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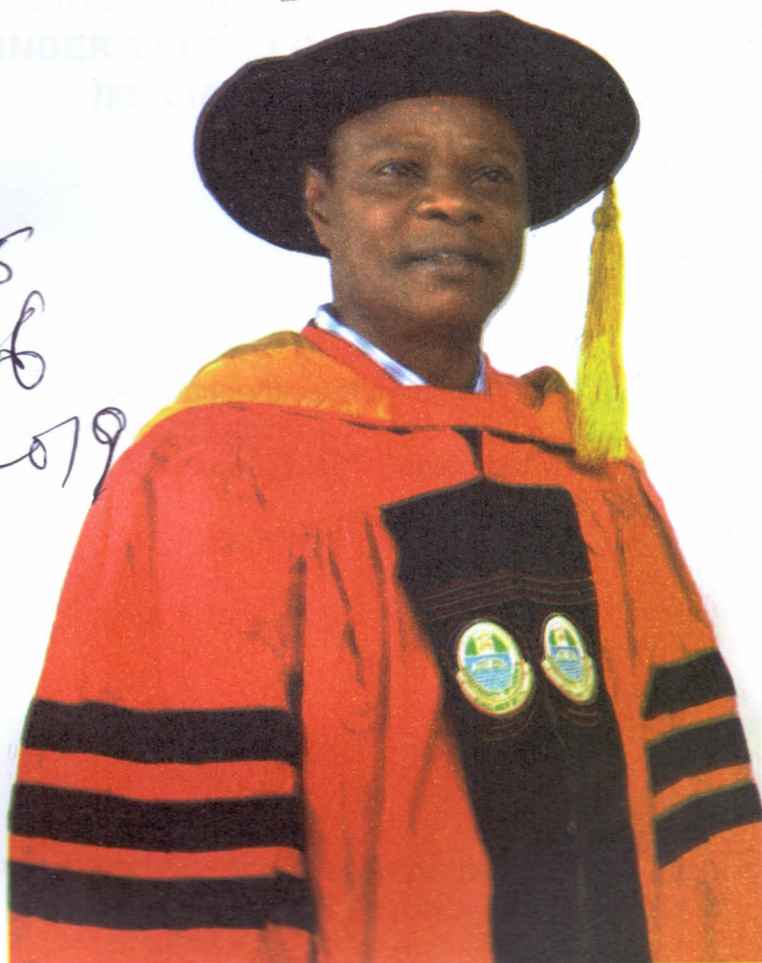
By

PROFESSOR OLAOSEBIKAN ABIDOYE OLAFADEHAN

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**PROFESSOR OF CHEMICAL AND PETROLEUM
ENGINEERING**

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MODELLING AND SIMULATION: THE UNDER-TAPPED GOLDEN RESOURCE AND IMPLICATIONS FOR PROCESS INDUSTRIES

An Inaugural Lecture Delivered at the
University of Lagos J. F. Ade-Ajayi Auditorium on
Wednesday, 18th September, 2019

By

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DEDICATION

This Inaugural Lecture is dedicated to the memory of my loving father, Pa Tewogboye Akanbi Olulaja Olafadehan, who instilled the virtues of hard work, honesty and discipline in me, and who made me understand at a tender age that education is the only legacy one can bequeath to one's children. He received the eternal call to glory on March 08, 2006. May his gentle soul continue to rest in the bosom of our Lord Jesus Christ, Amen.

PREAMBLE

It is a great pleasure for me to stand before you today with a feeling of excitement and fulfillment in life to deliver the 7th Inaugural Lecture from the Department of Chemical and Petroleum Engineering and the 11th Inaugural Lecture in the 2018/2019 academic session. I give the Almighty God, the Omnipotent, the Alpha and Omega, all the glory, honour and worship. I thank Him for His grace and favour. Coincidentally, today marks my 22nd wedding anniversary with my wife, Mrs. Olufemi Olafadehan. I thank Him for His grace and favour. I also thank my academic father and mentor, Emeritus Professor Alfred

PROTOCOL

The Vice Chancellor,
The Deputy Vice Chancellor (Management Services),
The Deputy Vice Chancellor (Academics and Research),
The Deputy Vice Chancellor (Development Services),
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Other Principal Officers of the University,
Your Lordships Spiritual and Temporal,
Your Royal Majesties and Highnesses,
Distinguished Academic and Professional Colleagues,
Distinguished Non-teaching Colleagues (Administrative and Technical),
The Great Akokites, past and present,
Members of the Press (Print and Electronic Media),
Family and Friends,
Distinguished Guests,
Distinguished Ladies and Gentlemen.

PREAMBLE

It is a great pleasure for me to stand before you today with a feeling of contentment and fulfilment in life to deliver the 7th Inaugural lecture from the Department of Chemical and Petroleum Engineering and the 11th Inaugural lecture in the 2018/2019 academic session. I give the Omnipotent, the Omniscient, the Alpha and Omega, all the glory, honour and adoration who made this day reality in my life. Coincidentally, today also marks my 22nd wedding anniversary with my heartthrob. Words are insufficient for me to express my profound appreciation to our amiable 12th Vice Chancellor, Prof. Oluwatoyin T. Ogundipe, FAS, for acceding to my request to present this inaugural lecture today. I also thank my academic father and mentor, Emeritus Professor Alfred

Akpoveta Susu, NNOM, FAE, FAS, for the encouragement and support.

Mr. Vice Chancellor, Sir, permit me to recount a brief history of what influenced my choice of Chemical Engineering as a chosen course of study in the University of Lagos, Lagos, Nigeria (the University of First Choice and the Nation's pride) and my choice of Modelling and Simulation of Chemical Reaction Systems as an area of specialisation. I loathe the popular saying "what will be will be". I strongly believe all and sundry has a part to play in achieving destiny. To realise this, it is imperative for the individual to identify his or her genius and exploit it completely. I do subscribe completely to the submission of many that the Providence has imbibed a unique genius in each person, which makes every person special in his/her right. There is always an innate strength or talent that brings out the best in each individual, and the challenge is to know and access that genius. So, when you see a child showing dexterity in a vocation, be it kicking the ball around skilfully like the renowned football stars of The Great King Pele of Brazil, Lionel Messi of Argentina/Barcelona and Cristiano Ronaldo of Portugal/Juventus, or another singing in the choir melodiously, it is a sign of the genius in that child screaming for recognition and accessibility. Identify the genius in you, access and leverage it and you would be astonished at the tremendous things you would achieve. At times, it takes others assisting one to identify this genius, as it was my case. My teacher in Primary 2 (my sincerest and unreserved apology to her for not remembering her name as I was only 6 years, 1 or 2 months old then) at Ibadan Municipal Government Primary School, Molete, Ibadan saw the traits of possessing excellent analytical skills in me when she would give some arithmetic tasks (sums, subtractions, divisions and multiplications) and ask who would give the answer mentally without putting down any calculation and I would answer correctly within a twinkle of an eye. I also remember vividly when she would tell me that the molecular formula of water is H_2O . Little did I know she was introducing me to Chemistry at a tender age: the subject later became my best subject in secondary school. She then encouraged me to pursue a

career that would utilise mathematical concepts and basic sciences. As I progressed to higher classes in primary school, all the teachers that taught me then also discovered what my primary 2 teacher found in me. The point I am making here is that everyone has a genius he/she must strive to recognise and access to hit the pinnacle of his/her career and demonstrate full ingenuity. The larger point is: it is never too late to check into your genius if you have not done so. My favourite subject in secondary school was Chemistry, with very good performances in Physics, Mathematics and the then Additional Mathematics. Even though my Additional Mathematics teacher, Mr. Amos Barimoh, had a self-adage (or axiom) that "Additional Mathematics creates additional problems", I was undaunted for I knew then that Applied Mathematics was a problem solver. Probably that made me be the best student in Additional Mathematics in secondary school, with no additional problem created, and to be nicknamed after the author of an Advanced Level Mathematics, Blakey, in my undergraduate days. The name I still cherish to be called! In as much as I desired to be an engineer, the question was: which of the engineering profession? Without much ado, I chose Chemical Engineering as I inadvertently stumbled on a textbook titled Introduction to Chemical Engineering when I was in form five and realised that it is a course whose tripod hinges on Mathematics, Additional Mathematics and physical sciences of Physics and Chemistry, the four subjects are still much relevant to my areas of research interest till date.

Mr. Vice Chancellor Sir, early at the University of Lagos, I did tap on the sound experience and engineering judgement of the analysis of chemical processes from Dr. V. O. Adeniyi. He inspired me to take research interests in modelling and computer simulation. This was found very useful to my undergraduate and postgraduate independent research works. My Bachelor of Science Thesis at UNILAG under the supervision of Prof. R. A. Bello was in mathematical modelling and computer simulation of bioengineering process. Later in my academic career, the research resulted in two published articles (Olafadehan et al., 2009; 2010). The simulation work could not have been achieved but for the

efforts and assistance of Prof. A. F. Ogunye, who provided almost 12 mini-computers for use and made his office available for most of us working in related topics. My M. Sc. Thesis, under the supervision of Dr. (Mrs.) T. O. Ajayi, looked at how solid waste could be utilised to generate electricity for a small community, as shown in Figures 1 and 2, with exergy analysis of the process, (Olafadehan, 1994; Olafadehan et al., 2012).

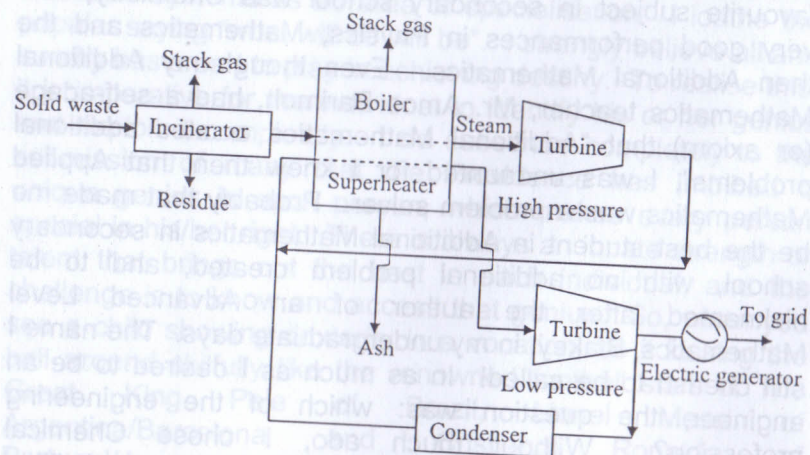


Figure 1. Energy-recovery systems with steam turbine-generator.

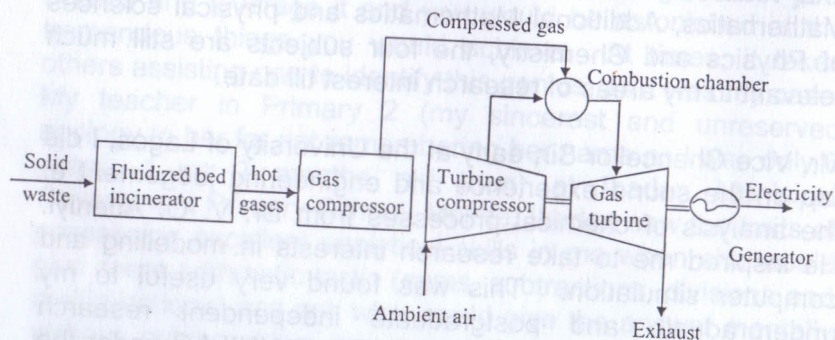


Figure 2. Energy-recovery systems with gas compressor-gas turbine-generator.

This was one of the earliest works to look at combined heat and power (CHP) systems, not even realising then that the nation would soon be plunged into an energy crisis. My Ph.D. Dissertation, under the indefatigable, erudite scholar of both national and international repute, the first Professor Emeritus of Chemical Engineering, UNILAG and a cornucopia of energy, Emeritus Professor Alfred Akpoveta Susu, was in modelling and simulation of multicomponent adsorption and reaction in porous media (Olafadehan, 2000). Eventually, the research resulted in seven publications after graduation.

Although all my independent research works at both undergraduate and postgraduate levels were on mathematical modelling and computer simulation of some selected chemical and biochemical processes, I had to acquire more knowledge in this rather difficult academic terrain to enable me execute significant research works and compete effectively with my counterparts nationally and globally. The worth of my contributions in this area has paved ways for me to be Editorial Board Members as well as a Reviewer in reputable peer-reviewed international and national journals. In recognition of my contributions in modelling and simulation, I was included in "Who is Who in Science and Engineering" in the Year 2006. It is therefore with delight that I stand before this august gathering as a Professor in the Department of Chemical and Petroleum Engineering to discharge my obligation to the University and present an inaugural lecture entitled: **MODELLING AND SIMULATION: THE UNDER-TAPPED GOLDEN RESOURCE AND IMPLICATIONS FOR PROCESS INDUSTRIES.**

Mr. Vice Chancellor, Sir, in this inaugural lecture, I will present the following: the components of mathematical modelling and computer simulation, my modest contributions to knowledge in environmental, renewable energy, and adsorption studies, and in modelling and simulation of investigated chemical and biochemical processes, conclusions and recommendations, and finally my expression of appreciation.

1. INTRODUCTION

A chemical process, which is the centre of chemical engineering, involves a series of operations/activities for the transformation of raw materials (input feedstock) into finished products of inestimable value, as depicted in the block diagram of Figure 3, using available sources of energy most economically.

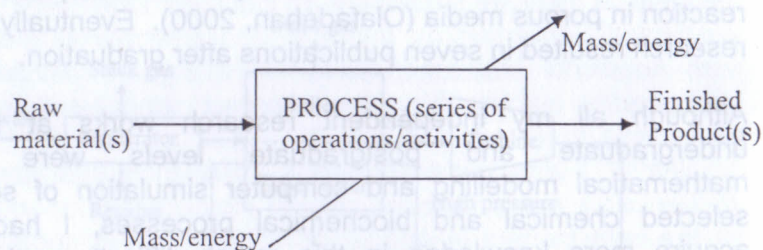


Figure 3. A chemical process.

In Chemical Engineering, a real chemical process can be represented by some equations or perhaps solely by experimental data, thereby establishing relationships amongst process variables. A chemical plant is an arrangement of processing units (reactors, heat exchangers, pumps, distillation columns, absorbers, evaporators, tanks, etc.) integrated systematically and rationally. This is a major industry, and a vast number of commercial products are obtained by chemical synthesis. Tetraoxosulphate (VI) acid, trioxonitrate (V) acid, trioxophosphate (V) acid, ammonia, ethylene, propylene, chlorine, urea, benzene, methanol, ethanol, and ethylene glycol are examples of chemicals produced in Nigeria. These, in turn, are used in the large-scale manufacture of fibres, paints, detergents, plastics, rubber, fertilizers, insecticides, and so on. The chemical engineer is familiar with chemical processes, reactor design and operation. That is why a chemical engineer is sometimes referred to as a process engineer. The role of a chemical engineer can be defined with its purpose to develop, design, construct, optimise and man any process and make the process lucrative without violating environmental balance (or regulations). Modelling and simulation are the tools assisting

to explore all the design options and thus define the optimal one. Consequently, there is a demand for chemical engineers in many sectors of the industry, including the traditional processing industries, chemicals, polymers, fuels, foods, pharmaceuticals and paper, as well as other sectors such as electronic materials and devices, consumer products, mining and metals extraction, biomedical implants, and power generation. The reason that companies in such a diverse range of industries value chemical engineers so highly is the following: "Starting from a vaguely defined problem statement such as a customer need or a set of experimental results, chemical engineers can develop an understanding of the important underlying physical science relevant to the problem and use this understanding to create a plan of action and set of detailed specifications, which if implemented, will lead to a predicted humongous financial outcome". Then, the question arises: why are engineers, with no exception to chemical engineers, and some experts in allied disciplines, interested in mathematical modelling and simulation of (chemical) processes? What benefits result from using this approach rather than just making engineering/scientific decisions intuitively? This inaugural lecture seeks to provide the answer(s) to these questions.

2. DEFINITION OF PERTINENT TERMS

Mr. Vice Chancellor, Sir, the following terms are used in this inaugural lecture and are briefly explained here for the large audience to understand.

Unit operation: The different chemical, physical, or biological processes of Figure 3 can be broken down into a series of separate and distinct steps referred to as Unit Operations.

Adsorption: In this inaugural lecture, the adsorption process is viewed from two perspectives: separation (mass transfer operation) and kinetic perspectives. As a separation technique, adsorption belongs to a more general class of unit operation, which is sometimes called percolation. A percolation process is any process in which a fluid is passed

through a bed of material which can alter the concentration of the fluid, as illustrated in Figure 4.

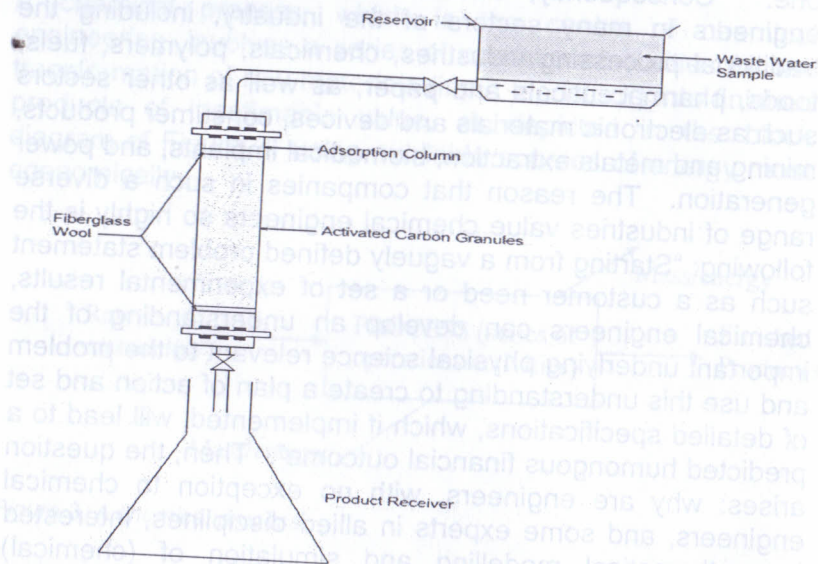


Figure 4. Fixed bed adsorption column.

Adsorption is a process that occurs when a gas or liquid or solute (called adsorbate) accumulates on the surface of a solid or more rarely a liquid (adsorbent), forming a molecular or atomic film (adsorbate), and separation is accomplished. Hence, adsorption processes may be regarded as consisting of three phases: the fluid phase, the adsorbed phase, and the adsorbent phase. It is a surface phenomenon, as illustrated in Figure 5.

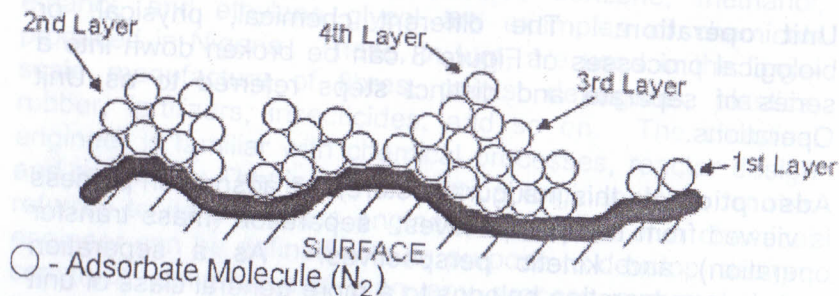


Figure 5. Different layers of adsorbate on the adsorbent surface.

The design of a column for adsorption starts with laboratory testing to establish the breakthrough curve. The fluid to be treated is usually passed down through the packed bed at a constant flow rate to adsorb components from the fluid, as depicted in Figure 4. The concentrations of the solute in the fluid phase and of the solid adsorbent phase change with time and position in the fixed bed as adsorption proceeds. At first, the adsorbent (usually activated carbon) is fresh with all its adsorption sites. Essentially, none of the material(s) to be removed escapes from the column. As time passes, some of the adsorption sites are used up, and the outlet concentration starts to rise with time. At time, t_b , the outlet concentration has risen to c_b , which is called the **breakthrough point**, (t_b, c_b) , as shown in Figure 6 for a typical breakthrough curve.

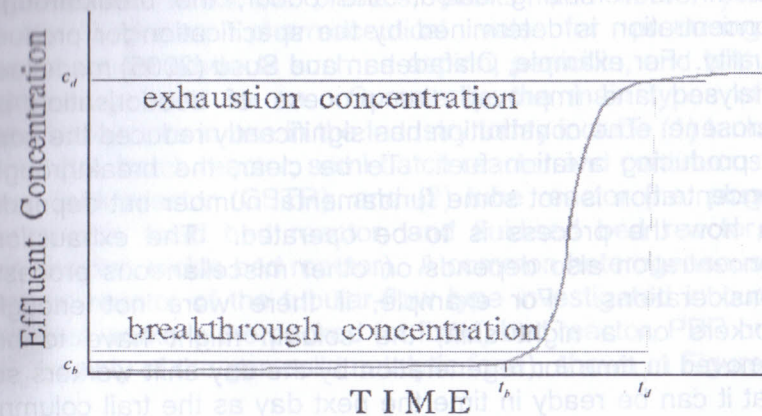


Figure 6. Breakthrough concentration profile.

Usually, it takes relatively long time before the effluent concentration rises sharply and then levels off. After the breakthrough point is reached, the outlet concentration c rises very rapidly up to point, c_d , which is the end of the breakthrough curve where the bed is adjudged ineffective. This implies that all the adsorption sites had been occupied. The breakthrough concentration represents the maximum that

can be discarded and is often taken as $0.01 \leq c_b/c_0 \leq 0.05$. The c_d/c_0 value is taken as the point where outlet concentration, c_d , is approximately equal to the inlet concentration, c_0 . The breakthrough (or allowable) concentration is determined by the process specifications. For example, if a pollutant is being removed, the breakthrough concentration, c_b , will be the government regulation for what the treatment plant can discharge to the environment without causing harmful effects to human being and watercourses. Such a process was exhaustively investigated experimentally and mathematically by Olafadehan and Aribike (2000) and Aribike and Olafadehan (2008) respectively for the treatment of wastewater effluent from a paint industry in Ikeja, Lagos, Nigeria (to mention but a few now). However, for a commercial product, where the column is removing colour and odour, the breakthrough concentration is determined by the specification for product quality. For example, Olafadehan and Susu (2005) modelled, analysed and improved the process of deodorisation of kerosene. The contribution has significantly reduced the cost of producing aviation fuel. To be clear, the breakthrough concentration is not some fundamental number but depends on how the process is to be operated. The exhaustion concentration also depends on other miscellaneous process considerations. For example, if there were not enough workers on a night shift, the column might have to be removed in time for regeneration by the day shift workers so that it can be ready in time the next day as the trail column. Note that the column could still adsorb some more material. However, little benefit accrues by running it for a longer time. One pays for labour, for electricity, for plant costs, etc. When the benefits are not worth the costs, the column is considered exhausted.

Isotherms: The results of adsorption experiments are most commonly presented in the form of adsorption isotherms. These are functions that relate the amount of adsorbate on the adsorbent to its pressure (if gas) or concentration (if

liquid) at constant temperature, i.e. the adsorption isotherm relates the concentration in the solid phase, q kg adsorbate (solute)/kg adsorbent (solid), to that in the fluid phase (gas or liquid), c kg adsorbate/m³ fluid. Different adsorption isotherms for different systems were used to correlate experimental data in our works.

