonds. Akintayo et al. (2005) determined the level of epoxidation of canola oil using ^1H NMR technique and found that maximum epoxidation took place after 8 h of reaction time. The epoxidation was carried out by reacting the oil with formic acid and hydrogen peroxide.

Epoxidised oils are very versatile industrial materials that may be used as plasticisers and stabilisers on polyvinyl chloride synthesis due to the heat and light stability imparted by the oxirane group (Akintayo, 2007; Gan, 1992). Epoxidised oils are also commonly used as starting materials to produce polyols, prepolymers in surface coatings and to synthesize polyurethanes.



Reaction scheme 1.0 : Typical epoxidation reaction of vegetable oil

Derivatives of Epoxidised oils

Alkoxyhydroxyl triglycerides (AHTG) have been found of immense importance industrially. They serve as useful emollients providing excellent skin care benefits in soap bars (Yarovoy et al., 2003), good fat substitutes for fat liquoring of leather (Schenkar and Rudolf 1997) and as emulsifiers in liquid detergents (Weerasooriya, 2000). Presence of hydroxyl groups in oils have been found to facilitate plasticization and adhesion of the triglycerides properties which are useful in a variety of applications such as plastics, inks and adhesives. The hydroxyl groups may also afford increased lubricity (Naughton, 1992). Akintayo and Akintayo (2007) studied a process for the production of alkoxyhydroxylated canola oil by epoxidising the oil followed by acid catalysed reaction of the epoxidised oil with desired alcohol, methanol, ethanol, propan - 2-ol and t-butyl alcohol in the presence of an acid catalyst. The higher the alcohol, the longer the time required for effective alcoholysis of the epoxidised oil. All the hydroxylated products had low flow point suggesting their application as lubricants.

Preparation of azido compounds from aliphatic and aromatic epoxides obtainable from petrochemicals are popular (Metzger and Furmeier 1999; Sabitha et al., 2002). Such compounds are good starting materials for preparing nitrogen heterocycles. In order to replace petrochemicals in this regard, we have successfully prepared azido compounds from a vegetable oil source, *Adenopus breviflorus benth* oil via epoxy cleavage (Akintayo et al., 2006). The azido compound prepared was an appealing straight forward access to preparation of vicinal hydroxyl triglyceride which is very versatile in the surfactant industries.

Petroleum derived polyols have been widely used in the manufacturing of polyurethane foams. Our interest is to replace the petrochemical with a renewable source like vegetable oil. Usually, hydroxyl groups have been introduced into vegetable oils through a two-step synthesis involving the epoxidation of unsaturated sites

with formic acid and hydrogen peroxide followed by epoxy ring opening (Monteavaro et al., 2005; Guo et al., 2000). Depending on the reaction conditions, polyols with high hydroxyl functionality (complete reaction) or epoxy-polyol esters with remaining epoxy groups (partial conversion) are obtained (Monteavaro et al., 2005). The epoxy-polyol esters were of interest to us because of their better oxidative stability. We therefore developed epoxy-polyol from *Jatropha curcas* oil (Akintayo et al., 2013) and the product had a high thermal stability.

The 1,5-sigmatropic rearrangement of the allylic hydrogen of an alkene (an 'ene') and a compound containing a multiple bond (an enophile) was first reported in by Alder (Alder et al., 1943). This six-electron pericyclic process is now known as Alder – ene reaction (Evan and Johnson, 2000). The reaction is compatible with many functional groups and has been widely used for the synthesis of complex molecules and natural products. The ene –reaction when applied to unsaturated plant oil triglyceride (Eren and Kusefoglul, 2004) was found not to consume the triglyceride unsaturation, but causes only the double bond to shift one carbon away that is, the migrating double bond is isomerized from the cis to the trans-geometry and becomes available for further functionalization under free radical conditions. Akintayo and Clark (2014) exploited this route to introduce acrylates and maleates moieties into the structure of *Jatropha curcas* oil and synthesized the maleinised and hydroxymethylated and acrylated hydroxymethylated *Jatropha curcas* oil. The possibility of appending polymerizable groups onto the triacylglycerol molecule of *Jatropha curcas* oil opens way for the pursuit of preparing polymers from the oil, thus extending the commercial viability of the oil.