Chemical Reactors: Of all the unit operations in a typical chemical process, one of the most important items of equipment is the chemical reactor. This is where conversion/change of a feedstock (raw material) to a product takes place. It is the very heart of any chemical process. Chemical reactors come in all colours, shapes, and sizes. They also vary in the method of operation, and are used for all sorts of reactions: the giant catalytic crackers for oil refining; the monster blast furnaces for iron making; the crafty activated sludge ponds for sewage treatment; the amazing polymerization tanks for plastics, paints, and fibres; the critically important pharmaceutical vats for producing pharmaceutical products such as aspirin, penicillin, and birth control drugs, and so on. Summarily, the main types of chemical reactors in use in the industry today include (1) tank reactor (i.e. batch reactor, semi-batch reactor and continuous stirred tank reactor (CSTR); and (2) tube reactor (i.e. plug flow reactor, fixed bed reactor, and fluidised bed reactor, slurry reactor, trickle bed reactor). A common heterogeneous chemical reactor of the tubular-flow type investigated in our numerous works is the packed (or fixed) bed reactor, PBR or FBR, (mainly of the gas-solid catalytic form), shown in Figure 7.

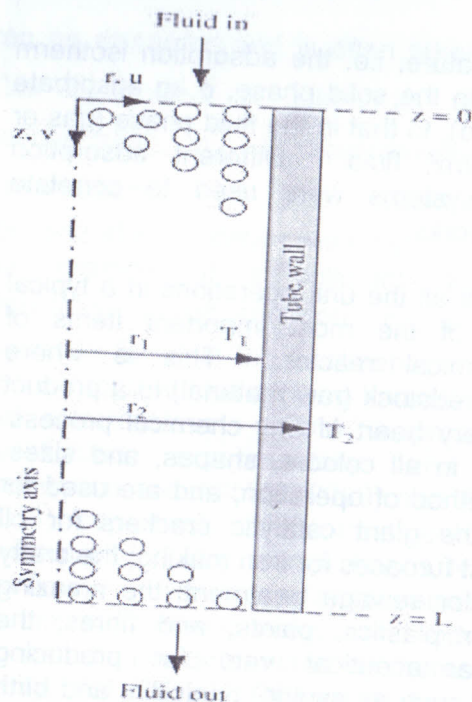


Figure 7. Schematic diagram of the catalytic packed bed tubular reactor.

In this reactor, the reacting fluid flows through a bed of relatively large catalyst particles (as sites for reactions) held in a stationary position (an inert support), e.g. the fixed bed reactor used for the oxidation of SO_2 with V_2O_5 particles for eventual manufacture of H_2SO_4 , which is a main process in the manufacture of detergents (the sulphonation plant). Similar in design and concept with the PBR is the packed bed bioreactor, PBBR, in which packings are used as supports for immobilising the active biological material (enzyme) that is responsible for the enzymatic process. The dynamics of PBBR was investigated by Olafadehan (1989), under the supervision of Prof. R. A. Bello; and Olafadehan et al. (2009; 2010). The mathematical model derived then is still being used for similar works in the literature (e.g. Silva et al., 2019 in Reaction Kinetics, Mechanisms and Catalysis: <https://doi.org/10.1007/s11144-019-01657-y>). Nowadays, the bioreactors are finding increasing use in the biotechnology industry for reasons of (i) enabling the enzyme

to remain on the support and be used as many times as possible, and (ii) improving the economics of the process. Similarly, immobilisation of microorganisms has been finding increasing application where the products are not adversely affected by immobilisation.

Fundamental Concepts in Reactor Modelling and Design:

The reactor's main phenomena that need to be included in reactor modelling and design are:

- Mass transfer, as a result of a change in concentration;
- Heat transfer, as a result of a change in temperature (or energy flow);
- Momentum transfer, due to velocity change; and
- Reaction equation.

These four can be used for analytical reasoning in mathematical forms. So, a chemical reactor engineer or designer would have to maintain a careful balance between analytical reasoning expressed in quantitative terms and sound engineering reasoning, gained by experience.

Model: This is a representation of real object or system of objects for purposes of visualising its appearance or analysing its behaviour, i.e. it is a virtual version of reality. In the literature, such definition as "an image of reality from a particular viewpoint" can be found. More precisely, a model is a simplified representation of those aspects of an actual process that are being investigated (Kafarov and Kuznetsov, 1976). There are different types of model: visual models (that simulate form and appearance such as graphical sketches, computer solid works); physical or iconic models (such as prototypes, mock-ups, miniature structures); mathematical/computational models (that use algebraic and/or differential equations to represent systems for computer simulations); and empirical models that establish functional relationships between variables as established by direct measurement (equations, charts or tables). Scientific models are often used in the construction of scientific theories.

From a practical point of view, the following three points are important to have in mind while developing a model and analysing the relationship between the model and the reality:

- (i) A model always has a certain deviation from the real process whose deviation must not be greater than 5% to achieve a 95% confidence level.
- (ii) Model definition and a mathematical tool are dependent on the chemistry and physics of the problem being explored;
- (iii) Reliability of the model is dependent on the technical know-how of the Engineers who work on the development of the model. The level of knowledge implies their skills (including intuition, mathematical prowess, and mastery of numerical techniques), experience and vision of the reality.

A perfect model does not exist, but having one that is close enough to mimic the reality can be a lot of assistance and a problem solution. For a model to be acceptable, it should be able to duplicate (replicate) the real system with minimum or acceptable error. Therefore, once a model has been put together, its predictive efficiency against experimental or real plant result (data) must be validated. Models are used for a variety of applications, such as the study of the dynamic behaviour, process design, model-based control, optimisation, controllability study, operator training and prediction. These models are usually based on physical fundamentals, conservation laws, and additional equations such as Newton's laws, and constitutive relations. In the development of a model, valid assumptions must be used, and all physical/chemical/biological factors affecting the process must be considered. Otherwise, process/plant failure may result, just as poor designs may lead to bridge collapse, structures collapse and even infrastructure collapse, and the damage could be colossal with human and material losses. Hazards that may be experienced in chemical plants include explosion during mixing operations, fire hazards and explosion of a chemical plant, as experienced in the Bhopal gas tragedy on the night of December 2-3, 1984 at the Union Carbide India Limited (UCIL) pesticide plant in Bhopal, India. Highly toxic substance, methyl isocyanate (MIC) gas, made

its way into and around the small towns located near the plant, killing thousands of people.

Modelling can be viewed from different perspectives:

- 1 as the act, art, or profession of a person who models clothes such as the fashion designer who uses his/her design equipment and experience;
- 2 as the treatment of volume or the process of producing the sculptured form with some (plastic) material such as clay before the master-piece;
- 3 as the technique of rendering the illusion of volume on a 2-D surface by shading;
- 4 as the representation, often mathematical, of a process, concept or operation of the system, often implemented by a computer program; and
- 5 It also includes imitation, psychological therapy in which a particular behaviour is elicited by the observation of similar behaviour in others or a technique in psychotherapy in which the patient is encouraged to model his/her behaviour after the therapist's.

Discussion about modelling so often goes into the direction of complex mathematical expressions. However, this is not always the case, although most models in engineering are qualitative. The modelling, I am talking about in this inaugural lecture, is in category 4 (complex qualitative mathematical expressions). It is the mathematical representation of a physical system using the fundamental laws of basic sciences: laws of conservation of mass, energy, momentum, combined in some cases, with the transport rate equations, equations of state, equilibrium, and chemical kinetics. It thrives on one's intuitive power to create and innovate to mimic the real situation with minimum loss of accuracy. Modelling of experimental results is mandatory to translate results to industrial perspectives. It is one of the ever-growing range of tools employed by engineers to meet the challenges posed by the fierce competition amongst process industries and the strong need to protect available markets. The advent of high-speed digital computers has made its application in process engineering very interesting and rewarding.

Moreover, the use of mathematical models makes the running of costly, time- and effort-consuming experiments unnecessary, though experimental results are required to validate the proposed model before it becomes acceptable to Engineers for improving the initial design of process equipment, and rationally scaling up the process. Engineers are then concerned with the enhancement of the operation of the plant once it is installed. Tangible benefits arise from improved plant performance, such as largest production, greatest profit, minimum operating cost, improved yields of valuable products (or reduced yields of contaminants), reduced energy consumption, and longer times between shutdowns. Here is a list of the most important activities of chemical engineering, which are somewhat impossible without mathematical modelling: process design; process development; reduction of time and costs in all stages of the process life cycle; an increase of process efficiency; calculations of operation benefits; process troubleshooting; and equipment sizing. Furthermore, modelling gives allowance for a better and deeper understanding of the process and its operation; as well as support for the solutions adopted during the process; it helps in decision making during the process development and exploitation; ensures an easy technological handling of the process; increases the quality of process management; reveals abilities to handle complex problems; improves process monitoring; and it predicts product qualities. Continuous process optimisation; contribution to reducing pollution; improving the safety of the plants; marketing new products faster; reducing waste emission while the process is being developed; improving the quality of the products; education of engineers; and ensuring a high quality of training of the operators are other activities impossible without modelling.

Simulation may imply different things amongst people, depending on the field of expertise. To the Mechanical Engineers, simulation is one of the major techniques to investigate a lot of product's properties such as mechanical performance, heat transfer properties etc. Equally, virtual prototyping belongs to the field of simulation. Even for the researchers in robotics, most of the robots are first tested

using simulation software and then apply to the physical ones. Electrical Engineers may think of simulation as some kind of circuit simulation, with some integrated circuits first built virtually in software to test the design logic and then obtain the physical production. The Industrial Engineers investigate the performance and behaviour of the service systems using discrete-event simulation or agent-based simulation. Others who concentrate on theoretical works use stochastic (i.e. probabilistic) simulation (variabilities in time and space) to test model performance or verify certain optimisation or statistical methods. The world football governing body, FIFA, considers simulation by a football player on the field of play as a fake foul committed on him/her and the referee issues a yellow card at first "simulation" and a red card is given for a second one or any other foul committed afterwards.

Mr. Vice Chancellor, Sir, in the context of this inaugural lecture, simulation implies a transition from a mathematical or computer model to a description of the system/process behaviour based on sets of input parameters. Process simulation uses mathematical models as a basis for analysis, prediction, testing, detection of a process behaviour irrespective of whether the process is existing in reality or not. Process simulation is there to increase the level of knowledge for a particular process. This is achieved by using an efficient and robust numerical translation of the mathematical model to computer algorithms and executable codes. Consequently, it provides a detailed study and examination of the process in the face of ever-changing process parameters in order to deeply understand its behaviour. To be precise, simulation is the only and best way to test models or methods to the extreme before implementation. In other words, it is the best cost-saving way to investigate the performance or test different configurations of the big system. This may otherwise cost a lot of money or require highly technical resources or outright impossible to investigate or change. Therefore, modelling and simulation are important techniques in engineering and science because the description of system behaviour by experimentation might not be feasible for reasons of:

1. inaccessible inputs and outputs;
2. experiments may be very dangerous;
3. cost of experiments might be too prohibitive;
4. time constants of the system may not be compatible with human dimensions; and
5. experimental behaviour might be obscured by disturbances.

Modelling and computer simulation (M&CS) pervades virtually all areas of human endeavours, without realisation. It stems from the fields of science through engineering to business analytics and other areas of life. M&CS refers to using models (physical, mathematical, or otherwise logical representation of a system, entity, phenomenon, or process) as a basis for simulation (methods of implementing a model) over time; to develop data as a basis for managerial or technical decision making. It facilitates understanding of a system's behaviour without actually testing the system in the real world. For instance, to determine which type of spoiler would improve traction the most while designing a race car, a computer simulation of the car could be used to estimate the effect of different spoiler shapes on the coefficient of friction in a turn. Useful insights about different decisions in the design could be gleaned without actually building the car. Besides, simulation can support experimentation that occurs totally in software, or in hardware-in-the-loop environments where simulation represents systems or generates data needed to meet experiment objectives. Furthermore, simulation can be used to train people in a virtual environment that would otherwise be difficult or expensive to produce. To ensure that the results of the simulation are applicable to the real world, the engineering manager must understand the assumptions, conceptualizations, and implementation constraints of this emerging field. Results of actual experiments must be considered to make models better. Summarily, the objective of numerical modelling and simulation of any system is to obtain a virtual realisation of the system that perfectly or almost perfectly describes what happens in real life. M&CS of chemical processes is the only straw with which I, like every other engineer, have to make the bricks. It is a powerful aid in designing new products and systems, in

improving existing designs, and in designing, developing and improving production processes. M&CS allows the study of a process (or a chemical reactor) performance under transient conditions such as start-up operations and quantitatively appraise process stability and reliability. This is illustrated in the work of Olafadehan and Alabi (2009) for methanogenic phase of an anaerobic digester under different operational conditions that can be extremely difficult to test experimentally. M&CS is a very powerful approach to studying complex systems, as will be highlighted in this inaugural lecture. When an engineering company is working on an incredibly intricate and expensive project, such as a new helicopter, satellite or submarine, chemical process/plant, modelling and simulation is massively advantageous. It saves time, allows the company to cut down on costs; and it means the solution can be tested in situations where physical testing would be impossible. M&CS solves real-world problems safely and efficiently. It provides an important method of analysis, which is easily verified, communicated and understood.

3. CONTRIBUTIONS TO KNOWLEDGE

3.1 Research and Development Studies on Local Raw Materials

Mr. Vice Chancellor, Sir, Extensive Research and Development studies on local agricultural and fishery wastes (which are pollutants) have been carried out to provide succinct data for the design of chemical processes for the commercial production of certain raw materials. The utilisation of these wastes would add value to the economy and open a potential avenue for small and medium scale industries thereby creating employment.

3.1.1 Production and Characterisation of Activated Carbon for Adsorption Studies

In Nigeria, like many other developing nations, activated carbon requirements are met by importation in enormous quantity at a very high cost since commercial activated

carbon is very expensive. However, vast quantities of low-cost lignocellulosic materials are generated annually as waste. These are precursors for the preparation of activated carbon to meet local demands and possibly for exportation.

The thrust of our studies (Olafadehan et al., 2012; 2018a; 2019a) was to create wealth from waste via converting these materials into a value-added product and resource for other industries. Amidst these materials, waste materials from agricultural by-products such as coconut shell, sawdust, bones of animals (cow and goats), and shells of crustaceans are economical and eco-friendly. This is due to their exceptional chemical composition, abundance, renewability, minimal cost of conversion as well as their efficiency in the treatment of industrial wastewater. Other raw materials that can be used for commercial production of activated carbon include wood, refinery residuals, peat, coal (bituminous, sub-bituminous, and lignite), coke, pitches, carbon blacks and nutshells. Many high carbon materials considered wastes that can also be used for producing activated carbon include: used bamboo, which can be found around many building construction sites in substantial quantity at almost no cost; old and worn-out automobile tyres (literature on its use as a precursor for the production of activated carbon is vast). Others are sawdust and wood shavings (many sawmills around the Lagos metropolis produce enormous quantity of particulate wood with no further utilisation but incineration); bagasse (enormous quantity of sugar cane fibre residue from sugar manufacturing industries) is produced in Nigeria with no real use except to be used as fuel; rice hulls and husk (from rice production and other grains); animal horns and bones (from meat production industries) which can be used for production of a special type of activated carbon of meso- and macro-pores called bone char, which is used in large quantity for sugar refining and to adsorb metals as well as organic chemicals from aqueous systems; palm kernel shell, which can be found in large quantities in palm oil producing communities. However, the palm kernel shell has found use in local foundries and blacksmith shops as an alternative to charcoal, hence, it has economic value and does not come cheap. Other vastly available raw materials are hard shells, cobs, pits, pods and capsules of nuts. Also, fruits and seeds,

either edible or not, including walnut, chestnut, acorn, hazelnut, corn, olive, peach, peanut, almond, hickory, pecan etc. are possible feedstocks for activated carbon production.

Coconut shell was used in our study (Olafadehan et al., 2012a) to produce powder and granular activated carbon according to Equation (1):



The coconut shell was obtained in enormous quantity as a by-product of copra processing, which is the method for producing coconut oil; discarded shells of the consumed edible white, fleshy coconut meat (the endosperm) and from other numerous uses of coconuts. The char produced was activated using 20% by weight zinc (II) chloride (ZnCl_2), followed by heating in the absence of air to produce ZnCl_2 -coconut shell carbon (ZCSC). The flowsheet for the development of activated carbon from coconut shell was given in Olafadehan et al. (2012a).

To measure the effectiveness of the activated carbon produced based on its application in our study for the treatment of brewery wastewater effluent (Olafadehan et al., 2012a), the chemical test methods of iodine number and methylene blue number were carried out to characterise the activated carbon. For liquid-phase adsorption, other product characterisation methods employed in our study included: % yield, ash content, specific surface area, and bulk density.

African walnut (*Tetracarpidium conophorum*) shell is a highly carbonaceous and fibrous material with little or no economic value, and its abundance and low cost make it a good source for the production of activated carbon. Its disposal is not only costly but also causes environmental problems. Hence, the production of char from walnut shells adds value to the walnut shells (waste). It also helps to reduce the cost of waste disposal and provides a potentially cheap alternative to the commercial carbonaceous adsorbents (Yevich and Logan, 2004). In the work of Olafadehan et al. (2018a), carbon was

produced from walnut shell according to Equation (2) for the carbonization process.



This was followed by surface modifications of the walnut shell carbon (WSC) via chemical activation using tetraoxophosphate (V) acid (H_3PO_4) to obtain acid-treated walnut shell carbon (AWSC), according to Equation (3):

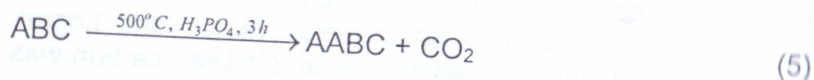


Subsequently, the WSC and AWSC were independently impregnated on the prepared chitosan (as discussed in Section 3.1.2) to obtain walnut shell carbon impregnated on chitosan (WSCC) and acid-treated walnut shell carbon impregnated on chitosan (AWSCC). The aim was to investigate the respective removal efficiencies of Zn (II) ions in aqueous solutions using the prepared adsorbents. Succinct characterisation of the different composite biosorbents prepared was carried out (Olafadehan et al. 2018a).

In furtherance of our contributions in the quest for low-cost and eco-friendly commercial adsorbents for industrial applications, Olafadehan et al. (2019a) prepared char from animal (cow) bone (a waste) from our abattoirs, (referred to as animal bone carbon, ABC) through carbonization process, according to Equation (4):



The produced char was chemically activated using H_3PO_4 acid and ZnCl_2 , to obtain acid-treated animal bone carbon (AABC) and ZnCl_2 -treated animal bone carbon (ZABC) respectively, according to Equations (5) and (6):



Furthermore, these products were surface modified by impregnation on chitosan obtained from shrimp (as discussed in Section 3.1.2) to produce acid-treated animal bone carbon impregnated on chitosan (AABCC) and ZnCl_2 -treated animal bone carbon impregnated on chitosan (ZABCC) respectively. Detailed information on the characterisation properties of the five prepared adsorbents were provided in the work of Olafadehan et al. (2019a).

Comprehensive characterisation studies were carried out on the raw coconut shell (RCS), raw walnut shell (RWS) and raw animal bone (RAB) via proximate and ultimate analyses, as presented in Table 1.

Table 1. Ultimate and proximate analyses of the raw materials used (Olafadehan et al., 2012a; 2018a; 2019a).

Materials	Ultimate analysis (%)					Proximate analysis (%)			
	C	H	N	S	O	Moisture content	Ash content	Volatile matter	Fixed carbon
RCS	50.80	1.90	0.15	0.05	47.10	12.78	0.62	72.90	13.70
RWS	45.90	5.90	0.25	0.00	47.95	11.60	1.40	70.50	16.50
RAB	49.70	1.72	0.20	0.10	48.30	5.50	0.40	75.40	1.50

From the ultimate analyses, the precursor for the preparation of the different adsorbents investigated in our studies had very low nitrogen and very low sulphur contents. Thus, they cannot contribute to environmental issues involving oxides of nitrogen and sulphur such as photochemical smog formation and acid rain phenomenon respectively. The lignocellulosic composition of the RCS, RWS and RAB was obtained as % of cellulose, hemicellulose and lignin for coconut shell, walnut shell and animal bone were (33.00, 36.50 and 30.50), (41.40, 20.00 and 17.60) and (45.90, 39.20 and 14.90) respectively. Thus, the lignin content of the animal bone used in this study was least. It is useful to note that materials with a low content of lignin are good candidates for the production of

microporous activated carbon (Daud and Ali, 2004; Gergova et al., 1994).

Similarly, the prepared char and the activated carbon were characterised and the results are presented in Table 2.

Table 2. Proximate analyses and physicochemical properties of the prepared char and the activated carbon (Olafadehan et al., 2012a; 2018a; 2019a).

Adsorbents	Proximate analysis, %				Physicochemical properties			
	Moisture content	Ash content	Volatile matter	Fixed carbon	Surface area/m ² g ⁻¹	Bulk density/g mL ⁻¹	pH	Iodine value/mg g ⁻¹
WSC	5.14	6.20	9.88	15.45	650	0.65	9.0	150
ABC	6.72	6.50	10.56	17.08	620	0.30	9.0	135
ZCSC	22.50	6.65	7.76	62.42	300	1.008	8.0	310
ZWSC	5.00	6.05	9.80	12.05	728	0.90	9.1	180
AWSC	6.00	2.05	8.76	16.90	580	0.40	8.5	138
AABC	21.20	8.24	7.74	13.10	310	1.1907	8.1	330
AWSC	5.10	1.49	9.28	16.54	634	0.50	7.6	168
AABC	17.35	6.00	7.76	12.20	387.40	1.088	8.33	360

The complementing results from Fourier-Transform Infrared (FTIR) are presented only for ABC and AABC in Figures 8 and 9.

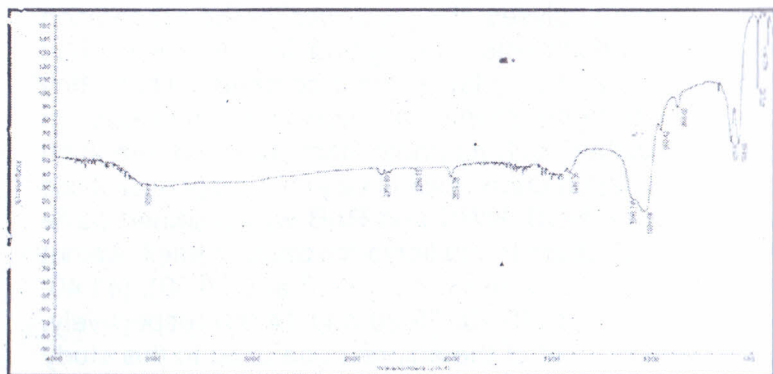


Figure 8. FTIR spectra of animal bone carbon (ABC)

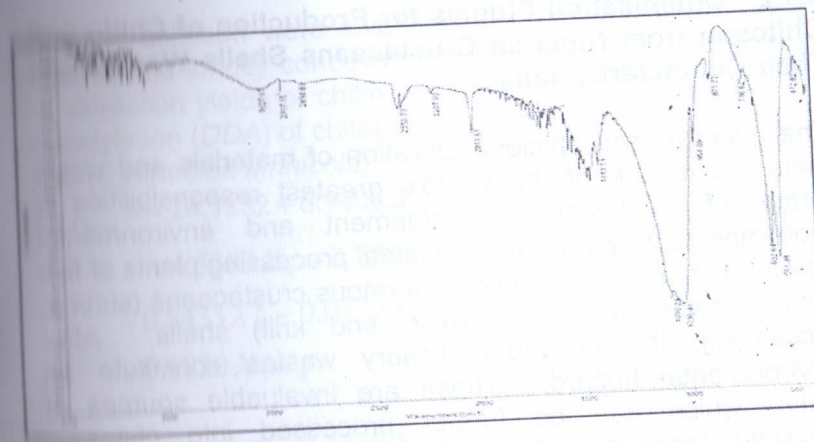


Figure 9. FTIR spectra of acid-treated animal bone carbon (AABC)

Scanning Electron Microscope (SEM) and Electron-dispersive X-ray Spectroscopy (EDX) analyses were reported in Olafadehan et al. (2012a; 2018a; 2019a). The absorption bands of the standard biosorbents from Sigma-Aldrich in Germany and the experimentally prepared ones (in our investigations) in the range of 4000 to 400 cm⁻¹ (indicating the various functional groups) were in excellent agreement.

Mr. Vice Chancellor, Sir, the import of producing activated carbon from carbonaceous materials (agricultural, plant and animal waste (bone)) is that a lot of income can be generated from activated carbon production, with the price of activated carbon at about USD450.00-USD2,000/ton, depending on its applications. The annual global activated carbon market size was estimated at USD 4.72 billion in 2018 with an expected expansion at a compound annual growth rate of 17.5% from 2019-2025 (published by Global View Research in May 2019). The production of activated carbon locally, which can treat industrial wastewater, will not only reduce the cost of treating wastewater by local industries but also increase the gross domestic product (GDP) of our nation.

3.1.2 Optimisation Studies for Production of Chitin and Chitosan from Nigerian Crustaceans Shells Wastes and Their Characterisations

The effective and efficient utilisation of materials and waste material is one of the world's greatest responsibilities in terms of sustainable development and environmental protection. Every year, the industrial processing plants of fish and the fish markets produce enormous crustaceans (shrimp, crab, prawns, lobster, crayfish and krill) shells. After processing, the discarded fishery wastes constitute an environmental hazard. These are invaluable sources of chitin, which can be further processed into chitosan. However, there is a dearth of detailed information on the extraction and characterisation of chitin and chitosan that can be obtained from crustaceans of Nigeria origin. Crustaceans shell wastes are available in abundance along the river banks and coastal lines. In our works (Olafadehan et al., 2018a; 2019a; 2019b; Amoo et al., 2019), shrimp and UNILAG lagoon snail and crab shell wastes were independently utilised to produce chitin and chitosan. These added-value products possess physiological and biological properties that could be exploited in several major research areas. These include pulp and paper, textiles, medical, cosmetics, biotechnology, agriculture and food industries. Other possible areas of application are chemical production, separation, and environmental sanitation (Gerente et al., 2007). For the production of chitin and chitosan from the shell wastes, Olafadehan et al. (2019b) and Amoo et al. (2019) determined the optimum conditions of the process variables for the extraction processes using the statistical strategy of factorial design of the Box-Behnken design of experiments using response surface methodology. The effect of four process variables: HCl molar concentration, X_1 , demineralisation time, X_2 , NaOH molar concentration, X_3 , and deproteinisation time, X_4 , on the yield of chitin was studied. Equally, the effects of three process variables: NaOH concentration, X_5 , deacetylation temperature, X_6 , and deacetylation time, X_7 , on the yield of extracted chitosan and degree of deacetylation

(DDA) of chitosan were investigated. We obtained robust, concave and strictly concave quadratic models for predicting the extraction yields of chitin and chitosan and the degree of deacetylation (DDA) of chitosan. The models are for: crab (*Callinectes amnicola*):

$$(Y_{ch})_{pred} = -24.7882 + 6.9408X_1 + 0.9496X_2 + 4.2338X_3 + 4.5383X_4 - 0.7708X_1^2 - 0.0223X_2^2 - 0.5896X_3^2 - 0.8433X_4^2 - 0.0379X_1X_2 - 0.32X_1X_3 - 0.2225X_1X_4 - 0.1850X_3X_4 \quad (7)$$

$$(Y_{cs})_{pred} = -23.1967 + 0.3658X_5 + 0.4364X_6 + 0.0131X_7 - 0.0034X_5^2 - 0.0026X_6^2 - 0.00004867X_7^2 \quad (8)$$

$$(DDA)_{pred} = 50.7283 - 2.0063X_5 + 1.0932X_6 + 0.2354X_7 + 0.0233X_5^2 - 0.0073X_6^2 - 0.0004X_7^2 + 0.0057X_5X_6 - 0.0008X_5X_7 - 0.0008X_6X_7 \quad (9)$$

The optimised chitin extraction conditions based on the yield (4.84 g or 19.36%) were obtained to be $X_1 = 3.25$ M HCl solution, $X_2 = 18.55$ h demineralisation time, $X_3 = 2.39$ M NaOH solution and $X_4 = 2$ h deproteinisation time. The maximum chitosan yield (5.98 g or 13.29%) was obtained at modelled optimised conditions of $X_5 = 50\%$ w/w NaOH solution, $X_6 = 85.05^\circ\text{C}$ deacetylation temperature, and $X_7 = 133.64$ min deacetylation time. The modelled optimisation conditions for the highest DDA of chitosan produced from crab shell waste were $X_5 = 50\%$ w/w NaOH solution, $X_6 = 84.46^\circ\text{C}$ deacetylation temperature, and $X_7 = 187$ min deacetylation time, with the corresponding predicted DDA of 84.20% (Olafadehan et al., 2019b).

Pink shrimp (*Penaeus notialis*):

$$(Y_c)_{pred} = -20.3650 + 0.2985X_5 + 0.4349X_6 + 0.0180X_7 - 0.0050X_5^2 - 0.0031X_6^2 - 0.0001X_7^2 + 0.023X_5X_6 \quad (11)$$

$$(DDA)_{pred} = 41.4627 + 0.4623X_5 + 0.5794X_6 + 0.0371X_7 - 0.0044X_5^2 - 0.0037X_6^2 + 0.0035X_5X_6 - 0.0004X_5X_7 - 0.0004X_6X_7 \quad (12)$$

The respective modelled optimisation conditions for the maximum yields of chitin and chitosan and for the highest *DDA* of chitosan from shrimp (*Penaeus notialis*) shell wastes were obtained as: $X_1 = 3.25$ M HCl solution, $X_2 = 19.03$ h demineralisation time, $X_3 = 2.43$ M NaOH solution, and $X_4 = 2.03$ h deproteinisation time), ($X_5 = 50\%$ w/w NaOH solution, $X_6 = 87.9^\circ\text{C}$ deacetylation temperature, and $X_7 = 145.26$ min deacetylation time) and ($X_5 = 50\%$ w/w NaOH solution, $X_6 = 97.2^\circ\text{C}$ deacetylation temperature, and $X_7 = 90$ mins deacetylation time) (Amoo et al., 2019).

In Equations (7)-(12), only the process variables with significant effects at 95% confidence levels were revealed while those with insignificant effects have been eliminated. Moreover, in both cases of extraction of chitin and chitosan from crab and shrimp, excellent agreements were achieved between the experimental responses (extraction yields of chitin and chitosan, and *DDA* of extracted chitosan) and their predicted values with % error $< \pm 5$ in all cases. These optimised conditions were subsequently used for the extraction of chitin and eventual production of chitosan by partial deacetylation of chitin under strong alkaline solution of NaOH, as shown in Figure 10, and the chemical reaction involved shown in Figure 11.

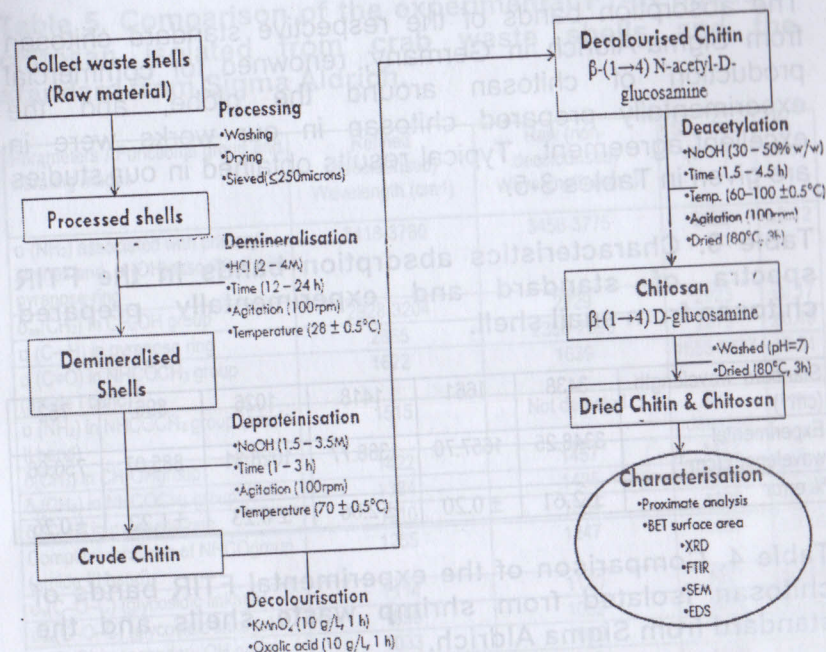


Figure 10. Experimental procedures of extracting chitin from crustacean shell waste, chemical conversion to chitosan and characterization tests carried out.

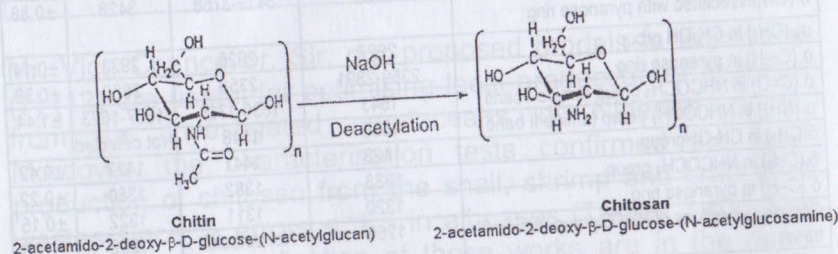


Figure 11. Conversion of chitin to chitosan by chemical deacetylation.

Comprehensive characterisation studies were carried out on the prepared chitin and chitosan via proximate and ultimate analyses, Fourier-Transform Infrared (FTIR), X-ray Diffraction (XRD), Scanning Electron Microscope (SEM) and Electron-Dispersive X-ray Spectroscopy (EDX), Brunauer-Emmett-Teller (BET), and Transmission Electron Microscopy (TEM) analyses (Olafadehan et al.; 2018a, 2019a; Amoo, 2019).

The absorption bands of the respective standard chitosan from Sigma-Aldrich in Germany, renowned for commercial production of chitosan around the globe, and the experimentally prepared chitosan in our works were in excellent agreement. Typical results obtained in our studies are given in Tables 3-5.

Table 3. Characteristics absorption bands in the FTIR spectra of standard and experimentally prepared chitosan from snail shell.

Standard wavelength (cm ⁻¹)	3438	1661	1418	1026	896	752
Experimental wavelength (cm ⁻¹)	3348.25	1657.70	1388.77	1028.31	885.07	750.06
% error	± 2.61	± 0.20	± 2.06	± 0.23	± 1.22	± 0.26

Table 4. Comparison of the experimental FTIR bands of chitosan isolated from shrimp waste shells and the standard from Sigma Aldrich.

Parameters / Functional group and vibrating modes	Refined (decolourised) Wavelength (cm ⁻¹)	Raw (non-decolourised) Wavelength (cm ⁻¹)	Standard (cm ⁻¹)	% error
ν (NH ₂) associated with primary amines and ν (OH) associated with pyranose ring	3458	3419-3768	3428	±0.88
ν_{as} (CH ₂) in CH ₂ OH group	2927	2925	2923	±0.14
ν (C—H) in pyranose ring	2359-2891	2358	2880	±0.38
ν (C=O) in NHCOCCH ₃ group (amide I band)	1643	1630-1785	1667-1623	±1.44
ν (NH ₂) in NHCOCCH ₃ group (amide II band)	1550	1548	Not detected	—
δ (CH ₂) in CH ₂ OH group	1428	1441	1422	±0.42
δ_s (CH ₃) in NHCOCCH ₃ group	1383	1382	1380	±0.22
δ (C—H) in pyranose ring	1320	1311	1322	±0.15
Complex vibrations of NHCOC group (amide III band)	1260	Not detected	1262	±0.16
ν_s (C—O—C) (glycosidic linkage)	1143	Not detected	1155	±1.04
ν_{as} (C—O—C) (glycosidic linkage)	1073	1086	1077	±0.37
ν (C—O) in secondary OH group	1069	1029	1074	±0.47
ν (C—O) in primary OH group	1030	742-951	1031	±0.10
Pyranose ring skeletal vibrations	885	888	897	±1.34
δ (NH) out of plane	660	Not detected	664	±0.60
δ (OH) out of plane	614	Not detected	616	±0.32

Table 5. Comparison of the experimental FT-IR bands of chitosan isolated from crab waste shells and the standard from Sigma Aldrich.

Parameters / Functional group and vibrating modes	Refined (decolourised) Wavelength (cm ⁻¹)	Raw (non-decolourised) Wavelength (cm ⁻¹)	Standard (cm ⁻¹)	% error
ν (NH ₂) associated with primary amines and ν (OH) associated with pyranose ring	3418-3780	3458-3775	3422	±0.12
ν_{as} (CH ₂) in CH ₂ OH group	2928-3204	2929	2923	±0.17
ν (C—H) in pyranose ring	2865	2356-2890	2879	±0.49
ν (C=O) in NHCOCCH ₃ group (amide I band)	1622	1639	1655-1627	±0.31
ν (NH ₂) in NHCOCCH ₃ group (amide II band)	1515	Not detected	Not detected	—
δ (CH ₂) in CH ₂ OH group	1422	1457	1422	0
δ_s (CH ₃) in NHCOCCH ₃ group	1384	1425	1382	±0.14
δ (C—H) in pyranose ring	1310	1384	1322	±0.91
Complex vibrations of NHCOC group (amide III band)	1255	1247	1257	±0.16
ν_s (C—O—C) (glycosidic linkage)	1114	1120	1077	±3.44
ν_{as} (C—O—C) (glycosidic linkage)	1090	1052	1073	±1.58
ν (C—O) in secondary OH group	1033	1010	1030	±0.29
ν (C—O) in primary OH group	1025	945	1029	±0.39
Pyranose ring skeletal vibrations	890	876	897	±0.78
δ (NH) out of plane	660	654	662	±0.30
δ (OH) out of plane	601	Not detected	605	±0.66

Mr. Vice Chancellor, Sir, our proposed models in Equations (7)-(12) are useful for optimising local production of chitosan from the investigated crustaceans of Nigerian origin. Moreover, the characterisation tests confirmed the local production of chitosan from the snail, shrimp and crab shell wastes since % errors < ± 5 in all cases (Tables 3-5). The implication and application of these works are in the direct use of the current drive to produce chitosan from the underutilised crustacean shells to ameliorate health hazard. Moreover, it provides alternatives to the heavy reliance on imported chitosan. Chitosan finds extensive use as an agent for sanitising the environment. It is also used in surgical medicine due to its enhanced healing properties (Muzzarelli and Peter, 1997). Pharmaceutically, it is used in cholesterol control, tumour inhibition, artificial skin, contact lens,

controlled drug release, and plaque inhibition in the dental field (Akbuga and Bergisadi, 1996; Ko et al., 2003). In agriculture, chitosan is used to improve the yield of rice and orchid production (Kim, 2010). It is a significant ingredient in weight loss products or fat reducers in food industries (Illum, 1998; Seo et al., 1988; Teixeira et al., 1990). Other areas of chitosan applications are in seed coating (Hirano et al., 2001); leaf coating, hydroponic fertilizer (Ren et al., 2001); food preservatives (Rhoades and Roller, 2000; Omara et al., 2019); and biodegradable packaging (Srinivasa et al., 2002).

Ironically, our country is not currently amongst the key market players in chitosan production and supplies as profiled by Allied Market Research (2018), which are Advanced Biopolymers AS (Norway), Heppe Medical Chitosan GmbH (Germany), GTC BioCorporation (China), Primex ehf (Ireland), Kitozyme S.A. (Belgium), Novamatrix (Norway), Agratech International Inc. (USA), Golden-Shell Pharmaceutical Co. Ltd. (China), Qingdao Yunzhou Biochemistry Co. Ltd. (China) and Panvo Organics Pvt Ltd. (India). Hence, it is high time we repositioned ourselves as a major player in the value chain of chitosan as the only known key player in the country, the National Institute of Oceanography and Marine Research, Victoria Island, Lagos, is no longer producing chitin for local uses. Japan accounted for the highest market share in the Asia-Pacific chitosan market: she generated a revenue of \$499 million in the year 2015 and is expected to reach \$956 million by the end of 2022, growing at a compound annual growth rate (CAGR) of 9.1%. Hence, local production of chitosan (as revealed in our studies) can be a source of forex earning as the annual chitosan market size was valued at \$5.71 billion in 2018 and is anticipated to expand at a CAGR of 20.8% from 2019 to 2025 (as published by Grand View Research in June 2019). The Nigeria-chitosan product can compete favourably for export in the African and world markets thus opening a window for improved foreign exchange earnings. It is only when we export that our foreign exchange earnings can improve the strength of the naira against stronger currencies like pounds, dollars and euro, and save us from the present foreign exchange imbalance.

3.1.3 Development of Composite Biosorbents

Mr. Vice Chancellor, Sir, in furtherance of the works carried out in Subsections (3.1.1) and (3.1.2), we recorded huge successes in the development of a diversity of composite biosorbents by impregnating the respective activated carbon on the prepared chitosan for adsorption studies. Comprehensive characterisation studies were carried out on the composite biosorbents via proximate and ultimate analyses, Fourier-Transform Infrared (FTIR), Scanning Electron Microscope (SEM) and Electron-dispersive X-ray Spectroscopy (EDX) analyses (Olafadehan et al., 2018a; 2019a, Amoo, 2019).

3.1.4 Improvement of Rheological Properties of Drilling Fluid Using Locally Based Materials

For some countries that are endowed with fossil fuel deposit, for example Nigeria, energy supply depends on the extent of exploration and exploitation of oil and gas reserves and other natural resources. Also, in the case of Nigeria, these resources are the mainstay of the economy. For exploration, drilling is often used to confirm the presence of most natural resources below the earth crust. It is the process of making a hole in the earth's surface to create access to the desired resource. One of the important materials used in drilling for oil and gas prospecting is the drilling fluid/mud. This fluid comes in two types: water-based mud and oil-based mud. In Nigeria, companies involved in the design and production of drilling fluid for the oil and gas sector have over the years imported the material, adjusted its properties with some additives to suit the formation requirements for the area to be drilled. This has been a major challenge to the indigenous companies. Owing to the high cost of imported drilling mud, the indigenous companies have been incapacitated to compete favourably with their foreign counterparts. Thus, research into the area of designing and producing drilling mud locally or finding suitable local substitutes is timely and necessary. Efforts to produce drilling fluid using strictly indigenous materials have yielded partial success due to low gel strength of the drilling fluid produced as well as high fluid

loss. These made the produced drilling fluid quite unsuitable for drilling processes. The gel strength of drilling fluid is a very important property that determines if the drilling fluid can adequately suspend the cuttings and transport them to the surface while supporting the stability of the formation. In our work (Olatunde et al., 2012), considering the fact that bentonite clay is the base material for all water-based drilling fluids, we developed four water-based drilling fluids locally: spud (or bentonite water suspension) mud, three separate mixtures of spud mud with 1g, 2g and 3g guar gum, three separate mixtures of spud mud with 1 g, 2 g and 3 g polyanionic cellulose (PAC), and three separate mixtures of spud mud with 32 g, 64 g and 96 g gum Arabic separately. The aim is to determine the compatibility of bentonite with other materials. The rheological property of each of the formulated drilling muds was determined at 120°F, as presented in Table 6 for typical analyses.

Table 6. Rheological properties of the developed drilling muds at 120°F.

Property	Spud mud	Mix of spud mud with 1 g guar gum	Mix of spud mud with 1 g PAC	Mix of spud mud with 32 g gum Arabic
Viscosity at different agitation speed (cp)				
600 rpm	5.0	47.0	64.0	84.0
300 rpm	3.0	38.0	34.0	59.0
200 rpm	2.0	34.0	26.0	49.0
100 rpm	1.0	30.0	16.0	36.0
6 rpm	-	22.0	4.0	9.0
3 rpm	-	21.0	3.0	8.0
Gel strength (lb/100 ft ²)				
At 10 s	-	24.0	5.0	10.0
At 10 min	1.0	35.0	9.0	15.0
At 30 min	1.0	45.0	20.0	20.0
Average viscosity (cp)	2.5	23.5	32.0	42.0
Plastic viscosity (cp)	2.0	9.0	30.0	25.0
Yield point (lb/100ft ²)	1.0	29.0	4.0	34.0

It can be seen that the spud mud had the least rheological properties at 120°F amongst the formulated drilling muds. Moreover, the developed drilling fluid combinations were hot-rolled using hot air rolling oven and ageing cells for 16 h at

150°F to study temperature stability of the drilling fluid additives. The results are presented in Table 7.

Table 7. Rheological properties of the developed drilling muds after hot-rolling at 150°F.

Constituent	Spud mud	Mix of spud mud with 1 g guar gum	Mix of spud mud with 1 g PAC	Mix of spud mud with 32 g gum Arabic
Bentonite/ppm	10.5	10.5	10.5	10.5
Water/ppm	322.7	322.7	322.7	322.7
Guar gum/ppm	-	1.0	-	-
PAC/ppm	-	-	1.0	-
Gum Arabic/ppm	-	-	-	1.0
Aging period/h	16	16	16	16
Temperature/°F	150	150	150	150
Viscosity at different agitation speed at 150°F (cp)				
600 rpm	17.0	52.0	53.0	26.0
300 rpm	11.0	44.0	34.0	17.0
200 rpm	9.0	39.0	26.0	15.0
100 rpm	6.0	31.0	17.0	10.0
6 rpm	2.0	16.0	5.0	5.0
3 rpm	2.0	15.0	4.0	5.0
Gel strength (lb/100 ft ²)				
At 10 s	4.0	15.0	6.0	9.0
At 10 min	8.0	16.0	10.0	11.0
At 30 min	20.0	22.0	20.0	20.0
Average viscosity (cp)	8.5	26.0	26.5	13.0
Plastic viscosity (cp)	6.0	8.0	19.0	9.0
Yield point (lb/100ft ²)	5.0	36.0	15.0	8.0
Filtration at 100 psi				
API fluid loss (ml s)	26.5	47.0	11.0	17.0
pH value	9.5	8.0	9.0	8.0
Filter cake 1/32"	2.0	5.0	1.0	1.0

Clearly, the rheological properties of the spud mud improved on hot-rolling. Furthermore, the rheological properties of the designed muds increased considerably on hot-rolling for 16 h at 150°F, except for the mix of spud mud with gum Arabic. Hence, gum Arabic is unstable with heat but it can be used as a stabilizer as well as a viscosifier to improve the hole-cleaning and solids-suspension capabilities of drilling fluids. This implies that with increase in temperature, the spud mud, mix of spud mud with guar gum and mix of spud mud with PAC would perform better as a drilling fluid than the mix of

spud mud with gum Arabic since the deeper the drilling operation is carried out beneath the earth crust, the higher the temperature (and pressure). The API fluid loss test carried out on the formulated drilling muds revealed that the PAC could be used to control fluid loss to the formation as well as to improve the viscosity of the drilling fluid. The guar gum was found not to be a good drilling fluid at high pressures since the more the filter cake, the higher the fluid loss. It is thus recommended to the companies involved in the design and production of drilling fluid for the oil and gas sector that in a mud system, guar gum should not be used in any way as a fluid loss agent at high pressures but as a viscosifier. However, the guar gum showed the highest gel strength and the most improved rheological properties. The pH of the filtrate obtained from the fluid loss test on the formulated drilling muds was found to be slightly basic. Hence, the use of these muds during drilling operation would be able to neutralise slightly acidic gases that are evolved from the formation (without damage to the environment). In other words, in any drilling operation, these muds can be used for surface drilling of depths not far enough where the emission of acidic gases is possible. Also, our findings revealed that indigenous water-based drilling fluid can be formulated since Nigeria is replete with so many varied raw materials that can be used for a variety of purposes with a view to improving the economic situation of the country and also to encouraging indigenous technological development with improved local content input in the oil and gas industry. The additives used in our study are readily available in commercial quantity in Nigeria, however, there is need to encourage the cultivation of guar gum tree as well as the processing of the crude gum Arabic for local use as well as to improve its export value.