Monomers derived from botanical sources are increasingly becoming attractive (Grivello and Narayan 1972). This is because polymers that would result from them would be environmentally friendly especially when the monomers could be converted to polymers using environmentally friendly techniques. Most vegetable

oils do not yield homo or copolymer by a radical initiated polymerization because the internal cis double bonds are too unreactive for polymerization. Also the allylic position and the naturally occurring tocopherols in the oil are excellent chain transfer agents and free radicals inhibitors (Eren and Kusefoglul 2004). To convert plant oil to a useful monomer therefore it must be suitably functionalized. Continuing with our efforts to functionalize some Nigerian oils, Akintayo et al. (2006) and Akintayo and Akintayo (2007) synthesized bromoacrylated and acrylated hydroxybrominated *Jatropha curcas* oil. These products apart from being able to polymerize through the reactive acrylate group, it was also expected that the presence of bromine should impart considerable flame resistance to polymers eventually prepared from them.

VEGETABLE OIL BASED POLYMERIC MATERIALS IN COATINGS

Surface coatings are materials applied normally in liquid form to substrates ranging from wood, metals and building surfaces (plaster, concrete), to plastics and composite materials (Gunstone and Hamilton, 2001). Coatings protect and decorate, often in equal measure, also identifying or disguising, providing light reflection or even hygiene in the form of cleanable surfaces. The commonly used polymeric materials in coatings include alkyd, polyetheramides, polyesteramides and polyurethanes.

Alkyds

Alkyds were first synthesized in mid 1920s by Kienle and introduced in the 1930s as binders for paints. Alkyd resins, a class of polyester coatings are derived from the reaction of a polyol, a polyvalent acid or acid anhydride and fatty acid derivatives. Alkyd paints have dominated the architectural coating market for a long period until the appearance of polymer dispersion called latex paints. Though, some new polymeric composition have replaced alkyds, wood and metal

application alkyd paints continued to be very popular. This has triggered extensive development of traditional alkyd as well as development of new types of coating systems emerging from alkyds. Some of the main issues for traditional alkyds are reduction of drying times, new drier systems as a replacement of cobalt driers, reduced dark yellowing, improved film properties and fire retardant ability. Akintayo and Adebawale (2004a) investigated the synthesis of acrylated *Albizia benth* medium oil alkyd via a monoglyceride method. Results revealed that the acrylated resin exhibited improved characteristics in terms of drying time, flexibility and adhesion, scratch, impact and chemical resistance.

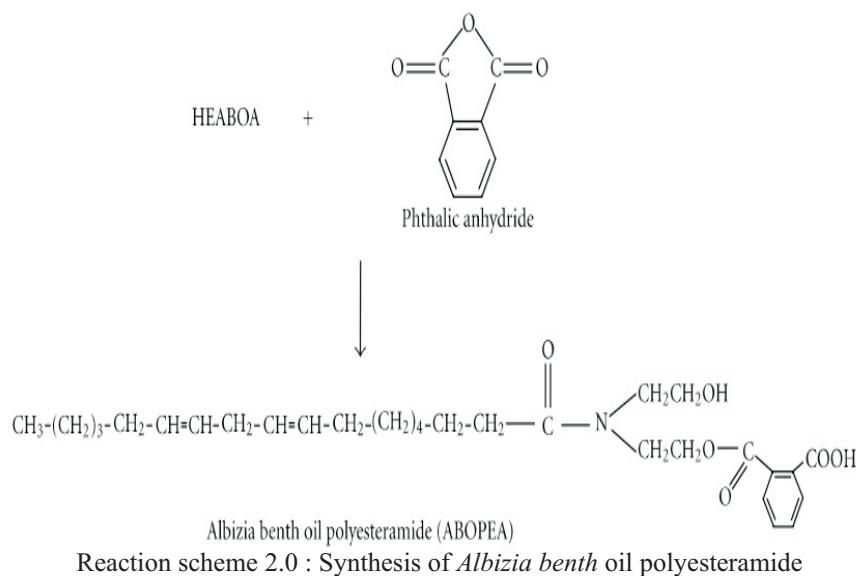
A good remedy to enhancing the durability of alkyd paint is to improve its weather resistance through chemical modification with acrylic resin. This way offers the possibility of combining the desirable application and film forming properties of the alkyd with the weathering and general resistance properties of acrylic systems. Flame retardants alkyd paints are also becoming popular for various reasons. A technique for preparing flame retardant polymer is based on the scavenging of radicals formed during combustion. This can best be achieved by halogenated compounds. Among halogens, fluorine cannot be used for flame retardance because of its very high electronegativity and thus difficulty in breaking its bonds. Iodine however is a very large atom and can easily separate from compounds its bonded to even at low temperature. Therefore, chlorine and bromine are the best radical scavengers (Gunduz et al., 1999). We synthesized chlorinated alkyd by direct chlorination of *Albizia benth* oil (ABO) alkyd of 50% oil length (Akintayo and Adebawale 2004b). It was confirmed by infrared spectroscopy (IR) that chlorine entered only into the aliphatic portion of the alkyd chain by addition and substitution reactions. The results revealed that the chlorinated resins possessed superior drying properties, scratch hardness, water, acid and alkali resistances than the unchlorinated alkyds. However, the flexibility and adhesion of the alkyd decreased on chlorination.