3.1.5 Production and Characterisation of Metakaolin for Zeolite Synthesis

Kaolin is a versatile industrial mineral with numerous technological applications and it is abundantly available in Nigeria. Nigeria is blessed with 3 billion metric tons of high-quality kaolin clay, with almost every state having at least one known viable deposit of kaolin (Onwualu and Ibrahim, 2010).

Presently, there are few kaolin processing plants in Nigeria. They are located in Katsina, Edo and Plateau States. The largest user of kaolin in Nigeria is the paper industry, where it is utilised as a filler and coating agent; kaolin also finds extensive use in the pharmaceuticals and wastewater treatment. There is a growing interest in the use of kaolin (as a combined source of silica and alumina) for zeolite synthesis. However, there has not been any major (or reported) work in the literature on the use and proper characterisation of Okpella kaolin deposits in Etsako East, Edo State, Nigeria, (hitherto referred to as Nigeria Okpella kaolin, NOK), to synthesise zeolite. In our work, we investigated the suitability of Nigeria Okpella kaolin and metakaolin for the synthesis of zeolite (Okolie et al., 2016). Refined kaolin of $<14 \mu\text{m}$ particle size and an estimated kaolinite content of 90.23 % were obtained. The optimal calcination parameters were obtained as 750°C and an exposure time of 15 minutes. The conversion of the kaolinite to metakaolinite was confirmed through XRD and TGA/DTA and BET analyses of the raw and thermally treated kaolin samples. These are depicted in Figures 12-15. The respective BET surface areas of NOK and thermally treated metakaolin were within the published acceptable range of $(14.5773 \pm 0.0894) \text{ m}^2/\text{g}$, $(11.7811 \pm 0.1245) \text{ m}^2/\text{g}$ and $(11.8714 \pm 0.1197) \text{ m}^2/\text{g}$.

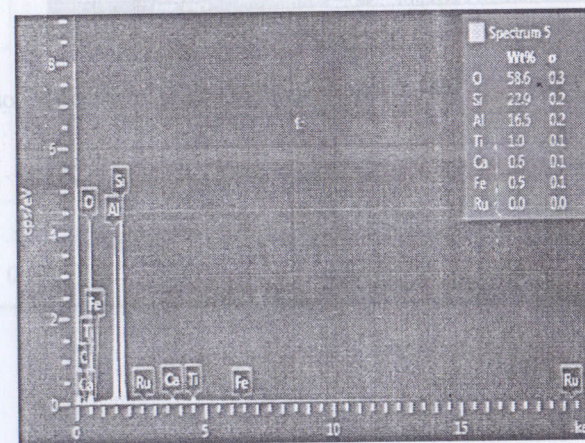




Figure 12. (a) EDS; (b) SEM analysis, and (c) SEM micrograph of raw NOK.

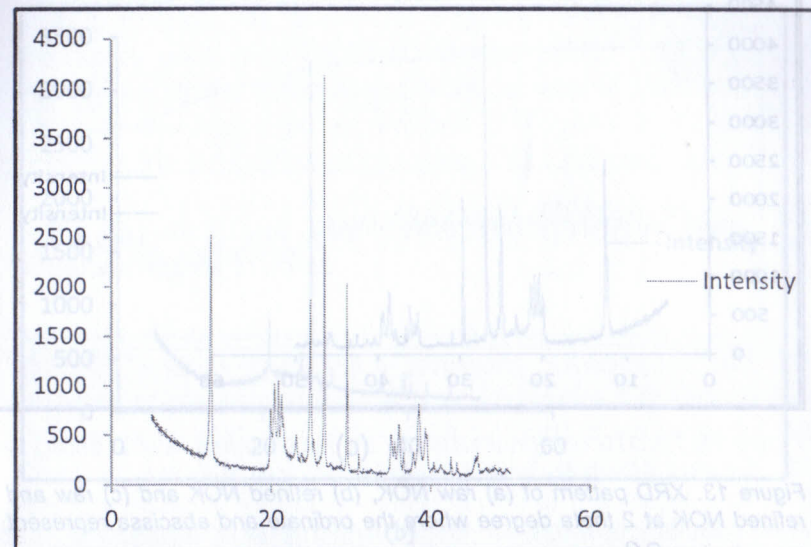
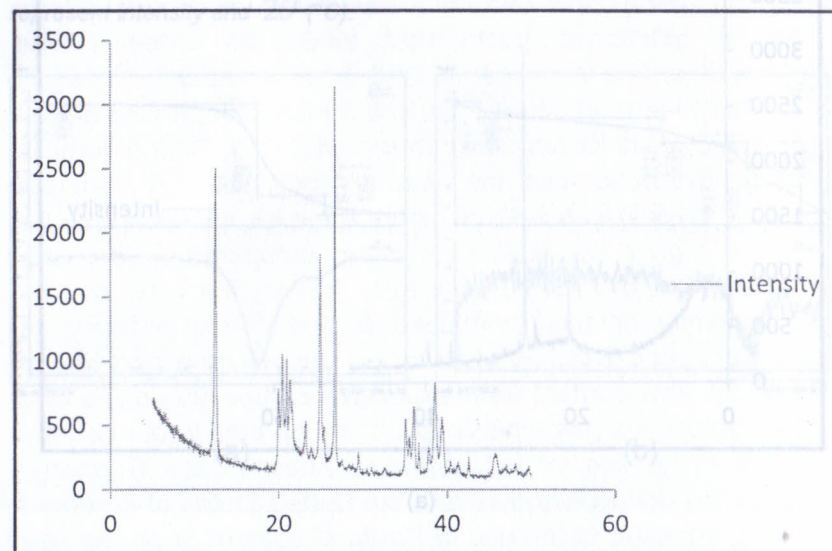
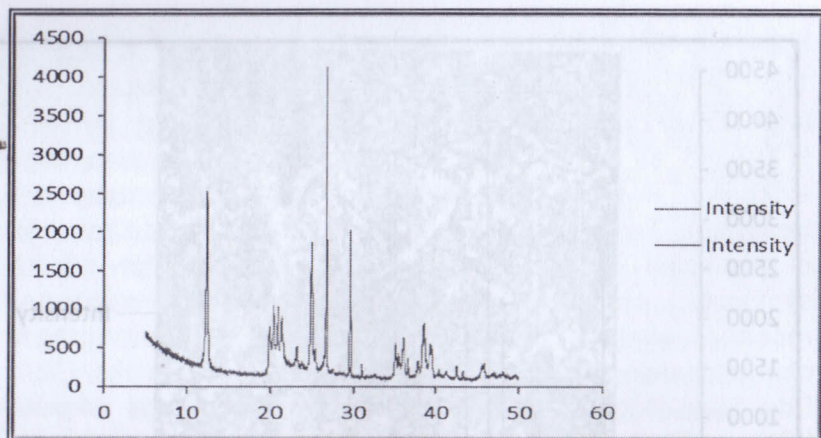


Figure 14. XRD pattern of metakaolin (a) T50°C for 15 minutes (b) T4K750

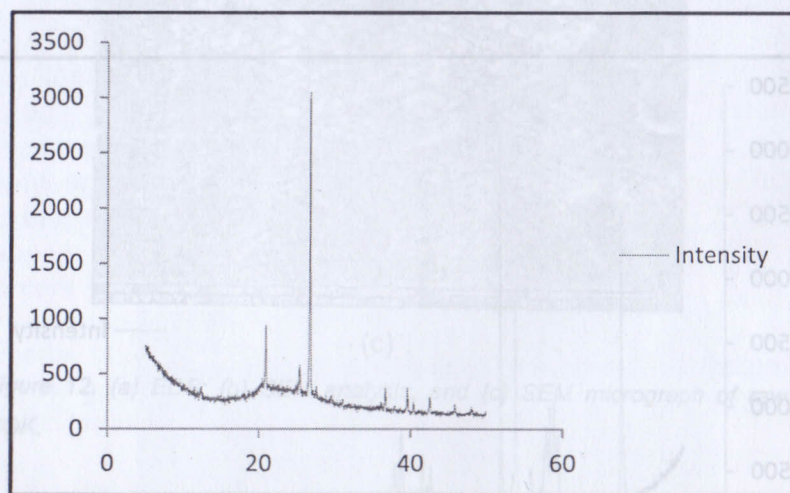


(b)

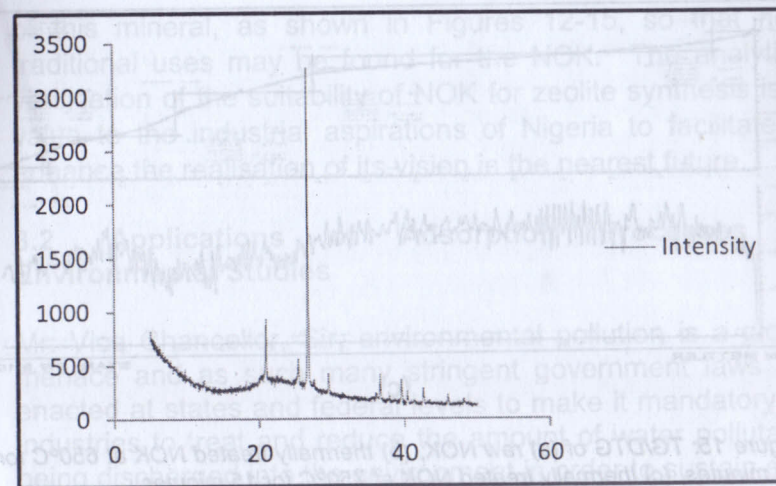


(c)

Figure 13. XRD pattern of (a) raw NOK, (b) refined NOK and (c) raw and refined NOK at 2 theta degree where the ordinate and abscissa represent intensity and 2θ ($^{\circ}\text{C}$).

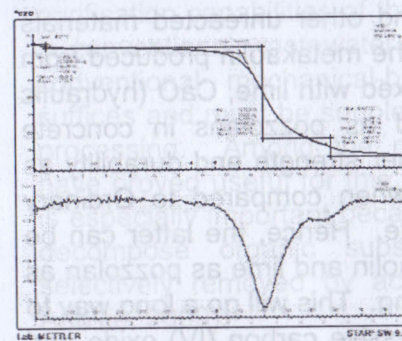


(a)

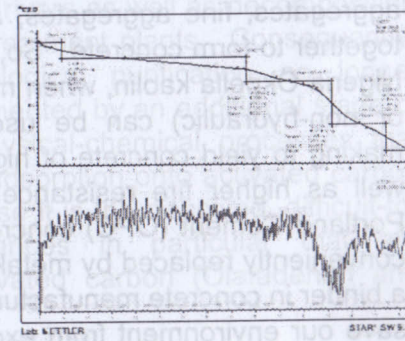


(b)

Figure 14. XRD pattern of metakaolin at (a) 750 $^{\circ}\text{C}$ for 15 minutes (MK750) (b) 650 $^{\circ}\text{C}$ for 60 minutes (MK650), where the ordinate and abscissa represent intensity and 2θ ($^{\circ}\text{C}$).



(a)



(b)

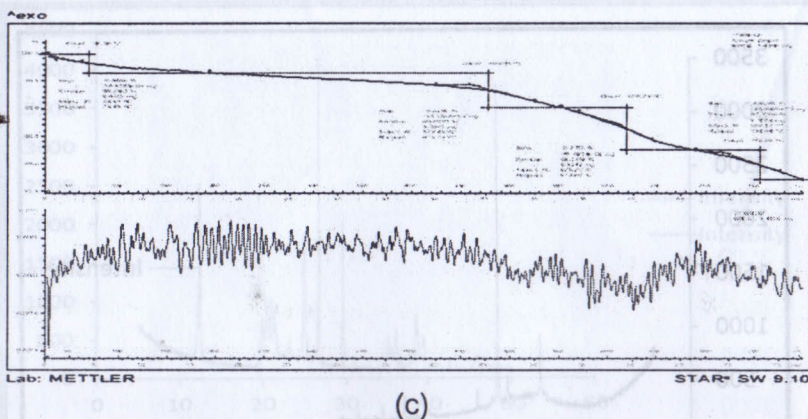


Figure 15: TG/DTG of (a) raw NOK, (b) thermally treated NOK at 650°C for 60 minutes, (c) thermally treated NOK at 750°C for 15 minutes.

The results obtained for kaolin and metakaolin showed that NOK is a good precursor for zeolite synthesis with minimal impurity. It needs to be stressed here that kaolin is a material that shows chemical and physical resemblance to Portland cement. Metakaolin can react easily with alkaline liquids to form a gelatinous paste that binds the loose coarse aggregates, fine aggregates, and other unreacted materials together to form concrete. So, the metakaolin produced from Nigeria Okpella kaolin, when mixed with lime, CaO (hydraulic or non-hydraulic) can be used as pozzolans in concrete making to yield concrete of higher strength and durability as well as higher fire resistance when compared to Ordinary Portland Cement (OPC) concrete. Hence, the latter can be conveniently replaced by metakaolin and lime as pozzolan as a binder in concrete manufacturing. This will go a long way to save our environment from excessive carbon (IV) oxide and other poisonous gas emissions. It is high time in our country to follow the line of industrialised nations (like Germany, Japan, the United Kingdom and the United States of America) on the reduction of the use of Portland cement or on the use of alternative to Portland cement as done in some developing countries like Malaysia, Singapore and Brazil to mention but a few. Summarily, our work has filled the gap in the exploitation of NOK deposits, giving detailed structure and characteristics

of this mineral, as shown in Figures 12-15, so that non-traditional uses may be found for the NOK. The analytical verification of the suitability of NOK for zeolite synthesis is of value to the industrial aspirations of Nigeria to facilitate or enhance the realisation of its vision in the nearest future.

3.2 Applications of Adsorption Processes to Environmental Studies

Mr. Vice Chancellor, Sir, environmental pollution is a global menace and as such many stringent government laws are enacted at states and federal levels to make it mandatory for industries to treat and reduce the amount of water pollutants being discharged into the environment in order to sustain eco-friendly society. Water pollution is one of the major problems faced globally due to the random release of domestic and urban wastewaters, agricultural wastes and industrial effluents into watercourses. The current problems in water and wastewater treatment stem from the increasing pollution of waters by organic compounds that are difficult to decompose biologically because they resist the self-purification capabilities of the rivers as well as decomposition in conventional wastewater treatment plants. Consequently, conventional mechanical-biological purification no longer suffices and must be supplemented by an additional stage of processing. Among the physical-chemical processes that have proved useful for this, adsorption onto activated carbon is especially important because it is the dissolved, difficult-to-decompose organic substances in particular that are selectively removed by activated carbon (Olafadehan and Aribike, 2000).

In our investigative study, adsorption process was successfully applied in the treatment of wastewater effluent from a paint industry in Ikeja, Lagos, Nigeria, using commercially available granular activated carbon (GAC) of multiple particle sizes 1-2 mm and >2 mm. The schematic diagram of the experimental set up for this purpose is already shown in Figure 4. Details of the configurations of the glass column used as fixed bed, experimental procedures carried out at a temperature of 28°C and solution pH of 8.0, gravimetric

determination of the chemical oxygen demand (COD) of the effluent from the bed, and the batch adsorption equilibrium studies were reported in Olafadehan and Aribike (2000). Our results showed that carbon loads of between 8.44 g/L and 108.48 g/L, which were respectively equivalent to organic removal of 2.23-4.47 mg by 1 g of activated carbon lent credence to the effectiveness of GAC as adsorbent in the removal of organic contaminants in wastewater effluent from a paint industry in Lagos, Nigeria. The experimental equilibrium data determined for this system was accurately correlated by the Freundlich isotherm. Breakthrough times of between 40 and 160 minutes were obtained for the continuous adsorption of organic pollutants on GAC in a fixed bed adsorption column. Our findings imply that the maximum concentration of these pollutants that can be discharged into the environment, especially watercourses, without causing harmful effects to the aquatic life would be achieved at these times.

Brewing industries are one of the major industrial users of water. These industries have one of the wastewaters that is difficult to treat satisfactorily. The high organic content of brewery effluent classifies it as a very high-strength waste in terms of chemical oxygen demand (COD), ranging from 1000 mg/L to 4000 mg/L and biochemical oxygen demand (BOD) of up to 1500 mg/L. In order to meet government regulations and to practise environmentally-friendly manufacturing, the treatment of brewery wastewater effluent is a costly task for the brewer. The untreated effluent discharge from these industries is coloured and highly intoxicating due to the presence of alcohol and can be toxic to aquatic life in receiving waters. Hence, it is necessary to treat brewery wastewater effluent before being discharged into watercourses. Olafadehan et al. (2012a) proffered resounding environmental solution to the wastewater effluent from a brewery around Iganmu area of Lagos, Nigeria, using the activated carbon produced from coconut shell, enunciated in Subsection (3.1.1). The kinetics of the adsorption of organic pollutants in brewery wastewater effluent was also established in the work. Equally, the influence of various production parameters and optimum conditions for the production of activated carbon from coconut shell by chemical

activation were investigated. From a batch adsorption experiment, the nature of equilibrium that existed in the brewery wastewater-activated carbon system was established using powdered activated carbon prepared by chemical activation method from coconut shell. Our results revealed that COD removal of 98% would be achieved for carbon dosage of 15 mg carbon/100mL of brewery wastewater solution. This would be of immense benefit not only to the manufacturing industry in terms of minimising the cost of COD treatment, but also to minimise the impact on the environment. For the design of a treatment plant for this kind of wastewater, we gave information on the experimental adsorption equilibrium data suitable and applicable for correlating the batch adsorption data of the brewery wastewater solution, as $q_e = 2.1845c_e^{0.5178}$, with the regression coefficient being 0.9868 and mean absolute deviation (MAD) of $\pm 1.6\%$.

One of the main impacts of water pollution is the enormous amount of heavy metals in effluents released by industries like electroplating, plastic and paint manufacturing, mining and metallurgical operations, pulp and paper production, petrochemical and battery manufacturing industries. These are summarised in Table 8 for eight common heavy metals.

Table 8. Sources of the eight most common heavy metals (Nasir, 2010).

No	Source	As	Cd	Cr	Cu	Pb	Hg	Ni	Zn
1	Mining and ore processing	√	√			√	√		√
2	Metallurgy	√	√	√	√	√	√	√	√
3	Chemical industry	√	√	√	√	√	√		√
4	Alloys					√			
5	Paint		√	√		√			√
6	Glass	√				√	√		
7	Pulp and Paper Mills			√	√	√	√	√	
8	Leather	√		√			√		√

9	Textiles	√	√		√	√	√	√	√
10	Fertilizers	√	√	√	√	√	√	√	√
11	Petroleum Refining	√	√	√	√	√	√		√
12	Coal-burning	√	√	√	√	√	√	√	

The groups of transition and post-transition elements are referred to as heavy metals. They have atomic weights between 63.5 and 200.6 and a specific gravity > 5.0 (Barakat, 2011). These include cadmium, chromium, copper, manganese, nickel, mercury, lead and zinc and the metalloids arsenic and selenium. These metals are toxic and non-biodegradable and can cause environmental pollution. Hence, they have been classified as priority pollutants by the United States Environmental Protection Agency (USEPA) and have been grouped under dangerous substances by the Commission of European Communities (CEC). At higher concentration, they are poisonous and pose a major threat to the aquatic ecosystem due to their toxic nature (Crini, 2005). Also, due to their high solubility in the aquatic environment, heavy metals can be absorbed by living organisms thus creating a means to enter the food chain via bioaccumulation. Once they enter the food chain, a large concentration of heavy metals may accumulate in the human body. If the metals are ingested beyond the permissible concentration, they can cause serious health disorders (Babel and Kurniawan, 2004). This can lead to a reduction in growth and development, cancer, organ, nervous system and irreversible brain damages, and in extreme cases, death. Exposure to some metals, such as mercury and lead, may also cause the development of autoimmunity, in which a person's immune system attacks its cells. This can lead to joint diseases such as rheumatoid arthritis, and diseases of the kidneys, circulatory system, nervous system, and damaging of the fetal brain. So, be wary of consuming untreated borehole water or untreated water from any other well as one may be consuming heavy metals present in such waters ignorantly. Hence, the removal of these heavy metals from water/wastewater is essential for protecting the environment and human health. However, trace concentrations of some of

these heavy metals, like zinc and copper, in the human body are important for the physiological functions of living tissue and regulation of many biochemical processes. For example, World Health Organisation recommended the maximum acceptable concentration of zinc and copper in drinking water to be 5.0 mg/L (Hawari et al., 2009) and 1.5 mg/L (Rao, 1992; Farouq and Yousef, 2015) respectively.

Olafadehan et al. (2018a), Adeleke (2018) and Njoku (2018) investigated the removal of Zn (II) and Cu (II) ions in industrial wastewater (from an electroplating company in Minna, Niger State) using the derived composite biosorbents from walnut and snail shells, and from animal bone and shrimp shells respectively. The effects of operational parameters (such as solution pH, adsorbent dosage, initial metal ion concentration, agitation time, agitation speed and temperature) on the respective Zn (II) and Cu (II) ions removal from an industrial wastewater were obtained. The increasing order of Zn (II) ions removal efficiency was obtained as WSC<AWSC<WSCC<AWSCC while for the Cu (II) ions, the increasing order of removal efficiency was obtained as ABC<AABC<ABCC<AABCC. Thus, it was concluded that acid-treated carbon (whether from walnut shell or animal bone) impregnated on chitosan was a potential alternative and tremendously-efficient low-cost biosorbent for the remediation of heavy metals of Zn (II) and Cu (II) ions contamination in wastewater. For the cases of Zn (II) and Cu (II) adsorption, the Langmuir isotherm fitted the adsorption data excellently for the derived composite biosorbents, giving an indication of monolayer coverage on the derived composite biosorbent. The kinetic modelling of Zn (II) and Cu (II) ions adsorption showed that the pseudo second-order kinetic model gave the best fit amongst the investigated kinetic models. In addition, the thermodynamic parameters indicated that the adsorption of Zn (II) and Cu (II) ions on the derived composite biosorbents was exothermic, endergonic, favourable, non-spontaneous with changes in enthalpy, ΔH , negative, entropy, ΔS , nearly zero (though negative), and Gibbs free energy, ΔG , positive, for all the prepared adsorbents.

Other environmental studies investigated by us included the remediation of contaminated groundwater. Naturally, groundwater is clean but it can be polluted or contaminated as a result of human activities and/or of natural conditions thereby making it unsuitable for use. Groundwater is the source of about 75% of Nigerian's drinking water (as public water services are somewhat moribund), excluding water for power plant cooling. Historically, the natural filtering resulting from water working its way through the subsurface was believed to provide sufficient protection from contamination to allow untreated groundwater to be delivered to customers. The dramatic epidemic incidents in the 1970s made us realise that our groundwater was contaminated with hazardous substances from hundreds of thousands of leaking underground storage tanks, industrial waste pits, home septic systems, municipal and industrial landfills, accidental chemical spills, careless use of solvents, illegal midnight soil dumping and widespread use of agricultural chemical (Gibat,1991). Using contaminated groundwater causes hazards to public health through poisoning or spreading of diseases and the practice of groundwater remediation has been developed to address these issues.

The greatest threat to groundwater posed by modern landfills is leachate. Leachate consists of water and water-soluble compounds in the refuse that accumulate as water moves through the landfill. This water may be from rainfall or from the waste. Leachate may migrate from the landfill, percolate through solids into the aquifers thereby contaminating soil and groundwater. This presents a risk to human and environmental health. Pollutants and contaminants can be removed from groundwater through the process of remediation thereby making it safe for use. In our work, Salami et al. (2013), we discussed details of recent advances and various remediation techniques for removing contaminants from groundwater. We identified possible contaminants in groundwater to include heavy metals (such as cadmium, chromium copper, iron, nickel, lead, uranium, zinc, arsenic, selenium, mercury) as well as nitrate, phosphate, sulphate. Other contaminants identified are nitrogen, chloride, vinyl chloride and phenol. Remediation of

groundwater contaminants can be achieved by biological, chemical or physical treatment or a combination of these treatment methods. Among these remediation techniques, the biological method is economical, least harmful, uses naturally occurring organisms and preserves the environment in a more natural state. Conversely, the physical technique is costly, depends on the geology of the aquifer and takes a long time to remove the contaminants. Most advanced countries like the United States of America use sanitary landfills in which liners with a minimum barrier thickness are used to prevent percolation of leachate to groundwater. In Nigeria (Lagos inclusive), no sanitary landfills are present but dumpsites, the remediation of contaminated groundwater is not only important but urgent for the general well-being of the populace and environmental integrity of our water resources. The data needed to validate the models and to predict the future contaminant concentration are not available in the country. The data, if available, will help to fashion out applicable remediation strategies.