In order to further improve on the water, alkali and solvent resistance of alkyd resin when compared to other film formers, (Akintayo,

2006) studied the styrenation of *Albizia benth* oil medium alkyd. The styrenated alkyd obtained combined the film forming characteristics of an alkyd resin and the weatherability and chemical resistance of the styrene monomer.

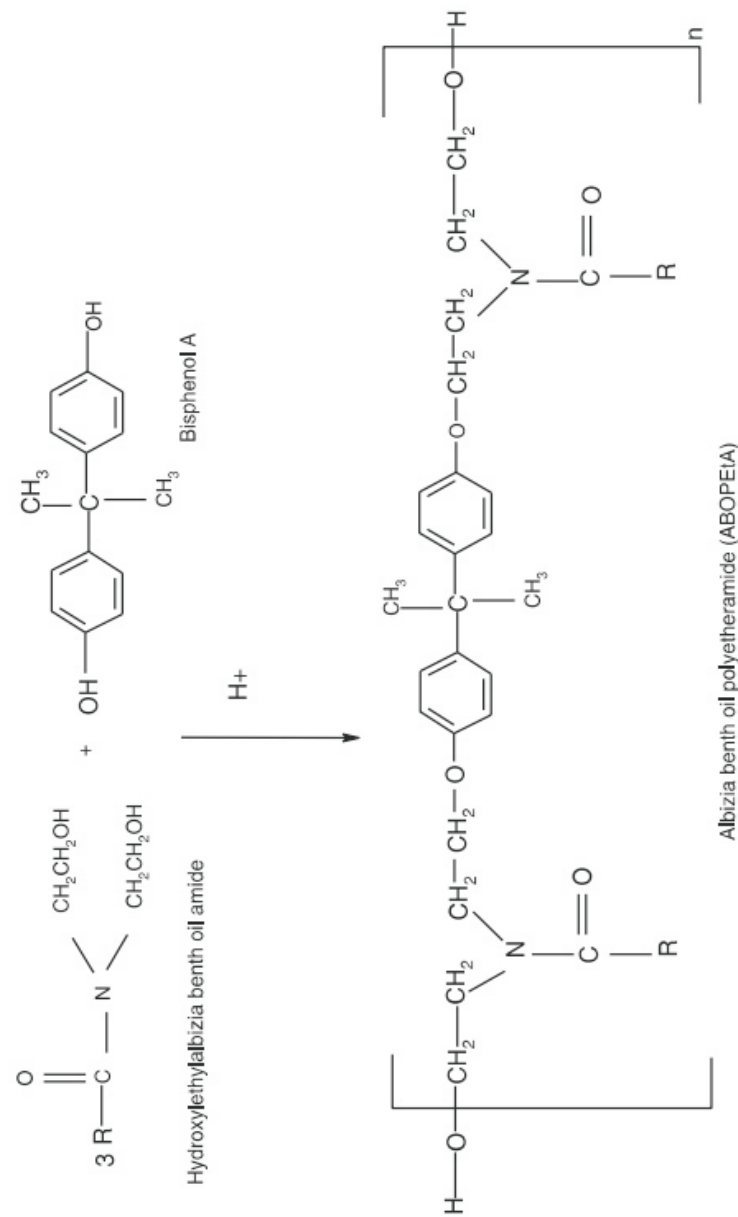
Polyesteramides

Polyesteramide (PEA) is modified alkyd containing repeating ester and amide units in their backbones and possess improved properties over alkyds such as hardness, ease of drying, water vapour resistance and resistance to chemicals, especially alkalis. In consonance with the aim of replacing petrochemicals with renewable resources, Akintayo et al., (2012) employed *Albizia benth* oil in the preparation of polyesteramide resin via the condensation of hydroxyethylamide derivatives of ABO fatty acids and phthalic anhydride. A malenized *Albizia benth* oil polyesteramide was prepared using malenized hydroxyethylamide derivatives of ABO and phthalic anhydride. The maleinated polyesteramide had improved properties such as drying, flexibility, scratch hardness, impact resistance, chemical resistance and lower curing temperature.



Polyetheramides

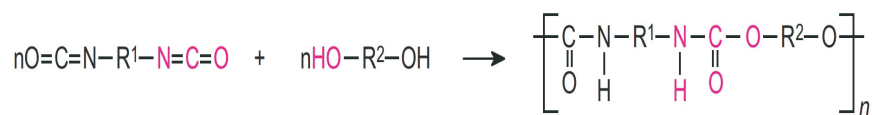
The polyetheramide (PE_rA) is another form of modified alkyd that contains ether and amide groups in its backbone, which provides adhesion and chemical resistance for the resulting coating. Akintayo and Akintayo (2010) reported the use of an under-utilized seed oil, *Albizia benth* oil for the preparation of polyetheramide and acrylated polyetheramide which when applied on mild steel strips showed improved mechanical behaviour and protective efficiency in acid, alkali and extreme weather conditions when compared with the coatings prepared from conventional alkyd resins. These newly developed polymeric materials could therefore be used as anticorrosive coating material. Adeniyi et al., (2017) carried out computational study to examine both the atomic and molecular changes that resulted in the improved resin properties for urethanated polyesteramides developed using *Albizia benth* oil in