3.3 Solid Waste Management and Control

Human beings cease to generate waste only when we become a disposable waste. Waste management and control in developing countries, Nigeria inclusive, is thus of grave concern. Hence, the subject of solid waste management and control is both timely and significant. The overall objective of solid waste management and control is to minimise the adverse environmental effects caused by the indiscriminate disposal of solid waste. Grievous effects of improper waste management and control include air pollution, contamination of drinking water supplies, the spread of diseases, and bad aesthetics of the environment.

In one of our works in solid waste management and control, we, Olafadehan and Salami (2011), proffered steps for effective solid waste management and control in Nigeria, identifying amongst other constraints, technical, financial, social and economic constraints mitigating against it, and suggestions were given for the way forward. Summarily, without adequately trained personnel, solid waste

management and control cannot be sustained; very limited funds are provided to the solid waste management sector by the governments, and the levels of services required for the protection of public health and the environment are not attained; insufficient funds for sustainable development of solid waste management and control owing to our weak economic bases, the weak industry base for recycling activities is a common constraint for the improvement of solid waste management in Nigeria: Nigeria loses N400 billion yearly to paper product importation (Punch Newspaper Report, 2010) owing to non-inculcation of the habit of recycling of waste paper by Nigerians. Equally, recommendations on the achievement of proactive solid waste management and control in Nigeria, as a way of environmental sustainability, were succinctly discussed in this work.

Since the composition of solid waste must be known especially by local authorities for decision making and planning as well as prevention of environmental degradation, we, Salami et al. (2011), carried out the characterisation of solid wastes within Lagos State as a case study. Table 9 shows the Lagos State solid waste components and percentage.

Table 9. Lagos State solid waste component and percentage

Component	Organic matter	Plastics	Paper	Glass	Silts	Ashes	Total
Tonnage	5580	1350	900	360	630	180	9000
Percentage	62	15	10	4	7	2	100

Source: Lagos State Waste Management Authority (LAWMA)

It can be seen that Lagos State solid waste comprises mostly 62% organic matter and 15% plastic, and a little of ashes which account for 2%. The moisture content of the waste was calculated to be 18.04%, which falls within the range of 10-35% expected of an industrial city like Lagos. The density of the solid waste was found to be 145.964 kg/m³. The

chemical formula of the solid waste with sulphur and without sulphur was found to be $C_{597.24}H_{872.26}O_{496.02}N_{15.12}S$ and $C_{39.50}H_{57.6891}O_{32.8052}N$ respectively. The volume of oxygen required to completely oxidise 100 kg of sulphur-free solid waste was determined to be 460 m³/100 kg solid waste. The anaerobic digestion of solid wastes produces gases mostly methane and carbon (IV) oxide, which are known to cause global warming and ozone layer depletion. With the chemical formula of solid waste without sulphur, the theoretical volume of methane gas that would be expected from anaerobic digestion of the solid waste was estimated to be 33 m³/100 kg of solid waste, which can be used for domestic purposes. All the parameters identified in our work, Salami et al. (2011), are useful for planning, economic analysis, design and subsequent management and operation of a disposal system, plant optimisation and emission monitoring of Lagos State solid wastes, in particular, and in the country generally. This would help to control environmental degradation.

3.4 Energy Studies

Mr. Vice Chancellor, Sir, energy studies carried out included the design of a Combined Heat and Power (CHP) plant, production of biodiesel using waste cooking oils and castor seed oil, and catalytic steam reforming of methanol, concentrated crude ethanol and glycerol for hydrogen production.

3.4.1 Design of a CHP Plant

Human being's current lifestyle is unsustainable; energy usage is on the increase with every technological advancement. There is, therefore, the need to enhance energy generation and one good source is biomass, regarded as waste. Moreover, sustainable development is one of the most significant issues facing society today. For new technologies to be sustainable, there is the need to save resources and avoid waste or better still use the waste from one component of the biogeochemical cycle as raw materials for another component: this causes ecological systems to

operate in a closed-loop with minimal interaction from and to the environment.

Globally, energy is required to maintain a good standard of living. Over the past hundred years, the world has been mainly dependent upon (i) the basic fossil fuels: coal, oil and natural gas; (ii) electricity generated by hydro- or nuclear means; (iii) wood and related low-grade fuels; and (iv) solar energy. Wood was the major energy source some hundred years ago, then coal became dominant until the early 1960s when oil became the major world energy source. The prospect of an oil famine and other world problems are of increasing concern to industrialised and developing nations. Coal and nuclear energy for electricity generation pose inherent environmental problems, which will become increasingly severe with time. Moreover, the nuclear contribution faces potential difficulties because of the apprehension of most countries toward the development of a nuclear plant.

Proposed alternative energy supplies suitable for heating and electricity generation being carried out worldwide include solar, wind, wave, biomass and tidal power. The use of combustible mass has been utilised in developed countries in Combined Heat and Power (CHP) plants to augment electricity generation. Figure 16 shows countries where CHP plants contribute to their total national electricity generation.

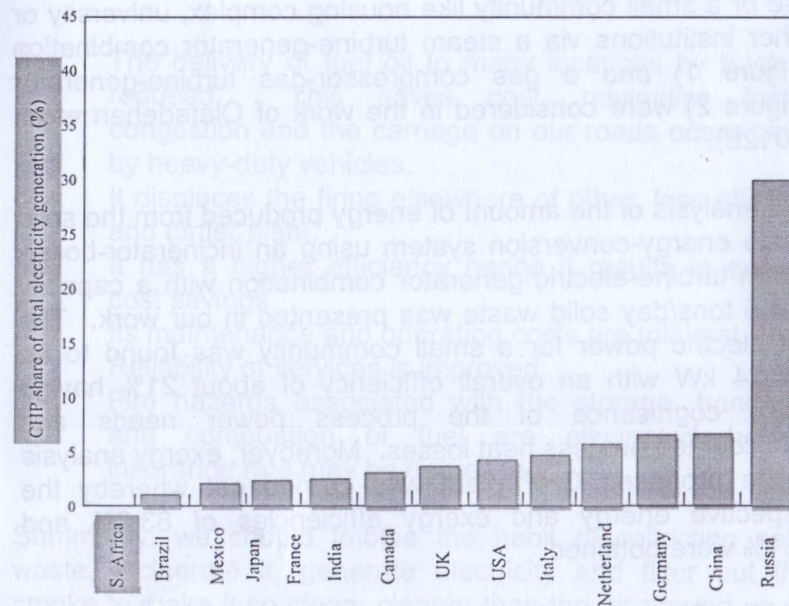


Figure 16. CHP share of total electricity generation in fourteen countries.

(Source: IEA data and analysis; data merged from years 2001, 2005, 2006).

The concept that the abundant heat currently lost in the incineration of solid waste can be recovered and used for other purposes rather than being wasted to the atmosphere, is not yet fully explored in Nigeria. Hence, the design of a feasible Combined Heat and Power plant was proposed for a small community in the work of Olafadehan et al. (2012b). Of the many alternatives solid-waste disposal methods available (which include hog feeding, open dumps, sanitary landfills, incineration, ocean dumping, composting, land-farming and deep-well injection), incineration of solid waste was recommended due to its potential ability to recover the heat released during solid waste incineration and other valuable by-products that can either be reused, recycled or marketed, among other advantages. As shown in Figure 1, the heat energy released during the incineration of solid waste was used to produce steam in a boiler, which in turn powered a turbine for the eventual generation of electricity. The two processes involved in the generation of electricity for in-plant

use or a small community like housing complex, university or other institutions via a steam turbine-generator combination (Figure 1) and a gas compressor-gas turbine-generator (Figure 2) were considered in the work of Olafadehan et al. (2012b).

The analysis of the amount of energy produced from the solid waste energy-conversion system using an incinerator-boiler-steam turbine-electric generator combination with a capacity of 4.5 tons/day solid waste was presented in our work. The net electric power for a small community was found to be 148.24 kW with an overall efficiency of about 21% having taken cognisance of the process power needs and unaccounted process heat losses. Moreover, exergy analysis of the proposed CHP plant was carried out whereby the respective energy and exergy efficiencies of 83.2% and 62.1% were obtained.

Mr. Vice Chancellor, Sir, this work is one of the possibilities of opening new frontiers on numerous alternative sources of electricity. It is, therefore, of great relevance to a small community for power generation thereby reducing heavy reliance on the national grid for heating and power supply. It can also augment electricity on the national grid and help to improve the epileptic power supply in our nation. In particular, it can provide affordable electricity for small communities as well as rural regions which are embedded in undulating terrains and long distances from the grid infrastructure and thus limit them access to electricity supply. Many unemployed will seize this opportunity to key into jobs that are electricity-driven without having to incur extra cost in running generating sets. The advantages of using a well-designed CHP plant include the following:

1. The dual system for generating electric power and heat makes possible overall energy utilisation efficiencies above 70%, as contrasted with about 35% for the generation of electricity alone.
2. A well-designed CHP plant results in correspondingly reduced emissions of pollution and combustion products.

3. The delivery of fuel oil to many locations by truck is reduced. This saves cost, minimises traffic congestion and the carnage on our roads occasioned by heavy-duty vehicles.
4. It displaces the firing elsewhere of other, less efficient and dirtier plant.
5. It has a higher efficiency hence it results in energy cost savings.
6. Its maintenance and operating costs are minimal.
7. Reliability of services is improved.
8. Fire hazards associated with the storage, handling, and combustion of fuel are eliminated hence, insurance rate may be decreased.

Summarily, we should imbibe the habit of collecting solid waste, incinerate it, generate electricity and filter out the smoke to make it so clean, cleaner than the air around us so that the chimney at the incineration plant emits very clean air. By this process, 90% of the solid waste disappears in a couple of hours and the remaining 10% turns to ash. The ash, just like the smoke, is toxic. It can be shipped to a far-away island where all of it is dumped into special water that does not touch the ocean water and there the ash stays underwater forever, hidden from everyone. This process is so clean that the integrity of the environment is not threatened, and the solid waste can disappear in 24 hours instead of 500 years! If every country could handle her trash and mine the same way Singapore does, then we will have a much cleaner world, a world where the trash/waste does not exist for more than a day.

3.4.2 Impact Analysis of Emissions during Biodiesel Production

Biodiesel, a generic term for alkyl esters of fatty acids, is a renewable biomass energy source. It is produced through transesterification process in which triglycerides of edible or non-edible plant oils (such as palm oil, sunflower oil, jatropha oil, castor oil etc.) react with alcohol, in the presence of an acidic or alkaline catalyst to produce biodiesel with glycerol as a by-product. As an energy source, biodiesel exhibits similar

performance as petroleum diesel. However, when used in a diesel engine, non-environmentally and non-friendly emissions from biodiesel are less compared to emissions from petroleum diesel. Hence, producing quality biodiesel with favourable environmental implications is of great importance to achieve sustainable energy management since the world economy depends on sustainable energy generation. In our work, Ayoola et al. (2016), we investigated the impact analyses of emissions on both man and environment during biodiesel production and washing water obtained in the alkaline catalysed transesterification of waste groundnut oil (WGO), waste soyabean oil (WSO) and crude palm kernel oil (CPKO) using SIMAPRO 7.33 software. The impact analyses were achieved by considering the life cycle assessment (LCA) during biodiesel production and the washing water obtained. Triglyceride compositions of WGO, WSO and CPKO are shown in Table 10 while the properties of the biodiesel produced from the transesterification of these oils are shown in Table 11.

Table 10. Triglyceride composition of WGO, WSO and CPKO.

Fatty acid	Triglyceride composition, wt %		
	WGO	WSO	CPKO
Linoleic acid, C ₁₈ H ₃₂ O ₂	0.42	34.86	-
Oleic acid, C ₁₈ H ₃₄ O ₂	90.21	39.14	9.29
Lauric acid, C ₁₂ H ₂₄ O ₂	-	10.30	42.58
Myristic acid, C ₁₄ H ₂₈ O ₂	-	-	10.64
Palmitic acid, C ₁₆ H ₃₂ O ₂	-	-	28.34

Table 11. Properties of biodiesel produced.

Property	ASTM method	WGO biodiesel	WSO biodiesel	CPKO biodiesel
Density @ 25°C (g/cm ³)	ASTM D4052	0.8903	0.8820	0.8760
Pour point (°C)	ASTM D97	-9	-6	-6
Flash point (°C)	ASTM D93	180	204	208
Water content (%)	-	0.005	0.006	0.004
Viscosity@ 40°C (mm ² /s)	ASTM D445	4.30-4.70	4.55-4.85	4.70-5.00
Cetane number		49.4-51.0	50.6-52.8	51.7-53.2

The results of the emissions to the environment during biodiesel production and the washing water are presented in Table 12.

Table 12. Substances, in mg/L, obtained during biodiesel production and washing water analyses.

Substance	WGO biodiesel	WSO biodiesel	CPKO biodiesel	WGO washing water	WSO washing water	CPKO washing water
Aluminium (λ=396.1 nm)	0.021	0.016	0.015	0.011	0.0150	0.009
Arsenic (λ=193.7 nm)	0.003	0.001	0.002	0.039	0.042	0.014
Beryllium (λ=234.9 nm)	0.011	0.007	0.009	-	-	-
Cadmium (λ=228.8 nm)	0.031	0.051	0.010	0.031	0.028	0.025
Calcium	-	-	-	0.760	0.550	0.860
Carbonate (µg/L)	-	-	-	500	530	430
Chloride	-	-	-	1.710	0.990	1.460
Chromium (λ=357.9 nm)	0.007	0.004	0.003	0.003	0.002	0.001
Cobalt (λ=240.7 nm)	0.004	0.003	0.002	-	-	-
Copper (λ=324.7 nm)	7	11	3	23	15	17
Hydroxide (µg/L)	-	-	-	0.810	0.750	0.680
Lead (λ=263.8 nm) (µg/L)	0.013	0.014	0.020	0.006	0.010	0.004
Nickel (λ=232.0 nm) (µg/L)	0.056	0.028	0.038	0.009	0.007	0.005
Nitrate (µg/L)	-	-	-	0.048	0.420	0.520
Phosphate (µg/L)	-	-	-	0.028	0.270	0.190
Sulphate (µg/L)	-	-	-	0.065	0.700	0.640
Zinc (λ=213.9 nm) (µg/L)	0.078	0.042	0.013	0.141	0.093	0.138
Water turbidity (NTU)	-	-	-	210	207	207
Colour of water (PCU)	-	-	-	307	307	307

The characterisation results of the emissions during biodiesel production, and from washing water were presented in Ayoola et al. (2016) in which seven midpoint categories were considered for characterising the non-environmentally and non-friendly substances that were identified as carcinogens, non-carcinogens, respiratory inorganics, aquatic ecotoxicity, terrestrial ecotoxicity, terrestrial acidification and global warming. Global warming, as a phenomenon, results from the release of greenhouse gases (GHGs) into the atmosphere. The GHGs resilience permanence in the atmosphere leads to the entrapment of heat on the earth's surface. The most significant examples of greenhouse gases are CH₄, H₂O, CO₂, NO₂ and fluorinated compounds. Table 13 presents the seven midpoint categories for characterising emissions during biodiesel production.

Table 13. General characterisation of emissions during biodiesel production.

Parameters	WGO	WSO	CPKO
Carcinogens	5.69×10^{-6}	3.55×10^{-6}	3.21×10^{-6}
Non-carcinogens	8.13×10^{-5}	5.74×10^{-5}	5.06×10^{-5}
Respiratory inorganics	7.25×10^{-8}	9.92×10^{-8}	4.94×10^{-8}
Aquatic ecotoxicity	2.59×10^{-1}	3.12×10^{-1}	2.66×10^{-1}
Terrestrial ecotoxicity	1.55×10^{-1}	1.24×10^{-1}	5.38×10^{-2}
Terrestrial acidification	2.32×10^{-6}	3.04×10^{-6}	1.75×10^{-6}
Global warming	1.18×10^{-6}	1.32×10^{-6}	1.54×10^{-6}

For example, considering carcinogens (arsenic, cadmium and chromium), during WGO-biodiesel, WSO-biodiesel and CPKO-biodiesel productions, the amounts of non-environmentally and non-friendly substances released were 5.69×10^{-6} kg (100%), 3.55×10^{-6} kg (62.4%), and 3.21×10^{-6} kg (56.4%) respectively. Using the single score based on the seven midpoint categories, it is evident in Table 13 that the emissions during WGO and WSO diesels production had pronounced effect on terrestrial ecotoxicity while the pronounced effect of the emission during CPKO-biodiesel production was aquatic ecotoxicity. The impacts of the non-environmentally and non-friendly substances released were assessed by grouping them into three categories: damage to human health, damage to ecosystem quality and damage to the climate. Our results showed that the emissions during WGO-biodiesel production had the most pronounced impact on human health with 2.94×10^{-10} kg (100%) emissions, WSO-biodiesel released 2.40×10^{-10} kg (81.6%) non-environmentally friendly substances while CPKO-biodiesel released 1.85×10^{-10} kg (62.9%) emissions. On damage to ecosystem quality, emissions of non-environmentally and non-friendly substances during WGO-biodiesel, WSO-biodiesel and CPKO-biodiesel production were obtained as 1.25×10^{-3} kg (100%), 9.95×10^{-4} kg (79.7%) and 4.39×10^{-4} kg (35.1%) respectively, revealing that during the production of WGO-biodiesel, the most severe threat to ecosystem quality was obtained. The results of damage to climate

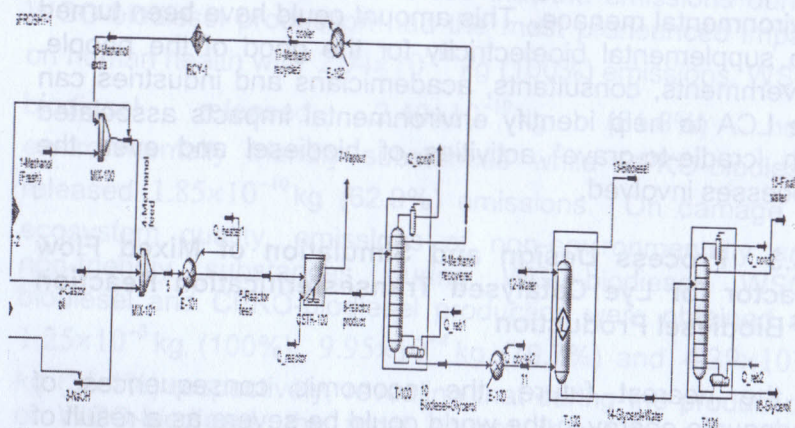
change showed that the emissions during WSO-biodiesel production contributed the most with 1.54×10^{-6} kg CO₂ (100%), followed by the processes of WGO-biodiesel and CPKO-biodiesel production with 1.32×10^{-6} kg CO₂ (85.7%) and 1.18×10^{-6} kg CO₂ (76.6%) respectively. Single score result of our study showed the increasing order of damage on the three factors considered. This was in the order of health < climate < ecosystem quality, i.e. human health experienced the least damage, followed by climate change and then ecosystem quality during the biodiesels production.

In conclusion, our findings showed that the order of preference of usage of the three kinds of biodiesel for diesel engine was CPKO, WSO and WGO since the higher the degree of saturation of the carbon bonds of the feedstock, the better the performance of the biodiesel as diesel engine oil and the less the release of non-environmentally and non-friendly substances into the environment. This is because most of the carbon atoms in CPKO are saturated while the carbon atoms in WGO and WSO are mostly unsaturated. These findings will aid in the decision-making process by incorporating green design objectives into engineering-related projects and thus provide opportunities for environmental improvement since over 3 million tonnes of spent cooking oils are produced in Nigeria annually, which constitute an environmental menace. This amount could have been turned into supplemental bioelectricity for the good of the people. Governments, consultants, academicians and industries can use LCA to help identify environmental impacts associated with 'cradle-to-grave' activities of biodiesel and even the processes involved.

3.4.3 Process Design and Simulation of Mixed Flow Reactor for Lye Catalysed Transesterification Reaction for Biodiesel Production

In the nearest future, the economic consequences of inadequate energy in the world could be severe as a result of the predominant dependence on fossil fuels. Moreover,

ecosystem and life quality degradation associated with the use of fossil fuels have become a lingering global challenge. These have prompted world leaders, organisations, industries and educational institutions to look for alternative or complementary energy sources that are sustainable, among which is biodiesel. A lye-catalysed esterification reaction is a sodium methoxide-fatty acid chemical interaction for the synthesis of environmentally benign fuel known as biodiesel. The biodiesel process is, however, fraught with its high cost of production (Ibrahim, 2015; Canakci and Van Gerpen, 2001). This has thus militated largely against industrial-scale biodiesel production and wide acceptance as a complete substitute for fossil fuel. Exploration of methods that reduce the production cost of biodiesel should, therefore, be the trend of current research. Olafadehan et al. (2018b) carried out the design of a process for the lye-catalysed synthesis of castor oil-based biodiesel in mixed flow reactor (MFR) at the rate of 1 kmol/h castor oil feed. The process layout, shown in Figure 17, was used to evaluate the process financial feasibility at mild operating conditions. Thus, a cost-effective mini-reactor for the process was designed. Castor oil is a readily available and inedible oil extracted from rapidly growing castor plant. Similar reports on the design of a transesterification process for biodiesel production using castor oil to the best of our knowledge are either unavailable or in closed literature.



used successfully to test run a fossil diesel generator for a few hours (Belewu, 2011). Mr. Vice Chancellor Sir, this is a challenge to us (UNILAG). The Department of Chemical and Petroleum Engineering is in a position to drive this feat. The Department is strategically positioned to access jatropha and castor seeds feedstocks.

3.4.4 Mechanistic Kinetic Models for Catalytic Steam Reforming of Methanol, Crude Ethanol and Glycerol for Hydrogen Production

The combustion of non-renewable energy resources, such as fossil fuels, constitutes the supply of most of the current energy needs. The gradual depletion of the fossil fuels reserves and efforts to combat pollution and GHG emissions have stimulated our interests in investigating a promising route for an alternative source of energy (i.e. hydrogen) production via catalytic reforming of methanol, ethanol and glycerol (a by-product in biodiesel production) since a new eco-friendly reservoir of hydrogen is needed if a global cycle of clean and sustainable production of energy is envisaged. Furthermore, since methanol, ethanol and glycerol do not contain heteroatoms (such as nitrogen and sulphur that can form different oxides in the presence of oxygen) and metals, their respective uses as sources of energy do not result in emissions of greenhouse gases (GHG) especially NO_x , SO_x , particulate matters and other toxic chemicals (hydrocarbons) to the indoor and outdoor atmosphere, when compared with the combustion of fossil fuels. Methanol is potentially a good source of hydrogen for mobile fuel cells since it is a liquid at ambient conditions. It has high hydrogen to carbon ratio.

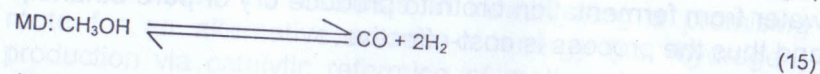
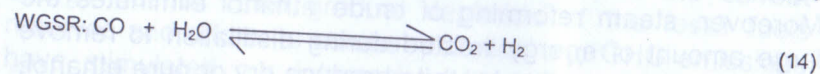
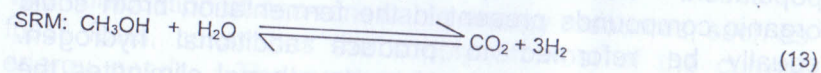
Ethanol can be produced renewably from several biomass sources, including energy plants, waste materials from agro-industries or forestry residue materials, organic fraction of municipal solid waste, etc. As a result, it can be a hydrogen source for countries that lack fossil fuel resources but have a significant agricultural economy. Ethanol provides an environmentally responsible energy source that can significantly reduce GHG emissions. The process of bio-ethanol conversion to hydrogen has the significant advantage

of being nearly CO_2 neutral since the CO_2 produced is consumed for biomass growth. It thus offers a nearly closed carbon loop. Moreover, ethanol is economically, environmentally and strategically attractive as an energy source since its complete combustion to produce power yields little or no CO . Unlike hydrocarbons, ethanol is easier to reform and is also free of sulphur, which is a catalyst poison in the reforming of hydrocarbons. Also, unlike methanol, which is produced from hydrocarbons and has relatively high toxicity, ethanol is completely biomass-based and has low toxicity and as such it provides less risk to the population. Besides, by using crude ethanol, the other organic compounds present in the fermentation broth could equally be reformed to produce additional hydrogen. Moreover, steam reforming of crude ethanol eliminates the large amount of energy wasted during distillation to remove water from fermentation broth to produce dry or pure ethanol, and thus the process is cost-effective.

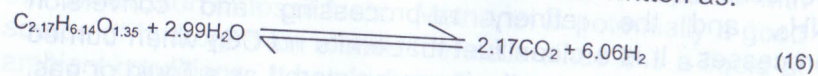
The transesterification of oils produces fatty acid methyl esters (biodiesel) and a 10% by weight glycerol as a by-product. Although glycerol is used as a sweetening agent, in medicine and cosmetics, the world demand for glycerol is limited. As such, a novel way of utilising glycerol to keep up with an increase in biodiesel production is to convert it to other products such as hydrogen for the production of energy. Hydrogen is predicted to be a major source of energy in the future. It is an important raw material in the chemical and petrochemical industries, for instance, in the manufacture of NH_3 , and the refinery re-processing and conversion processes. It is a clean fuel that emits no CO_2 when burned or used in $\text{H}_2\text{-O}_2$ fuel cells, it can be stored as a liquid or gas, and has been described as a long-term replacement for natural gas. Globally, efforts are geared toward commercialisation of the use of fuel cells. An example is the proton exchange membrane (PEM) fuel cell. This commercialisation can be used for the generation of electric power for both electric vehicles and distributed electric power plants (Creveling, 1992). This is due to the high-energy efficiency of the fuel cell, which is about 85% (Whitaker, 1994). With an equally strong interest in the use of hydrogen

as fuel, PEM fuel cells are the most certain to meet future ultra-low NO_x, SO_x, CO, CH₄ and CO₂ emission targets (Creveling, 1992).

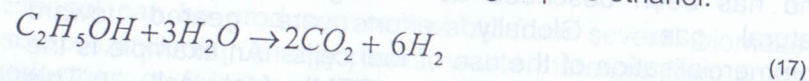
Consequently, kinetic studies investigated by us included (i) steam reforming of methanol (SRM) over a Cu/ZnO/Al₂O₃ (10/5/85 wt. %) catalyst in a fixed bed reactor over the temperature range of 433-573 K at atmospheric pressure and molar methanol to steam ratio of 1:1.4 (Olafadehan et al., 2009b). The main reactions that occur on this type of catalyst are reforming (SRM), water-gas shift reaction (WGSR) and methanol decomposition (MD):



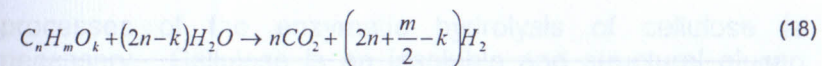
(ii) kinetics of steam reforming of concentrated crude ethanol on a Ni-based commercial catalyst at atmosphere pressure in the temperature range of 673-863 K, and at different catalyst weight to the crude ethanol molar flow rate ratio (in the range 0.9645-9.6451 kg catalyst h/kg mol crude ethanol) in a stainless steel packed bed tubular microreactor (Olafadehan et al., 2015). Based on our investigation, the molecular formula of the concentrated crude ethanol mixture was found to be C_{2.17}H_{6.14}O_{1.35}. Thus, the stoichiometric equation for the reforming of concentrated crude ethanol was written as:



as against the conventional reforming of pure ethanol:



(iii) kinetics of steam reforming of glycerol (C₃H₈O₃) (a by-product of biodiesel production) on Ru/Alumina catalyst (Peter et al., 2018). The general chemical reaction for steam reforming of alcohol and bio-oils is represented thus:



In the three cases, mechanistic kinetic models were postulated and plausible Langmuir-Hinshelwood-Hougen-Watson reaction rate expressions were developed based on atomic and molecular adsorption of hydrogen. The optimisation routines of Nelder and Mead simplex method and Levenberg-Marquardt were used to estimate kinetic parameters inherent in the models by fitting exceedingly well the experimental rates of reactions, and methanol, ethanol and glycerol conversion independently with simulated results, as shown in Figures 18 and 19 for steam reforming of methanol and crude ethanol respectively.

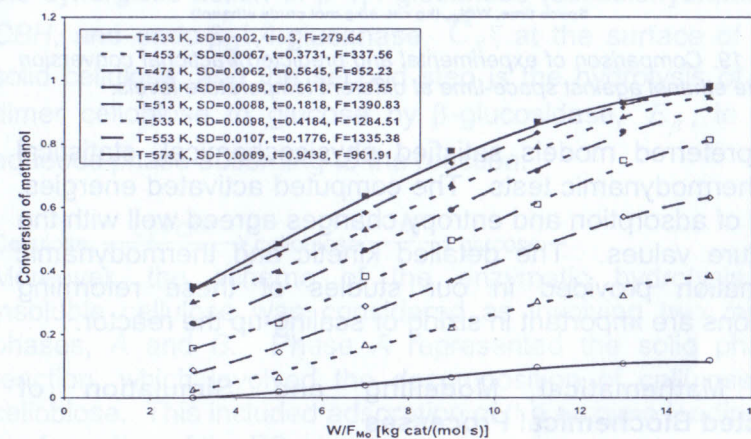


Figure 18. Comparison of experimental and predicted methanol conversion against contact time at different temperature levels during steam reforming of methanol on Cu/ZnO/Al₂O₃ (10:5:85) catalyst (S/M=1.4, $p_T=1$ atm).

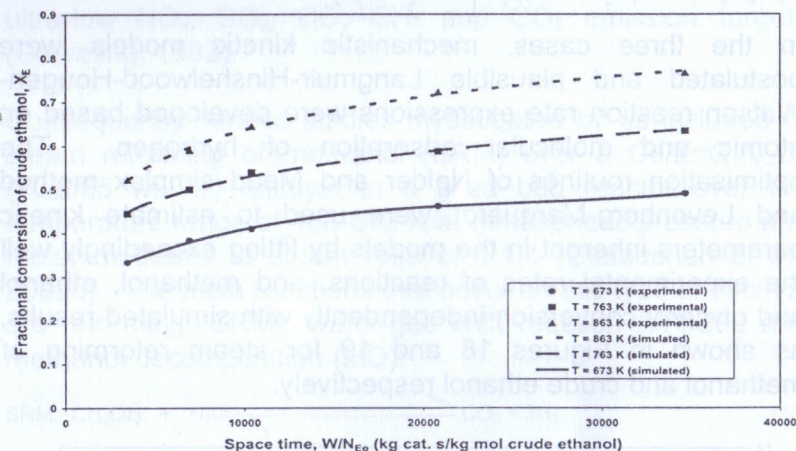


Figure 19. Comparison of experimental and predicted fractional conversion of crude ethanol against space-time at different temperature levels.

The preferred models satisfied physicochemical, statistical and thermodynamic tests. The computed activated energies, heats of adsorption and entropy changes agreed well with the literature values. The detailed kinetic and thermodynamic information provided in our studies of these reforming reactions are important in sizing or scaling-up the reactor.

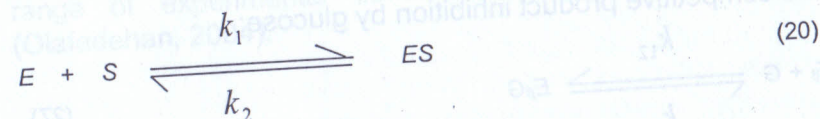
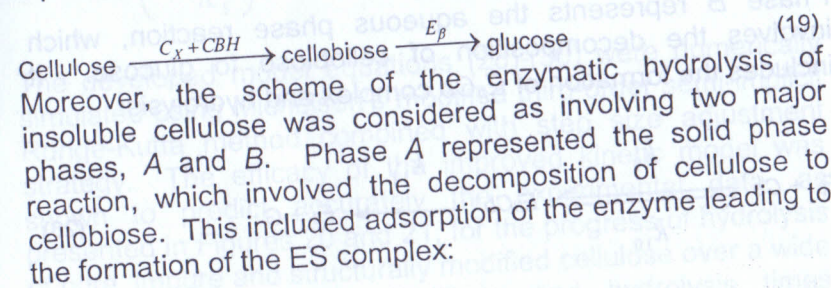
3.5 Mathematical Modelling and Simulation of Selected Biochemical Processes

Mr. Vice Chancellor, Sir, my contributions in the area of Biochemical Engineering are on the studies of hydrolyses of cellulose and lactose ($C_{12}H_{22}O_{11}$) by the enzymes, cellulase and lactase respectively, kinetics of enzymatic hydrolysis of oils (palm oil and sunflower oil), and methanogenic phase of an anaerobic digester. The emphases were in the utilisation of resources that are at our disposal in Nigeria for the bioengineering processes in consideration.

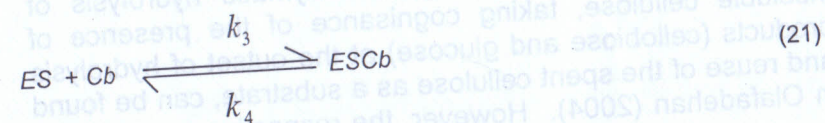
3.5.1 Enzymatic Hydrolysis of Cellulose

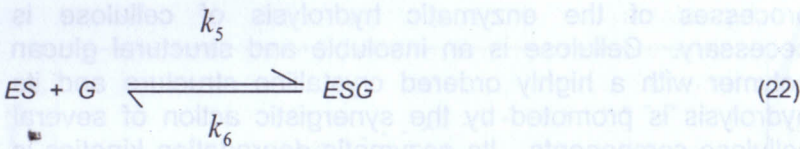
For better and ease of design as well as for rationally scaling-up the hydrolysis reactor, deeper understanding of the basic

processes of the enzymatic hydrolysis of cellulose is necessary. Cellulose is an insoluble and structural glucan polymer with a highly ordered crystalline structure and its hydrolysis is promoted by the synergistic action of several cellulase components. Its enzymatic degradation kinetics is yet to be fully understood. This presents the most difficult problem in the hydrolysis of cellulose. Olafadehan (2004) developed an improved, feasible, reliable and comprehensive mechanistic kinetic model for the enzymatic hydrolysis of cellulose. Considering cellulose crystallinity and nature and the composition of the cellulolytic enzyme system, a two-step hydrolysis of cellulose was proposed: the first step is the conversion of the insoluble cellulose into cellobiose through the synergistic action of β -1,4-glucanase (cellobiohydrolase), CBH, and endo- β -1,4-glucanase, C_X , at the surface of the solid cellulose, and the second step is the hydrolysis of the dimer cellobiose to glucose by β -glucosidase, E_β , in the aqueous phase according to the reaction:



Inactivation of the ES complex by non-competitive product inhibition:

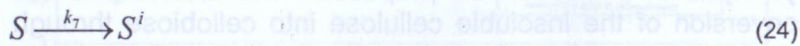




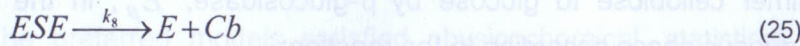
The effective portion of the ES complex is given as:

$$c_{ESE} = c_{ES} - c_{ESCb} - c_{ESG} \quad (23)$$

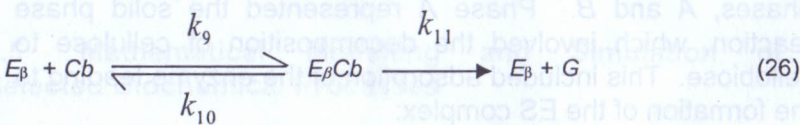
The transformation of the cellulose into a less digestible form is given as:



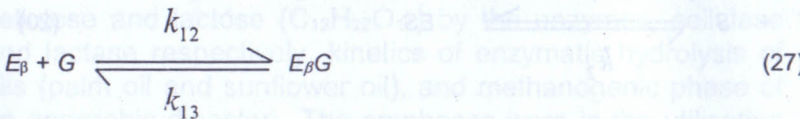
and hydrolysis of the effective portion of the ES complex into cellobiose:



Phase B represents the aqueous phase reaction, which involves the decomposition of cellobiose to glucose. It includes the formation of $E_\beta Cb$ complex and hydrolysis:



and competitive product inhibition by glucose:



From the mechanisms above, the summary of the generalised rate expressions for enzymatic hydrolysis of insoluble cellulose, taking cognisance of the presence of products (cellobiose and glucose) at the outset of hydrolysis and reuse of the spent cellulose as a substrate, can be found in Olafadehan (2004). However, the respective overall rates

of degradation of cellulose, S , and of production of the product (reducing sugar), P , and glucose, G , are presented in Equations (28)-(30) respectively:

$$\frac{dc_S}{dt} = 0.9k_8\phi_o \left[1 - \left(\frac{c_{SO} - c_S}{c_{SO}} \right)^n \right] \frac{c_{ESO}c_S}{c_{SO}} (1 - k_Gc_G) \times \exp[-k_{Cb}(c_P - c_G)] \quad (28)$$

$$R = \frac{dc_P}{dt} = k_8\phi_o \left[1 - \left(\frac{0.9c_P}{c_{SO}} \right)^n \right] \frac{c_{ESO}(c_{SO} - 0.9c_P)}{c_{SO}} \times (1 - k_Gc_G) \exp[-k_{Cb}(c_P - c_G)] \quad (29)$$

$$\frac{dc_G}{dt} = \frac{k_{11}c_{E\beta O}(c_P - c_G)}{K_4 \left(1 + \frac{c_G}{K_5} \right) + (c_P - c_G)} \quad (30)$$

The developed model equations (28)-(30) were numerically simulated using Michelsen's modified third-order semi-implicit Runge-Kutta method combined with step size adjustment strategy. The efficacy of the improved kinetic model was shown to predict accurately the experimental data, as presented in Figures 20 and 21, for the progress of hydrolysis of pure, impure and structurally modified cellulose over a wide range of experimental conditions and hydrolysis times (Olafadehan, 2004).

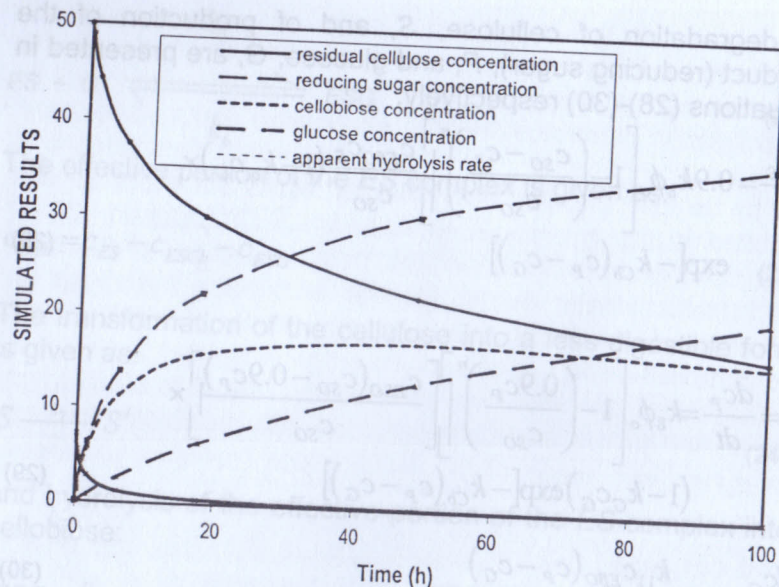


Figure 20. Comparison between simulated results and experimental data for the progress of hydrolysis of cellulose under normal hydrolysis conditions.

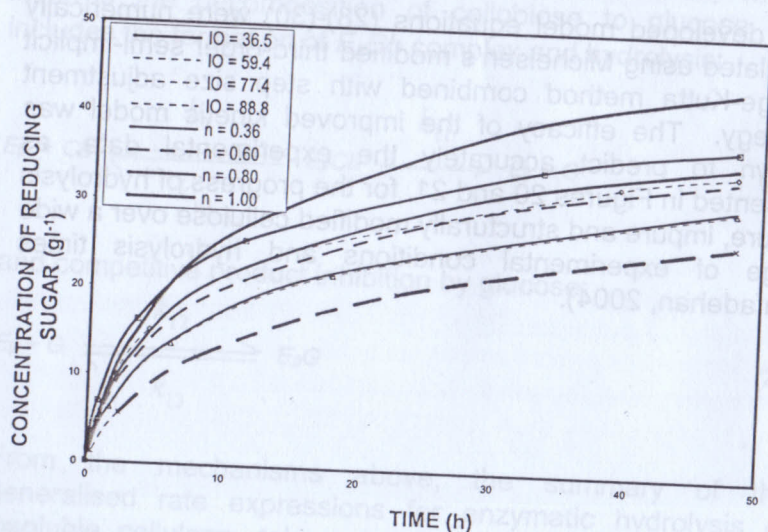


Figure 21. Effects of changes in initial crystallinity index on the hydrolysis of insoluble cellulose, and sensitivity of the model in response to the variation of the of the parameter, n , for the 96 h ball-milled cellulose.

Moreover, the improved kinetic model was used in estimating not only the changes in the concentrations of glucose and cellobiose, but also changes in other parameters including the extent of soluble protein adsorption, the extent of unadsorbed soluble protein, and the digestibility of spent cellulose (Olafadehan, 2004). Equally, an optimal cellulase complex with increased cellobiase activity was designed (Olafadehan, 2005) to minimise inhibition by cellobiose and thus maximise glucose formation during the enzymatic hydrolysis of insoluble cellulose, since glucose, and not cellobiose, is the preferred final product for most practical applications and is also a milder reaction inhibitor. The proposed model and the numerical solution presented in our works (Olafadehan, 2004; 2005) are most useful for a deeper understanding of biological reactor performance, ease of design, simulation and optimisation studies through the use of less complex kinetic equations that describe the hydrolysis reaction of insoluble cellulose.

3.5.2 Enzymatic Hydrolysis of Lactose

Lactose was discovered in milk in 1619 by Fabriccio Bartoletti, and identified as a sugar in 1780 by Carl Wilhelm Scheele (Linko, 1982). Lactose is a disaccharide that occurs naturally in both human and cow's milk. When milk is consumed, lactose breaks down in the small intestine under the influence of β -galactosidase (lactase) into two different monosaccharides: galactose and glucose. However, in adult human (or even starting from ages 5-7 and above), there is a reduction of the lactase present in the bowel leading to lactose intolerance, that is, the body is incapable of digesting lactose. Lactose intolerance affects millions of people worldwide. If the deficiency of lactase is very high, lactose escapes into the large intestine where it provides food for bacteria to thrive on. The fermentation of lactose by bacteria produces water, carbon (IV) oxide, lactic acid, methane, hydrogen gas and several other acids. This causes fermentative diarrhoea in the human victim who thereby experiences diarrhoea, flatulence, cramps, and general impairment of digestion. Several undesirable physical

properties are also implanted in dairy products due to the limited solubility of lactose in these products. Even though it exists as a true solution in milk, lactose easily precipitates out of these products giving them a gritty texture. Non-utilisation and disposal problem of whey, a by-product of cheese manufacture, is another lactose-caused problem. Souring of milk on brief exposure to ambient air is due to the conversion of lactose to lactic acid by bacterial action.

There are several solutions and methods of alleviating the problems of lactose presence in milk. These include the addition of enzyme and enzyme-substitutes to milk; fermentation of milk and milk products; and total abstinence from milk and milk by-product and/or a switch to goat milk in preference to cow milk. The enzymatic hydrolysis of lactose is an important biotechnological process in the food industry since it provides a good route of circumventing the limitations of the enumerated solutions. During the processing of milk or milk products for human consumption, lactose in the milk is usually hydrolysed by the action of β -galactosidase (lactase) into two simple sugars. These simple sugars are sweeter and more soluble than the product and thus make milk sweet so the overall requirement of sweeteners during the process is reduced. This makes the enzymatic hydrolysis of lactose more profitable in a dairy plant.

In our studies (Olafadehan, 1989, Olafadehan et al., 2009a; 2010), we developed a feasible and comprehensive mathematical model for lactose-lactase hydrolysis in a fixed bed, as presented in Equation (31), and the necessary numerical solution methods using Runge-Kutta-Gill and orthogonal collocation for the plug and dispersion flow models respectively.

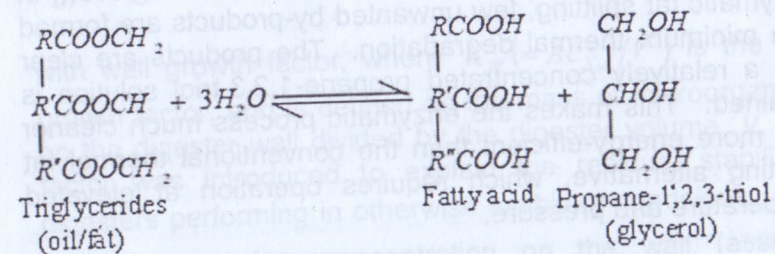
$$\frac{\partial C_s}{\partial t} = -D_L \frac{\partial^2 C_s}{\partial z^2} + U_f \frac{\partial C_s}{\partial z} - D_r \left(\frac{\partial^2 C_s}{\partial r^2} + \frac{1}{r} \frac{\partial C_s}{\partial r} \right) + (-r_s) \quad (31)$$

The design and analyses of such system were carried out to identify the flow system in a fixed bed. The β -galactosidase of

Kluyveromyces fragilis was immobilised on spherical chitosan beads using glutaraldehyde in an isothermal packed bed at 43°C, with a water recirculation jacket and a heating water bath. Different reaction rates of zero, first, Michaelis-Menten without inhibition, Michaelis-Menten with competitive product inhibition kinetics were used, taking cognisance of mass transfer resistances for the first time in such studies. The reliability of the model simulations was tested using experimental data, where it was revealed that dispersion flow model and using Michaelis-Menten kinetics with competitive product inhibition were appropriate to interpret the experimental results and simulate the process of lactose-lactase hydrolysis in a fixed bed (Olafadehan et al., 2010). Moreover, the results of this study can be used as a design tool to predict the effects of varying operating conditions (initial substrate concentration, superficial velocity/substrate input flow rate) on reactor performance, which can be taken up for application by the interested organisations and manufacturing outfits.