order to provide some insights into the improved qualities of the resin observed experimentally. The computed properties clearly showed that the urethane linkage group in urethanated *Albizia benth* oil polyetheramide (UABOPE_rA) acted as a strong electron withdrawing group, consequently causing the rest of the molecule to be nucleophilic. This leads to increase in the stability and hydrophobicity of the UABOPE_rA.



Reaction scheme 3.0 : Synthesis of *Albizia benth* polyetheramide

Polyurethanes

Polyurethanes are versatile plastic materials. The nature of their chemistry allows polyurethanes to be adapted to solve challenging problems e.g to be molded into unusual shapes; to enhance industrial and consumer products by adding comfort, warmth and convenience to our lives. It does not matter where you look, you are likely to find polyurethanes. Polyurethanes can be found in mattresses, couches, insulation, liquid coatings and paints, tough elastomers such as roller blade wheels, soft flexible foam toys, some elastic fibers, and many other places.



Reaction scheme 4.0: Formation of Polyurethane from polyol and poly isocyanate

As shown in the reaction scheme 4, polyurethanes are formed by reacting a polyol (an alcohol with more than two reactive hydroxyl groups per molecule) with a diisocyanate or a polymeric isocyanate in the presence of suitable catalysts and additives. The physical properties, as well as the chemical structure, of a polyurethane depend on the structure of the original reactants, in particular the R¹ and the R² groups. The characteristics of the polyols - relative molecular mass, the number of reactive functional groups per molecule, and the molecular structure - influence the properties of the final polymer, and hence how it is used. Siyanbola et al., (2016) prepared polyurethane from *Thevatia peruvianah* seed oil and evaluated the product for its antimicrobial and anti-corrosive properties. The non drying nature of the *Thevatia peruvianah* oil made the partial glyceride urethane prepared from it to be brittle at low isocyanate incorporation. The urethanes were however of good thermal stability and exhibited good antimicrobial and anticorrosive properties.

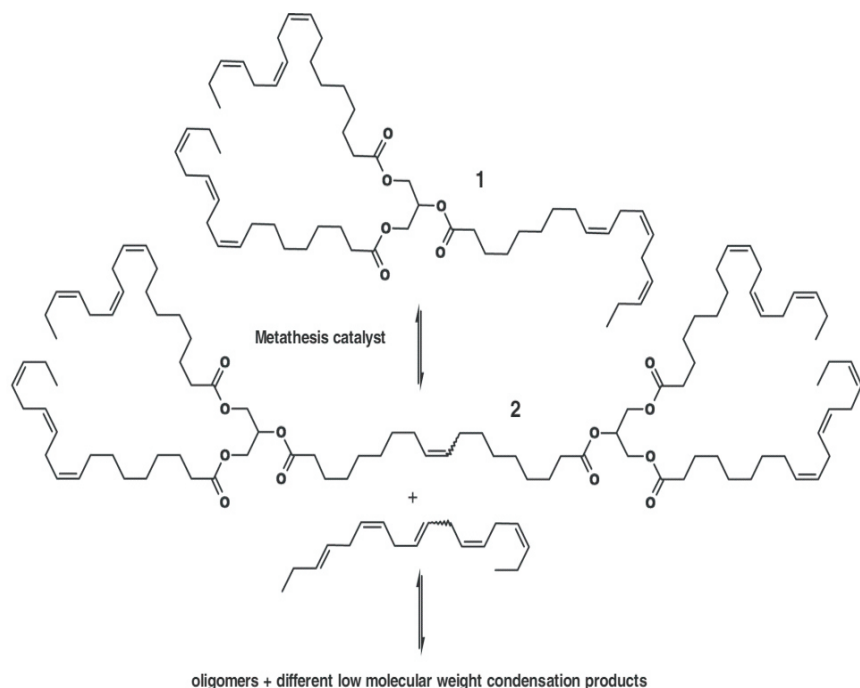
Lubricants

Vegetable oils have proved to be excellent lubricants and functional fluids (Willing 2001) due to their low volatility, high molecular weight of the triacylglycerol molecule, narrow range of viscosity change with temperature, good lubrication characteristics which may be attributed to the polar ester group and high solubility power for polar contaminants and additive molecules (Sharma et.al 2009) . In spite of the above enumerated advantages of vegetable based oil lubricants, the high degree of unsaturated fatty acid in the composition of many vegetable oils however causes them to have low thermal and oxidative stability (Akintayo, 2007). Sharma et al. (2006) had reported a novel synthetic approach for introducing sulphur containing compound at the double bond of triglycerides as organic sulphur compounds have been widely used in improving the thermal and oxidative stabilities of lubricants. Akintayo et al., (2015) therefore reported the synthesis of thioether hydroxyl derivative of *Plukenetia conophora* oil. Because of the high level of unsaturated sites in *Plukenetia conophora* oil, the resulting derivative from the oil possess potential for application in formation of lubricants and industrial fluids.

POLYMERS AND POLYMERIC COMPOSITES FROM TRIGLYCERIDE OIL

Polymer and polymeric composite materials have uses in aerospace, automobile, marine infrastructure, military, sports and industrial fields. These light weight materials exhibit excellent mechanical properties, high corrosion resistance, dimensional stability and low assembly cost. Polymers and polymer composites are popularly derived from petroleum sources, but as the number of applications increases, alternative sources of these materials become more important (Khot et al., 2000). The polymer obtained from natural oils are biopolymers in the sense that they are generated from renewable natural sources, they are often biodegradable as well as non-toxic, so such materials have environmental as well as economic advantages (Vaidya et al., 2012.)