3.5.3 Kinetics of Enzymatic Hydrolysis of Oils

Mr. Vice Chancellor, Sir, the most important amongst the applications and significance of lipase in the oleo-chemical industry is its use for the production of fatty acids from oils according to the chemical reaction:



Although the fatty acids processing technology has been an established industry for over a century, there exists a dearth of kinetic data on this process in the literature. Olafadehan et al. (2008b) developed a detailed, feasible and generalised

mathematical model for the enzymatic hydrolysis of palm oil and sunflower oil in a mechanically stirred bioreactor at any enzyme concentration (whether low or high). The model predicted interfacial saturation at high-enzyme concentration for both palm oil and sunflower oil. It was used to determine, under different operating conditions, the enzyme concentration at which the interface between the oil and aqueous phase containing the enzyme would be saturated, that is, the critical enzyme concentration. Moreover, excellent agreements were achieved between the simulated results and experimental data for the hydrolyses of palm oil and sunflower oil by lipase in a stirred bioreactor. It was also shown that the quasi-steady-state approximation for the intermediates was applicable under the operating conditions used in this study. The sensitivity of the model predictions to the values of the kinetic parameters was also investigated. This study provided a technical survey to generate the necessary chemical kinetics and process data for the production of fatty acids. Equally, these data elucidated the process dynamics that form the basis for further studies in the development of an indigenous fatty acids processing technology as the enzymatic hydrolysis of oils by lipase for the production of high value-added products and heat-sensitive fatty acids is an energy-saving method due to mild reaction conditions with enzymes. It also reduces the financial constraints encountered in the process and the construction of the process equipment. Moreover, in enzymatic fat splitting, few unwanted by-products are formed with minimum thermal degradation. The products are clear and a relatively concentrated propane-1,2,3-triol solution is obtained. This makes the enzymatic process much cleaner and more energy-efficient than the conventional thermal fat splitting alternative, which requires operation at elevated temperature and pressure.

3.5.4 Modelling and Simulation of Methanogenic Phase of an Anaerobic Digester

Anaerobic treatment processes are rather complex microbiological processes, performed by specific groups of bacteria that function only in the absence of air. Such

processes are often used to dispose of wastes while generating useful fuel (methane, commonly called biogas). Three main steps are usually identified in anaerobic digestion as follows: hydrolysis of the complex organic matter; acidogenic phase (with the production of volatile acids); and methanogenic phase (where the methanogenic bacteria convert the volatile acids into the final products, CO_2 and CH_4). Amongst the volatile acids, ethanoic acid is the most significant precursor of methanogenesis; with methanogenesis considered as the rate-controlling step in modelling attempts. In our study (Olafadehan and Alabi, 2009), a biological dynamic model for the methanogenic phase of an anaerobic digester with and without wall growth factor was developed for the substrate and microorganisms concentration, and presented thus:

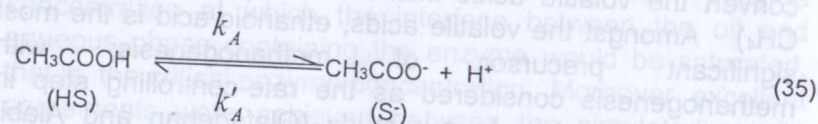
$$\left. \begin{aligned} \frac{dc_s}{dt} &= \frac{1}{\sigma}[(c_s)_0 - c_s] + \frac{\mu}{Y}c_x \\ \frac{dc_x}{dt} &= \frac{1}{\sigma}[(c_x)_0 - c_x] + c_x(\mu - K_d) \end{aligned} \right\} \text{without wall growth factor} \quad (32)$$

$$\left. \begin{aligned} \frac{dc_s}{dt} &= \frac{1}{\sigma}[(c_s)_0 - c_s] + \frac{\mu}{Y}[c_x + (A/V)c_{x_w}] \\ \frac{dc_x}{dt} &= \frac{1}{\sigma}[(c_x)_0 - c_x] + \mu[c_x + (A/V)c_{x_w}] - K_d c_x \end{aligned} \right\} \quad (33)$$

with wall growth factor, where $K_w (=Ac_{x_w}/V)$ is the wall-growth factor, and is defined as the mass of microorganisms on the digester wall divided by the digester volume, V . The factor was introduced to explain the residual stability of digesters performing in otherwise inhibitory conditions; c_{x_w} is the microorganism concentration on the wall (assumed constant), and A/V the ratio of wetted surface area, A , to volume of the digester. The microorganism specific growth rate, μ , is given by:

$$\mu = \frac{\mu_{\max}}{1 + \frac{K_s}{C_{HS}} + \frac{C_{HS}}{K_I}} \quad (34)$$

The dissociation of ethanoic acid is given by:



with acetic acid dissociation (or equilibrium) constant, k

$K_A = \frac{k_A}{k'_A}$. Hence, the derived specific growth rate of microorganisms was found to be:

$$\mu = \frac{\mu_{\max}}{1 + \frac{K_s(K_A + C_{H^*})}{C_{H^*}C_T} + \frac{C_TC_{H^*}}{K_I(K_A + C_{H^*})}} \quad (36)$$

The use of an inhibition function in the substrate and microorganisms mass balances is essential to develop a feasible model that predicts failure situations in sustained continuous anaerobic processes due to inhibition of biological growth. The model, which assumed a continuous feed of ethanoic acid to the continuously stirred anaerobic digester, was numerically solved, without pH restriction ($4 \leq \text{pH} \leq 10$), using the semi-implicit Runge-Kutta method combined with step-size adjustment strategy. The simulated results of this study showed that it was extremely imperative to avoid sudden changes in the feed (substrate) concentration in order to allow the process stabilise and metabolise the substrate concentration present, within a reasonable response time, coupled with the prevention of process failure and bioreactor instability owing to inhibitory unionised substrate concentrations at low pH values: low pH values (i.e. $\text{pH} < 7$) enhance bioreactor instability and thus lead to the failure of the process. However, at high pH values, the

microorganisms showed a shorter response time, which suggested that reactor recovery would be more difficult and long recovery times needed. Moreover, good process response was obtained by a gradual increase (ramp forcing) of the feed substrate concentration instead of a step increase. The presence of microorganism growth on the digester walls led to an improvement of the response of the reactor toward inhibition (i.e. less inhibitory conditions were observed). This implied robust stability of an anaerobic digester under drastic changes of its operational conditions. This study was necessitated for reason of this process becoming more popular in the water treatment industry as the anaerobic process has considerable advantages over aerobic processes. Some of the advantages include low sludge production, tolerance of start/stop operation, production of a useful fuel (methane, commonly called biogas) and relatively high throughput. The dynamic model presented herein allows the study of anaerobic digester performance under transient conditions, such as start-up operations, and quantitatively measures process stability under different operational conditions.

3.6 Modelling and Simulation of Selected Chemical Processes and Adsorption Kinetics

Fixed bed adsorption column, as depicted in Figure 4, is widely used for purifying liquid mixtures, especially industrial waste effluents. Hence, in our works, a detailed, feasible and comprehensive mathematical model was developed to describe the processes of monocomponent and multicomponent adsorption on different porous media in fixed-bed adsorption column (Olafadehan, 2000; Olafadehan and Susu, 2001a, 2001b). The model took into cognisance many of the factors neglected in the literature. These include effects of axial diffusion in the fluid and the external film and internal diffusion resistances of the particles. The resulting model was good for all manners of non-linear reaction rate expressions and all general non-linear adsorption isotherm relationships. The resulting model equations are hyperbolic and parabolic partial differential equations for the macro-

(fluid) and micro-systems respectively, as presented in Equations (37) and (38):

Fluid phase:

$$\frac{\partial C_i}{\partial t} = D_{Li} \frac{\partial^2 C_i}{\partial z^2} - U_f \frac{\partial C_i}{\partial z} - \left(\frac{1 - \epsilon_b}{\epsilon_b} \right) \left(\frac{3}{R} \right) K_{fi} (C_i - X_i) \Big|_{r=R} \quad (37)$$

Pore-fluid phase:

$$\frac{\epsilon_p}{r^2} \frac{\partial}{\partial r} \left(r^2 D_{pi} \frac{\partial X_i}{\partial r} \right) + f_{ri} = \epsilon_p \frac{\partial X_i}{\partial t} + \sum_{j=1}^n \left(\frac{\partial q_i^*}{\partial X_j} \right) \left(\frac{\partial X_j}{\partial t} \right) \quad (38)$$

In our studies, these equations were expressed for each of the components (pollutants) in a multi-component adsorption system.

3.6.1 Phenolic compounds adsorption without reaction in Fixed Bed

For the treatment of wastewater effluent from a paint industry in Ikeja, Lagos, Nigeria (explained in Section 3.2), the system under consideration was a multicomponent one as it involved removal of phenolic compounds from the wastewater. However, the complex multicomponent adsorption system was rationalised into a single system, which was simpler and easier to handle mathematically than the multicomponent system. The former is a pseudo monocomponent adsorption system in which the phenolic compounds have been lumped into one single component. In the experimental work of Olafadehan and Aribike (2000), the concentrations of the pollutants were lumped together as chemical oxygen demand (COD). This decision was hinged on the fact that the industrial wastewater employed in the experiment was found to contain mainly phenols. Hence, the developed models, Equations (37) and (38), were applied in conjunction with the already obtained adsorption isotherm in Olafadehan and Aribike (2000) to predict the lumped concentration of phenolic compounds removed from industrial wastewater in a fixed

bed of activated carbon adsorbent (Aribike and Olafadehan, 2008). This was achieved by solving the model equations using the orthogonal collocation method and third-order semi-implicit Runge-Kutta method combined with a grid refinement strategy. The simulated complete breakthrough profiles for phenolic compounds in pseudo single component adsorption system using particle sizes of 1-2 mm and > 2 mm were in excellent agreement with the pilot plant profiles studied by Olafadehan and Aribike (2000). The effects of particle sizes on breakthrough curves for the samples collected at three different effluent points revealed that a strong influence occurred at early breakthrough times. These were observed to be highest for particle size > 2mm for all the three samples of wastewater effluents and lowest for 1-2 mm particle size. Therefore, the particle sizes used in the column affected breakthrough times. Breakthrough times of 40, 25 and 150 minutes were predicted for phenolic compounds in wastewater samples I, II and III respectively for particle sizes of 1-2 mm. In the case of particle sizes greater than 2 mm, breakthrough times of 90, 90 and 160 minutes were obtained for samples I, II and III, respectively. There were indications that it would take the carbon bed between 1 and 3 hours to get saturated for the cases considered. Also, the relation between the solid phase and bulk liquid phase concentrations for phenolic compounds in the three wastewater samples revealed the formation of a primary monomolecular layer on the adsorption surface. Typical breakthrough concentration profiles obtained in our studies are shown in Figure 22.

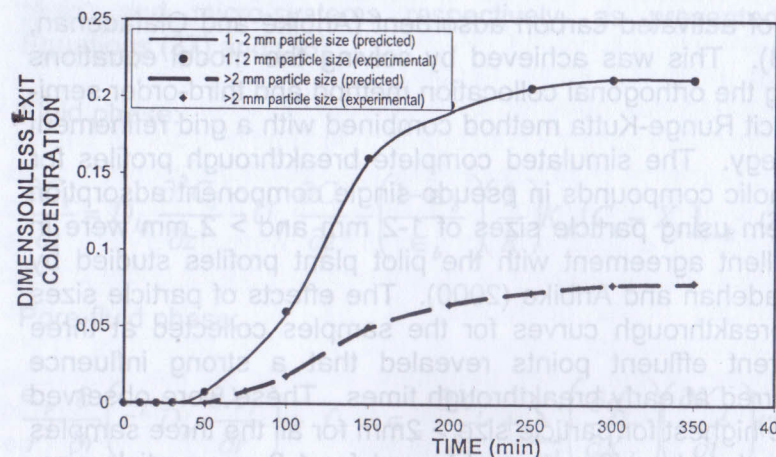


Figure 22. Predicted versus experimental breakthrough profiles for phenolic compounds in sample I.

3.6.2 Binary adsorption of aromatics and sulphur compounds without reaction in fixed bed

We, Olafadehan and Susu (2005), presented the simulation of the binary adsorption, without reaction, of aromatics and sulphur compounds onto a fixed bed of porocel clay for kerosene deodorisation, together with comparative analyses of linear, Freundlich and Langmuir isotherms using the developed models given in Equations (37) and (38). Excellent agreement was obtained between the simulated results and pilot plant data for the breakthrough profiles for the non-linear adsorption isotherms of Freundlich and Langmuir. However, no agreement was obtained for the linear isotherm. Also, competitive multicomponent adsorption occurred on the adsorbent surface in which sulphur compounds are selectively adsorbed onto porocel clay relative to the aromatics compounds. In this regard, our simulated results revealed the formation of multiple adsorption layers upon the primary monomolecular layer on the adsorbent surface as illustrated in Figure 5. An experimental breakthrough time of 8 h was also predicted for both aromatics and sulphur compounds using the non-linear Freundlich and Langmuir isotherms. The implication and application of this study are in the current drive of using

deodorised kerosene in the aerosol and aviation industries as aromatics and sulphur compounds impart odour to kerosene.

3.6.3 Ternary adsorption without reaction in fixed bed

The adsorption of a single component from an aqueous solution onto an adsorbent has been modelled successfully. Conversely, relatively little model development has been done for almost real multicomponent systems. Olafadehan and Susu (2004a) presented a computational procedure for solving the set of stiff hyperbolic and parabolic partial differential equations (37) and (38) describing the simultaneous adsorption of a ternary system in a column packed with adsorbent particles using non-linear adsorption isotherms of Fritz and Schlunder. We adopted orthogonal collocation method combined with Michelsen's modified third-order semi-implicit Runge-Kutta method with step-size adjustment strategy for the numerical solution of the resulting coupled ordinary differential equations modelling the simultaneous adsorption of butanol-2, tert-amylalcohol (2-methylbutan-2-ol) and phenol on activated carbon as the adsorbent in fixed beds of 0.41 and 0.82 m length. Excellent agreement was achieved between the simulated results of our study and the previously published experimental data of Balzli (1977). Typical results are shown in Figure 23 for a 0.41-m adsorber.

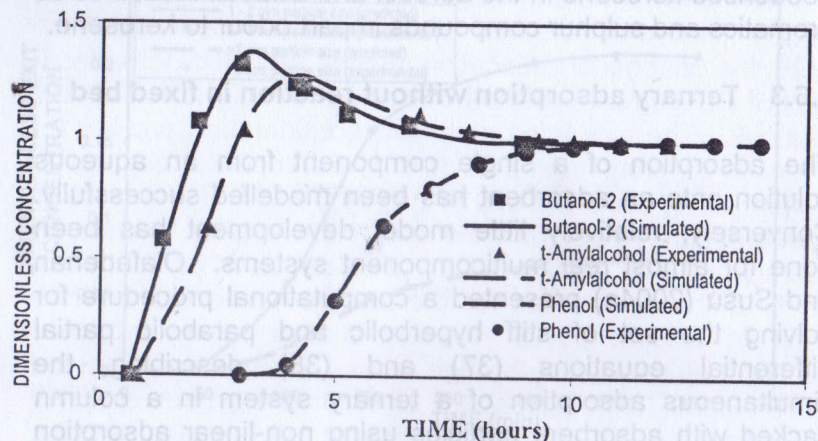


Figure 23. Breakthrough curves for simultaneous adsorption of butanol-2, t-amyl alcohol and phenol in a 0.41 m bed.

From Figure 23, it can be seen that phenol appeared in the effluent only after a very long time. This is due to its very strong adsorption affinity, and thus replaced the non-key components (i.e. butanol-2 and t-amylalcohol), which were first adsorbed onto the activated carbon in the bed: they appeared in the effluent as a concentration peak. Thus, phenol was the most selectively adsorbed component on the activated carbon. It was equally observed that the breakthrough curves were delayed by 1.5, 2.0 and 5.5 hours for butanol-2, t-amylalcohol and phenol respectively in a 0.82-m adsorber compared with the results in a 0.41-m adsorber. Hence, the bed length affected the breakthrough times and even heights of the peak as the peak heights for these components increase on doubling the bed length since the longer the bed, the larger the total amount of the non-key components displaced. Moreover, as peaks increased, the breakthrough times increased, and the separation between the wavefronts increased in the longer beds. Our results revealed a simple type of multiple layer formation, that is, adsorption on solid surfaces took place with the formation of secondary, tertiary and finally multiple layers upon the monomolecular layer. So physical adsorption must have occurred on the chemisorbed species with chemisorption

being completed at lower concentrations. The comprehensive model developed herein is most useful in the design and analysis of fixed-bed activated carbon adsorbers treating multicomponent aqueous wastes. Moreover, it can be readily extended to multicolumn and/or unsteady state process operation.

3.6.4 Binary and ternary adsorption with reaction

Many investigators have worked successfully on binary and multicomponent adsorption, without reaction, onto porous media in a fixed bed. These included some of our numerous works that were enumerated above. However, none of these models considered the adsorption-reaction process. In our studies (Olafadehan and Susu, 2004b; 2004c), adsorption-reaction of the dehydrogenation of cyclohexane to benzene and hydrogen on Pt-Re/Al₂O₃ catalyst in an inert (argon and helium) and active diluent (hydrogen) using pulse microcatalytic and continuous flow reactors were investigated. The catalytic dehydrogenation of cyclohexane (C₆H₁₂) to benzene (C₆H₆) is an important reforming reaction in the petroleum refining and petrochemical operations. The scheme of this consecutive reaction through the intermediate cyclohexene (C₆H₁₀) is presented in Figure 24 thus:

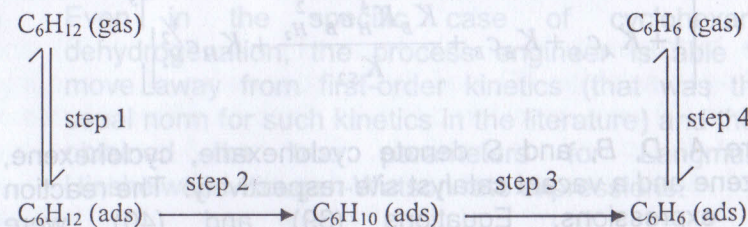


Figure 24. Consecutive reactions during the catalytic dehydrogenation of cyclohexane to benzene.

Olafadehan and Susu (2004b; 2004c) proposed reaction mechanisms for the reforming reaction based on unadsorbed and adsorbed hydrogen on the catalyst surface. Subsequently, mechanistic reaction rate equations were developed by assuming any of the elementary reaction steps

(outlined in Figure 24) was rate-determining. All the mechanistic reaction kinetic models were tried in the Nelder-Mead modified simplex method (a search algorithm). Also, discrimination among the rival rate expressions was based on the positive values of the rate and adsorption equilibrium constants, the goodness of fit and on the increase and decrease of the kinetic rate and adsorption equilibrium constants of the reaction with increase in temperature. Thus, we obtained the surface reaction of adsorbed cyclohexane to adsorbed cyclohexene (step 2) as the rate-determining step for the catalytic dehydrogenation of cyclohexane with unadsorbed hydrogen on the catalyst surface (a binary system with reaction) as:

$$(-r_1) = \frac{k_{s1}K_A(c_A - c_B c_{H_2}^3/K)}{1 + K_A c_A + (K_B/K_{S2})c_B c_{H_2}^2 + K_B c_B} \quad (39)$$

However, for the case where hydrogen was adsorbed on the catalyst surface (a ternary system with reaction), we obtained:

$$(-r_2) = \frac{k_{s1}K_A \left(c_A - \frac{K_{R2}^5 c_B c_{H_2}^3}{K} \right)}{\left[1 + K_A c_A + K_B c_B + \frac{K_B K_H^4 c_B c_{H_2}^2}{K_{S2}} + K_H c_{H_2}^{1/2} \right]^3} \quad (40)$$

where A, D, B, and S denote cyclohexane, cyclohexene, benzene and a vacant catalyst site respectively. The reaction rate expressions, Equations (39) and (40), were independently incorporated into the developed model equation (38) and solved together with the fluid phase mass balance, Equation (37), using orthogonal collocation and Michelsen's third-order semi-implicit Runge-Kutta method combined with step-size adjustment strategy. Numerical solutions for the ternary adsorption-reaction scheme were compared with the binary adsorption-reaction case where hydrogen adsorption was ignored. Our results revealed the surface reaction of adsorbed cyclohexane to adsorbed

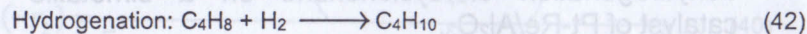
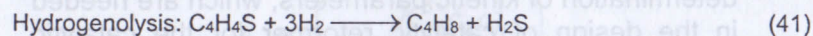
cyclohexene (step 2) was indeed the rate-determining step for the catalytic dehydrogenation of cyclohexane to benzene with dissociative adsorption of hydrogen atom on Pt-Re/Al₂O₃ catalyst in inert and active carrier gases using pulse and continuous flow techniques. Therefore, hydrogen adsorption is somewhat significant for the dehydrogenation of cyclohexane to benzene. Hence, it cannot be ignored. The activation and equilibrium adsorption energies were found to be higher for the case of dehydrogenation of cyclohexane with adsorbed hydrogen than with unadsorbed hydrogen as a result of autonomous cleaning of the catalyst surface by the hydrogen adsorbed. The adsorption-reaction processes studied here are of utmost significance to industrial processes where kinetics is Langmuir-Hinshelwood-Hougen-Watson so all mass transfer resistances that have been considered exist for such system hence the presentation here goes far beyond cyclohexane dehydrogenation on Pt-Re/Alumina catalyst. For the specific case discussed, the advantages of this adsorption-reaction method are as follows:

- (i) In a situation where one does not know mass transfer resistance is negligible, this method allows determination of kinetic parameters, which are needed in the design of catalytic reformer for the catalytic dehydrogenation of cyclohexane on a bimetallic catalyst of Pt-Re/Al₂O₃.
- (ii) Even in the specific case of cyclohexane dehydrogenation, the process engineer is able to move away from first-order kinetics (that was the usual norm for such kinetics in the literature) and thus obtained the true parameters for Langmuir-Hinshelwood-Hougen-Watson rate expressions.

In conclusion, the adsorption-reaction process is feasible in porous media. Although mathematically complex, the process can be treated with the methods developed in our work.

3.6.5 Mechanistic Kinetic Models for Hydrodesulphurization Processes

Hydrodesulphurization (HDS) is probably the most important hydrotreating process in petroleum refining industry to produce clean fuels devoid of heteroatom impurities such as sulphides, disulphides, polysulphides, thiophene, benzothiophene, mercaptans, and quinoline. However, the kinetic modelling of such process is lagging far behind, yet an exhaustive understanding of the kinetics of these sulphur-containing compounds will pave way for the design of improved hydrotreatment plant. Olafadehan and Oghenekaro (2008), and Olafadehan and Okinedo (2009) provided succinct information on the mechanistic kinetic models for hydrogenolysis of thiophene and benzothiophene on a commercial hydrodesulphurization Co-Mo/ γ -Alumina catalyst respectively. The following consecutive reaction schemes adopted for the hydrogenolysis of thiophene, C_4H_4S , into hydrogen sulphide (H_2S), butene (C_4H_8), and butane (C_4H_{10}) are given thus:



The hydrogenolysis of thiophene (T) into butene (B) and hydrogen sulphide (S), and the hydrogenation of butene into butane (A) were considered to take place on different kinds of active sites σ and τ respectively. Since no 1,3-butadiene and tetrahydrothiophene were detected in the effluent stream of the experimental work of Van Parijs and Froment (1986), it was inferred that they must be highly reactive intermediates. Therefore, for the kinetic analysis in our studies, thiophene and n-butane were chosen as the independent reaction components, and mechanistic kinetic models were developed. Amongst the rival models, the best fit of the experimental conversion/rate against space-time data with positive rate and equilibrium constants showed that the surface reaction between adsorbed thiophene and adsorbed hydrogen on σ sites in the hydrogenolysis, and the surface

reaction between adsorbed butene and adsorbed hydrogen on τ sites in the hydrogenation, when hydrogen was adsorbed molecularly, are the rate-determining steps.

The triangular reaction scheme for the hydrogenolysis of benzothiophene (C_8H_6S) to ethylbenzene ($C_6H_5C_2H_5$) and hydrogen sulphide (H_2S) is given in Figure 25.