Although more than 95% of all chemical reactions of triglycerides or the fatty acid esters are carried out at the carboxy function, transformation of unsaturated fatty acid esters by reactions of the carbon-carbon double bond such as hydrogenation, epoxidation, ozonolysis, hydroformylation and dimerization are becoming increasingly of industrial importance. Olefin metathesis offers another reaction at the carbon-carbon double bond that is much less explored as the reactions discussed above. Generally, olefin metathesis is a catalytic exchange reaction between two alkene molecules during which two alkylidene groups are interchanged as generally represented in Reaction scheme 5.0



Reaction scheme 5.0 : Olefin metathesis reaction

Akintayo et al., (2012) investigated the acyclic triene metathesis polymerization of *Plukenetia conophora* oil (walnut oil) to produce branched polymers. The oil which consists mainly of linolenic acid was polymerised via acyclic triene metathesis using different ruthenium benzylidene and indenylidene catalysts to yield highly branched and functionalized polyesters. The approach allowed the preparation of polymers that are fully along the lines of green chemistry. The imperfectly branched tree-like polymer structures were shown to have special structural and rheological properties that might lead to potential applications in various areas such as rheology modifiers and drug delivery.

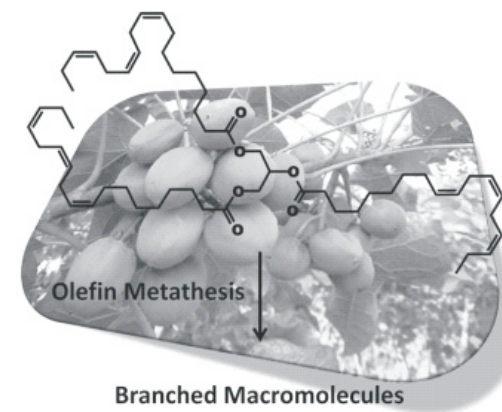


Figure 4.0: Branched Polyester of PKCO

Akintayo et al., (2015) also prepared a variety of new polymers ranging from soft to hard plastics by cationic polymerization of *Adenopus breviflorus* oil with styrene and divinyl benzene initiated by modified boron trifluoride etherate. The fully cured thermosets were found to contain between 78-92% cross linked materials that ranged from soft rubbers to hard plastics.

ANALYSIS AND APPLICATION OF SOME RENEWABLE RESOURCES

The consumption of cereal based foods such as biscuits and bread is very popular in Nigeria. These foods therefore provide an excellent means of improving nutritional quality through incorporation of vegetable proteins. Akintayo and Akintayo (1998) investigated the nutrient composition and susceptibility of biscuits fortified with pigeon pea flours. This was an effort to use legume proteins to increase the protein content of a cereal based food. Result revealed that pigeon pea flour could replace 35% of the wheat flour in biscuit formulation without adversely affecting sensory qualities and use of pigeon pea flour at this optimum level also increased protein and energy levels by 18.9 and 1.7 per cent respectively.

African yam bean (*Sphenostylis stenocarpa*) (AYB) is a widely cultivated legume in Nigeria and many other tropical countries. It is an important source of protein and dietary fibre (Aletor and Aladetimi, 1989). It is consumed in a variety of ways which include boiling rehydrated dry or fresh seeds alone or in combination with other foods like yam, plantain or maize. It however takes a long time and therefore excessive use of firewood or fuel to cook. In order to reduce cooking time and improve flavour and texture of this legume, Nigerians employ the use of kaun (trona) to tenderize AYB. Akintayo et al., (1999) studied the quality changes and mineral composition of AYB cooked in kaun solution and established the optimal cooking conditions (that is, best kaun concentration and minimum cooking time to achieve optimal quality) as 0.1% and 90 minutes respectively. Cooking at these optimal conditions were found to increase concentrations of Zn, Cr, Fe, Na and K in both the cooked beans and leached solids but decreased the concentration of Mg and Cu in the cooked beans.

In order to successfully introduce a new supplement into any food items, it is necessary to find out whether the supplement possesses appropriate functional properties. The flavour and functional

properties of food systems have been found to be impaired when legumes flours are used in large quantities as food supplements. To overcome this inadequacy, protein of the legume flour have become increasingly attractive as protein supplements as they have low flavour profiles and relative freedom from toxic factors and indigestible carbohydrate (Berk, 1970). Akintayo et al. (2000) did a comparative study on the functional properties of some Nigerian underutilized legume flour and protein concentrates and found out that the legume protein concentrates had higher protein solubility, foaming, emulsion, water and oil absorption capacities than the flours.

The current demand from starch is met by restricted range of crops, the most important of which are potatoes, maize, wheat and tapioca. The grain legumes are also recognized as important source of starch (Deshpande and Damodaran 1990). In our further effort to reveal the potentials of AYB, Akintayo (2008) investigated the preparation, composition and physicochemical characteristics of native and physically modified AYB starches. The hydrothermal treatments improved gelation capacity and amylase content while it decreased swelling and solubility of the AYB starches. Results further revealed that the process of annealing and heat moisture treatment can be selectively used to impart processing characteristics onto native AYB, thereby making the starch more versatile for industrial purposes.

As discussed above, starch modification may involve the alteration of the physical and chemical characteristics of the native starch to improve its characteristics. Chemical modification in particular can be used to tailor starches for application in a particular process (Hermansen and Svegmak, 1996). Akintayo and Akintayo (2009) investigated the preparation, composition and physicochemical characteristics of native, oxidized and acetylated African yam bean starches. We found that acetylated starches and highly oxidized starches had reduced gelatinization enthalpy and temperature. Such modified starches could therefore be employed in processes where a

thickening agent must gel at lower temperature. However slight oxidation of AYB starch led to increased swelling, increased initial pasting temperature and peak viscosity and higher gelatinization temperature. Such starch may find application in deep fried foods.

Starches are widely used in pharmaceutical tablets and fillers, binders and disintegration (Biliaderis, 1991). Afolabi et al. (2012) investigated the physicochemical and tableting properties of native, acetylated and oxidized finger millet starches with the objective of revealing its industrial potentials most especially as excipients in the pharmaceutical industries. Results obtained showed that the higher bulk and tap densities of acetylated and oxidised finger millet starch compacts enhanced the filling during tableting since high bulk volume is required in tablet formulation. The high bulk and tap density of oxidized finger millet starch coupled with its high flowability and solubility may find useful application as fillers in capsule formulations. The acetylated finger millet starch may also find wide application as pharmaceutical excipient when fast disintegration time and high crushing strength are desired..

Fibers like coir, oil palm bamboo and banana have proved to be very good and effective reinforcement in thermoset and thermoplastic matrices (Hornsby et al., 1997). Systematic studies of coir fibres in countries like India and Brazil have revealed differences in the properties of coir as a function of varieties, areas of production, climate etc (Silva et al., 2000). In order to properly evaluate coir, extracted from Nigerian grown coconut, Akintayo et al., (2016) investigated the spectroscopic, mechanical and thermal properties of native and modified Nigerian coir fibres. Results revealed that tensile strength and elongation of break of the fibres increased on chemical modification by acetylation, oxidation and mercerization. Thermal stability of the fibre also improved on chemical modification.

The physical properties of agricultural materials are necessary for the design and development of machines to be deployed for their processing. Olatunji et al. (2011) analysed for unit mass, unit volume,

true density, geometric mean diameter, bulk density, sphericity, porosity and projected area of *Thevattia peruvianah* seeds. The results obtained are useful for designing machines for the processing of the seeds for oil and flour extractions.

Recommendations

1. Nigeria being a tropical country is blessed with wide varieties of plants (trees, shrubs and vegetables) that produce oil bearing seeds. Because of the abundance of these oils, they are ideal alternative chemical feedstock for our industries. We therefore need to elevate our nation Nigeria from the present low level mono-product economy based on a non-renewable natural resource (crude oil) to a highly reliable and more desirable level of diversified economy based on systematic utilization of our renewable natural resources which include our local plant resources.
2. A modern bio-based chemical plant is capital intensive. In a developing country, it almost means that government must play a dominant role in providing funds for such project. If Nigeria will give priority of reserving some oil earnings to the development of a bio-based chemical plant instead of “prestige” projects that are without adequate social benefits to the common man, then the necessary finance can be raised. I venture to say that a large bio-based chemical plant satisfying most of the local chemical needs is an urgent requirement which is good for national prestige and is therefore worth making sacrifices for, even if it is only making modest profits. There is no reason why it may not make reasonable profits. Such bio-based chemical plant would reduce unemployment and stabilize our economic recessions and increased demands in the chemical industry of the developed world would not affect our access to chemicals.
3. Nigeria should invest more in her Universities especially in the area of research. For example, chemical research is a major factor on which chemical industrialization of the country would depend. It is research that will improve the existing technology that we are making current use of. Research will solve the day to day problems of the industries in the country. It will also look into problems of how currently

used raw materials can be replaced by other more abundant ones, especially those available locally

4. Given the high level of unemployment in Nigeria today, our industrial development should be tailored along labour intensive, classically low technology industries like bulk chemicals, iron, steel and other metal fabrication, cotton and leather, power generation and value addition industries like soap, paint, sugar, etc. Later, after overcoming the unemployment challenge, then labour saving, high technologically oriented chemical industries may be focused on.
5. To emphasize the theory and practical works as related to industrial products, the Chemistry curricula in our Universities will have to be drastically modified to emphasize industrial products and processes, industrial economics and more industrial visits and attachments to fit our graduates more into what new job opportunities will become available to them.
6. Mr Vice-Chancellor Sir, I will like to implore you being a classic academic, to add another feather to your cap of achievements for FUOYE by building and equipping a Central Research Laboratory to cater for interdisciplinary research. This will assist academics here and around here to be able to impact properly on our students, and make money for the university through laboratory services and society at large. University is not just a place where teachers teach what they were taught, Lecturers should have access to research facilities to do research and advance the frontiers of knowledge and teach their students also about their research findings.

7. My appeal to developing nations; in the end, Science and Technology among us is our responsibility. We must realize that our men and women of science are our precious assets. Prize them; give them opportunities, responsibilities for scientific and technological development of their own countries. At present, even the small numbers that we have are under-utilized. However the goal must be to increase their number tenfold, to increase the amount spent internally on Science and Technology tenfold. Science is not cheap and we must not also forget that technology in the conditions of today cannot in the long run flourish without science flourishing at the same time.

ACKNOWLEDGMENT

Mr Vice-Chancellor sir, I thank first and foremost God Almighty for ordering my steps in life and making me to address an august occasion like this today and also for giving me a very wonderful family. God has been so merciful and gracious to me and I am most grateful to Him.

My avalanche of gratitude goes to my father and mother (late Pa Luke Oyelami Ogundiran and Mrs Margaret Ogundiran) for their moral, financial and emotional investment into my life. The kind of discipline (administered with love) you meted to me and my siblings while we were young now means a lot to us as it has helped us to cut out a responsible niche for our lives. Thank you to all my siblings and their families, my elder brother, Deji Oyelami, and younger ones, Rev Fr. Antony Oyelami, Segun & Bisi, Lekan & Kehinde, Femi & Kemi and Drs Bayo (our all rounder last born) and Funmi Oyelami for all your supports and encouragements. I want to place on record that we had too many grown up relatives (about 18) living with us at most times while I was growing up in my father's house. I therefore didn't have opportunity of cooking much in the kitchen because I was seen as too young and anyway, there were too many skilled cooks in the house for them to allow me try my hands on cooking. Then it happened that I had to spend my holiday at my aunt's place in Ibadan after my Polytechnic education and it was there that my poor cooking skills got exposed. But my big mummy (Mummy Ibadan), Late Mrs Adewumi Rachael took up the task. For my poor cooking skill, she made me to serve the punishment of being the only one to cook for her whole family for about one and half months. Not only did my cooking skills improved, I also took interest in kitchen affairs. Kitchen chores became part of my life and I owe my adeptness in cooking today which my husband cherishes so much to her. My sincere appreciation goes to her for building in me one of the major skills a woman needs to have a stable home.

My appreciation goes to my Vice-Chancellor, Prof. Kayode

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Let me specially appreciate Prof Dipo Kolawole, former Vice-Chancellor of Ekiti State University for believing in me and facilitating my crossing over from the Polytechnic to the University system in 2008. In the same vein, I acknowledge Prof Chinedu Nebo, the first Vice-Chancellor of Federal University Oye - Ekiti, for his encouragement and support for my research endeavour.

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