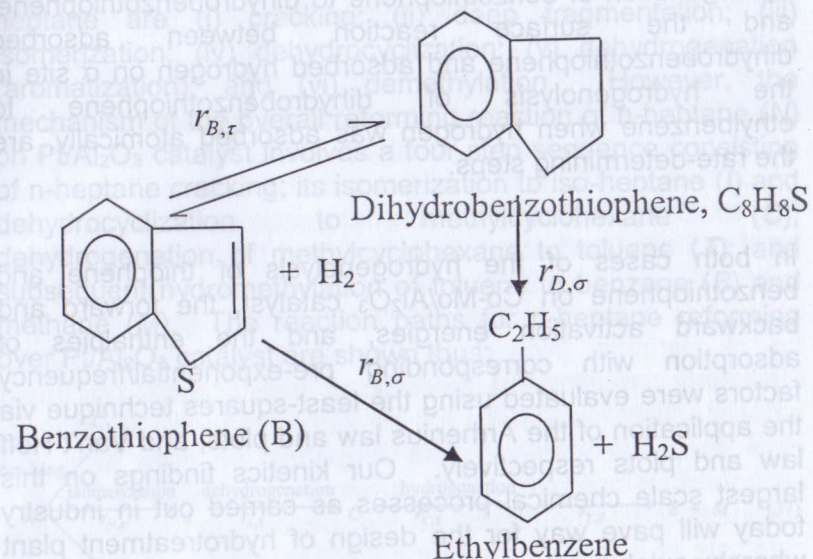
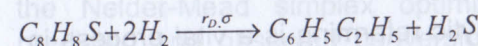
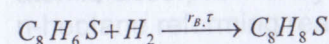
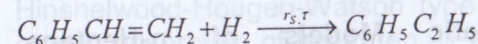
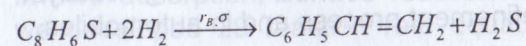


Figure 25. Reaction scheme for hydrogenolysis of benzothiophene on Co-Mo/ Al_2O_3 catalyst.

Hence, the reactions occurring during the hydrogenolysis/hydrogenation are given below, from which mechanistic kinetic models were formulated.



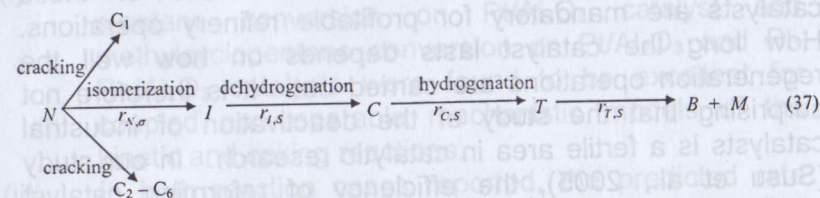
Amongst the rival models, the best fit of the experimental conversion against space-time data with positive rate and equilibrium constant revealed that the surface reaction between adsorbed benzothiophene and adsorbed hydrogen on σ sites in the direct hydrogenolysis of benzothiophene to ethylbenzene, the surface reaction between adsorbed benzothiophene and adsorbed hydrogen on τ sites in the hydrogenation of benzothiophene to dihydrobenzothiophene, and the surface reaction between adsorbed dihydrobenzothiophene and adsorbed hydrogen on σ site in the hydrogenolysis of dihydrobenzothiophene to ethylbenzene when hydrogen was adsorbed atomically, are the rate-determining steps.

In both cases of the hydrogenolysis of thiophene and benzothiophene on Co-Mo/Al₂O₃ catalyst, the forward and backward activation energies, and the enthalpies of adsorption with corresponding pre-exponential/frequency factors were evaluated using the least-squares technique via the application of the Arrhenius law and plots, and Van't Hoff law and plots respectively. Our kinetics findings on this largest scale chemical processes as carried out in industry today will pave way for the design of hydrotreatment plant whereby sulphur compounds can be removed. This is the call in various countries, including Nigeria, for an acceptable level of sulphur in petroleum fractions in a bid to minimise its effects as a primary source of air pollution. The presence of sulphur in many forms in petroleum fractions poses both technical and environmental risks to man and nature. Refining of the sulphur compounds, in particular, decreases the contributions to acid rain production upon fuel combustion. It is also valuable in preventing catalyst poisoning both in the refinement process and in automobiles.

3.6.6 Mechanistic kinetic Models of n-Heptane Reforming

As mentioned earlier, catalytic reforming is a vital process in petroleum refining. It is needed for the enhancement of octane number in gasoline production and also for the

production of aromatics for the petrochemical industry. The aromatization of n-heptane is an important reforming reaction, especially on supported platinum catalysts. Olafadehan et al. (2008a) comprehensively studied the kinetics of the reforming of n-heptane on a platinum/alumina catalyst in a pulse microcatalytic reactor at a total pressure of 391.8 kPa over a relatively wide temperature range of 420-500°C (Susu and Adenusi, 1997). The main reactions in the reforming of n-heptane are (i) cracking; (ii) deep fragmentation; (iii) isomerization; (iv) dehydrocyclization; (v) dehydrogenation (aromatization); and (vi) demethylation. However, the mechanism of the overall reforming reaction of n-heptane (N) on Pt/Al₂O₃ catalyst involves a four-step sequence consisting of n-heptane cracking; its isomerization to iso-heptane (I) and dehydrocyclization to methylcyclohexane (C); dehydrogenation of methylcyclohexane to toluene (T); and subsequent hydromethylation of toluene to benzene (B) and methane (M). The reaction paths for n-heptane reforming over Pt/Al₂O₃ catalyst are shown thus:



The dehydrogenation and hydrogenation steps occur on platinum sites, represented by S while the isomerization step occurs on the acidic alumina sites, represented by σ . The cracking is believed to occur by the free radical theory, which is a subject for further study by the Inaugural lecturer. The dehydrogenation, hydrogenation and isomerization steps involve adsorption, surface reaction and desorption. Thus, we developed 29 reaction rate equations of the Langmuir-Hinshelwood-Hougen-Watson type based on molecular and atomic adsorption of hydrogen. Parameter estimates for the n-heptane reforming reactions were obtained by application of the Nelder-Mead simplex optimisation technique to the predicted and observed conversion/production rates of the reaction components. Discrimination amongst rival kinetic

models was based upon physicochemical criteria, analysis of the residuals, statistical and thermodynamic tests. The rate-determining step was found to be the surface reaction of adsorbed iso-heptane to adsorbed methylcyclohexane with dissociative adsorption of hydrogen on the catalyst surface during dehydrocyclization of iso-heptane to methylcyclohexane.

3.6.7 Simultaneous Reaction-Deactivation Kinetic Studies

The deactivation of industrial catalysts adversely affects the profitability of industrial catalytic plants, as the catalytic process may represent a major cost component of the plant. For example, a catalytic reformer processing 100,000 bpd crude oil may cost about \$1 billion, and the platinum catalyst cost may be about \$278 million (Somorjai and Davis, 1982), at today's price of between \$27,263.83 and \$28,067.60 per kg of platinum (New York Times of August 23, 2019). Obviously, multiple regenerations and reuse of these catalysts are mandatory for profitable refinery operations. How long the catalyst lasts depends on how well the regeneration operations are carried out. It is therefore not surprising that the study of the deactivation of industrial catalysts is a fertile area in catalytic research. In our study (Susu et al., 2005), the efficiency of reforming catalyst utilisation was explored using the deactivation data collected in a CSTR at a total pressure of 101.325 kPa and W/F values up to 0.33 g min/cm³ from the multiple regenerations of platinum-containing catalysts. The deactivation models combined the kinetic equation with the coking equation; both equations were derived from mechanistic models. The reactive systems investigated were the reforming and coking of n-octane and methylcyclopentane on the monometallic Pt/Al₂O₃ and the bimetallic Pt-Re/Al₂O₃ catalysts. The coupling of the two models resulted in a dynamic expression, and the parameter estimates were carried out without decoupling the main reaction from the coking reaction. The model formulation afforded the estimation of the level of residual activity by the incorporation of a factor, f ,

representing incomplete deactivation. The residual activity, f , was found to be practically unity for n-octane and methylcyclopentane conversion, indicative of high utilisation efficiency of the Pt/Al₂O₃ and Pt-Re/Al₂O₃ catalysts for the two hydrocarbon reactants, regardless of the large difference in the coking abilities of the hydrocarbon species. For both reactants, these were ascribed to the existence of a predominant coke type, whose magnitude is a thousand-fold higher than the deleterious coke types. This predominant coke type is oxidisable coke, which is removable by an oxygen-containing gas. This coke is non-toxic to the reforming reactions, as regeneration restores the catalyst activity. As far as the industrial life of the catalyst is concerned, it was revealed in our study that the efficiency of catalyst utilisation would be high for as long as oxidisable coke predominates on the catalyst surface. In addition to the conclusion of efficiency utilisation of the catalysts studied, other major conclusions derivable from this work are:

- (i) The predictions of experimental deactivation data for n-octane conversion on Pt/Al₂O₃ catalyst and methylcyclopentane conversion on Pt/Al₂O₃ and Pt-Re/Al₂O₃ catalysts were found to be excellent for coupled non-separable mechanistic models of the kinetic and coking reactions.
- (ii) In both reaction cases reported, the predicted rate constants for the forward reaction were about five times higher than those for the reverse reaction.

3.6.8 Modelling Hydrocarbons Pyrolysis

Hydrocarbons pyrolysis reactions are described by several elementary reactions involving reactive intermediates which may be atoms or radicals. The kinetic equations derived for elementary reactions are normally complex and difficult to solve. The Steady-State Approximation (SSA) was therefore postulated to simplify complex equations. The SSA assumes that the concentrations of the reactive intermediates (radicals) are constant during the course of the reaction, and as such the rates of change of their concentrations are zero. The use of SSA converts the stiff ODEs associated with radical

species to non-linear algebraic equations to forestall the complex mathematics often encountered in the numerical integration of such equations. In this way, very useful and plausible solutions of the models could be obtained. Thus, in our work (Aribike et al., 2006), the application of the SSA in the modelling of n-hexane and n-heptane pyrolysis reactions was investigated, where two hundred and fifty four (254) mechanistic models were proposed. The experimental set-up consisted essentially of an annular stainless steel reactor, an electric furnace (Stanton Redcroft, U.K.), three gas chromatographs, a split flow valve and liquid nitrogen cold trap. A brief description, materials and experimental methods used in the study were given in our work, (Aribike et al., 2006) while the detailed description was given in Aribike (1986). The proposed reaction mechanism comprised mainly radical reactions. Some molecular reactions were equally included in the mechanistic model, since excluding them would result in erroneous results (Benson, 1976). These were then translated to two sets of stiff ordinary differential equations (ODEs) using a 'chemical compiler' code. The two sets of coupled non-linear ODEs were solved numerically using a stiff integration program based on the Adaptive Semi-Implicit Runge-Kutta (ASIRK) algorithm of Prokopakis and Seider (1981). Alternatively, SSA was applied to convert ODEs representing radical species to non-linear algebraic equations, which were subsequently solved simultaneously with the remaining ODEs representing molecular species. The major product distributions of n-hexane and n-heptane pyrolysis predicted by ASIRK showed excellent agreement with the experimental data, while those simulated by SSA and Newton-Raphson algorithm showed significant deviation from experimental data. Thus, the ASIRK technique is well suited for solving kinetic models of hydrocarbons pyrolysis reactions while SSA and Newton-Raphson algorithm were inadequate in the chemical reaction kinetics of hydrocarbon pyrolysis, i.e. radicals never really attain a steady state in the reactor in practice.

3.6.9 Kinetics of Smog Photochemistry

Photochemical smog is an atmospheric condition, which produces severe eye irritation and poor visibility, to mention but a few of its adverse effects. Three ingredients are needed for its formation: energy from a light source (ultraviolet), hydrocarbons and nitrogen oxides. Hydrocarbons and nitrogen oxides are produced through the burning of fossil fuels, most notably automobiles. There are two types of photochemical smog: oxidising smog due to a high concentration of an oxidizing agent (ozone); and reducing smog due to a high concentration of SO_2 . A generalised scheme for the formation of photochemical smog was presented in Olafadehan (2002), where for the first time, a reduced reaction mechanism (with minimal loss of accuracy for predicting ozone formation in photochemical smog systems) was applied to the modelling of the chemistry of photochemical smog in the troposphere. The resulting simplified mechanism contained nine key reactions and 11 species (NO_2 , NO , O_3 , CO , CO_2 , O_2 , singlet oxygen (O), charged form of singlet oxygen (OD), HNO_3 , HO_2^* and OH^*). Olafadehan (2002) showed that the simplified reduced mechanism gave excellent predictions for the stable pollutant species and radical species when compared to the measurement made for smog chamber experiments from Commonwealth Scientific and Industrial Research Organisation (CSIRO) outdoor smog chambers. Hence, the proposed simplified version of the Generalised Reaction Scheme can be used for predicting accurately ozone formation in photochemical smog systems. However, the current simplified reduced mechanism can be modified to include specific hydrocarbon species that will include selective reactivities that control radical production. So, further refinements of computationally efficient and rigorous mechanisms for photochemical smog modelling are being pursued by the Inaugural Lecturer.

3.6.10 Modelling of Cryogens Spills on Water Surfaces

In recent years, demand for natural and petroleum gases both as fuel and petrochemical feedstock has been on the increase. Cryogenic liquid mixtures such as LNG, LPG and NGL are extracted from natural gas at a very low-temperature condition. It is thus of utmost importance to understand and quantify the physical processes taking place during the extraction process. Thus far, no model has been developed to describe completely the behaviour of LNG on water in real situations. For the first time, we, Dosunmu et al. (2004), developed a detailed and feasible mathematical model for simultaneous spreading and vaporisation of cryogens on water surfaces using continuity and the general Navier-Stokes equations in cylindrical coordinates (r, z, θ) , applicable in real situations. The model accounted for gravity-inertia spread regime that predominates during the spreading process, maximum conditions at the leading edge, and neglected the compositional effect of the cryogenic liquid. Using LNG as the test liquid in our study and solving the resulting model equations with the method of characteristics, literature values of the dimensionless maximum radial extent of 1.23 and dimensionless duration of the entire spill process of 0.8 were accurately predicted. Since no significant variance existed between our model results and those of Conrado and Vesovic (2000), which considered the dynamic change in composition of LNG during vaporisation process to compute the thermodynamic and transport properties of LNG both in liquid and vapour phases, we concluded that the rate of vaporisation of LNG was not influenced by its composition in both liquid and vapour phases during spills on water surfaces. Moreover, useful information were provided in our study for the assessment and management of the explosive risk associated with the spillage of cryogens on water surfaces in the natural gas industry.

3.6.11 Compositional Hydrodynamic Modelling of Gas/Gas Condensate in Gas Pipeline

Natural gas must be found, produced, gathered, processed and transported for it to be available at the burner, be it in a home or the factory. Quite often, the collected natural gas has to be transported over a long distance in pipelines of various sizes. These pipelines cross undulating terrain with varying temperature profiles. When such pipelines operate in a single-phase-gas flow regime, design calculations are readily available. However, gas condensation in pipelines commonly occurs owing to the multicomponent nature of the transmitted natural gas and its associated phase behaviour, as well as the inevitable temperature and pressure variations that occur along the pipeline. Condensate subjects the gas pipeline to two-phase transportation. Therefore, Olafadehan and Fayanjuola (2010) presented the development and numerical solution of a non-isothermal one-dimensional steady-state compositional two-phase flow model to describe the problem of gas condensation and its resulting hydrodynamics in horizontal natural gas pipelines. Our simulated results demonstrated the appropriateness of such a model and its versatile characteristics in describing this rather complex problem. It was shown in our study that a critical point existed in pipelines where the maximum amount of liquid occurred; and we thus predicted the quantity and distribution of condensate in the pipeline, in addition to other commonly sought engineering design variables, which were unknown *a priori*. The model presented in this study can serve as a predictive and design tool for use in both the design and operation stages in gas pipeline design. The model is also useful in the prediction of flow patterns, liquid hold-up and pressure loss for two-phase flow in pipelines, which are important in designing gas-liquid transportation systems. It also assists to validate the functionality of measuring devices, which have been installed on the well-head.

3.6.12 Refinery Products/Waste Optimisation using a Synthesised Pinch Technique

Mr. Vice Chancellor, Sir, owing to high costs of refinery operations and increasing/fluctuating price of crude oil per barrel in international markets, the marginal profit of refinery operators is sometimes challenged. Hence, there is a need to optimise the desired products yield without retrofitting the plants. This was achievable using the application presented in our study (Abhulimen et al., 2012), which was based on the concepts of pinch, as demonstrated for optimising heat recovery in an operating refinery heat exchanger network. Therefore, an optimal waste minimisation exchange network was designed for the control of effluent, thermal and gaseous wastes generated from the process plant. The model used the concept of pinch technique, which was based on a weighted design superstructure that set design products production targets at 25%, 50% and 75% against an operating benchmark status, to optimise the product/waste production from a Crude Distillation Unit (CDU) of an existing operating refinery. Since it is practically impossible to demonstrate the concepts for the whole refinery operations, the Crude Distillation Unit (CDU) was selected based on data obtained from an operating refinery unit as a pilot case. The concepts discussed here applied the pinch technique to distinguish between refinery products (desired products, such as kerosene (HKK), gasoline (PMS), diesel (AGO)) and wastes (unwanted products, heavy oil, residual crude, and heavy crude). The Linear Programming (LP) model that resulted from the analysis of these waste systems and the composite plots were generated for thermal, gaseous and liquid effluent waste streams. The dynamics of waste recovery systems was investigated in relation to the movement of the pinch position as the process conditions were modified or changed based on design targets of 25%, 50% and 75% of the products production scheme. The pinch point was located and the high and low waste generating systems were identified and quantified. The analysis of the composite plots and the solution of the LP model showed that a design target that minimised the production of gaseous and liquid wastes was obtained when the deviation of the pinch

point favoured movement of product curve away from the waste curve. Thus, a new model that allows refinery designer to predict and minimise waste from a refinery process and maximise products production was developed.

3.6.13 Modelling and Simulation of Multicomponent Distillation Column for Acetone Chloroform-Methanol System

Mr. Vice Chancellor, Sir, we, Olafadehan et al. (2013), developed a steady-state mathematical model to describe the operation type of multicomponent distillation process by use of a plate-to-plate method involving Murphree plate efficiency and a condition of plate matching at the vapour composition on the feed plate. This approach contrasted the θ 's method proposed by Lyster and Holland (1959) where plate matching implied that the liquid composition on the feed plate obtained by calculation steps for both enriching and stripping sections of the column must be equal for all components. The developed model equations were applied to a ternary system of acetone-chloroform-methanol in a ten-stage distillation column. An algorithm for solving the operation type of this ternary distillation problem was presented. The corresponding numerical solutions were obtained in MATLAB environment using condenser's boundary condition as an initial guess. The simulated results of the variations of temperature, activity coefficient and mole fractions of acetone, chloroform and methanol in the liquid, with the number of theoretical stages in the 10-stage distillation column, conformed to the trends in the literature. The convergence behaviour of the method employed in this work showed that convergence was achieved within seven-ten iterations.

3.6.14 Grid Design and Numerical Modelling of Multiphase Flow in Complex Reservoirs using Orthogonal Collocation Schemes

Mr. Vice Chancellor, Sir, we, Olafadehan et al. (2018c), developed a new advanced gridding technique and numerical model to simulate reservoir flow performance and pressure profiles in complex reservoir using collocation grid points in a

triangular coordinate system to capture accurately the effects of geometrically complex features such as geological discontinuities and boundary irregularities. These include faults, pinch outs and inclined beddings. Others are well-related phenomena such as multilateral wells of general orientation. The orthogonal collocation method was used for simulating multiphase reservoir flow equations in triangular curvilinear coordinates $[\xi(r), \xi(\theta), \xi(z)]$ in a normalised domain as derived from Cartesian coordinates (x, y, z) . The approach was to accommodate irregular boundaries in the general three-dimensional deviated wells as well as complex reservoir geometry for the multiphase flow of hydrocarbon in natural reservoir formations. Based on the field data obtained from multinational oil and gas operator in Nigeria, the proposed model was used to predict saturation, production and petroleum productivity with time and distance in a MATLAB environment. The simulated plots revealed that pressure profile was parabolic at the centre of the reservoir with unusual characteristics at coordinates $\xi(r)=0.4257$, thereby reflecting the impact of geological features in the pressure and production flow performance hence complex geological features may be located at the centre of the reservoir. The main advantage of the developed innovative grid point methodology is that it uses orthogonal collocation in triangular grid coordinates such that points signatures represent important collocation nodes that track pressures profiles and reservoir production performance and link them with the profiles generated in other grid points. Therefore, a user can simulate accurate pressure and production profiles even if the geometry of the reservoir is irregular, unstructured and undefined because only grid points are required. In addition, our technique can allow users to infer the reservoir geometry and location of geological features that may have a significant impact on the production performance and pressure profile of the reservoir.

3.6.15 Modelling and Simulation of an Industrial FCCU-Riser Reactor for Catalytic Cracking of Heavy Oil

The fluid catalytic cracking unit, FCCU, as shown in Figure 26, is the heart of a modern refinery.

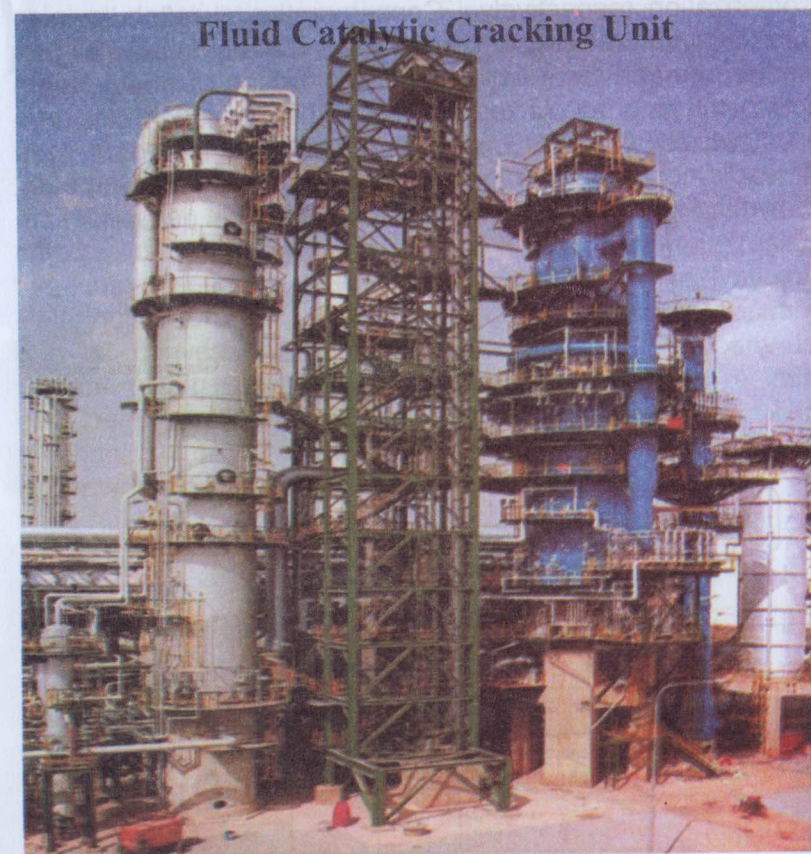


Figure 26. FCCU of KRPC.

Nearly every major fuels refinery, including the Old and New Port-Harcourt Refining and Petrochemical Company (PHRPC), Kaduna Refining and Petrochemical Company (KRPC), and Warri Refining and Petrochemical Company (WRPC), all in Nigeria, has an FCCU. The FCCU is one of the most significant and sophisticated contributions to

petroleum refining technology. Its capacity is usually one-third of atmospheric crude distillation capacity. Generally, FCCU contributes the highest volume (35 vol %) to the gasoline pool through the catalytic conversion of heavy oil feedstock in the riser reactor. The balance of 30, 20 and 15 vol % is contributed by the Reformer, Alkylation and Isomerization respectively. Consequently, oil refineries use fluid catalytic cracking to correct the imbalance between the market demand for gasoline and the excess of heavy, high boiling range products resulting from the distillation of crude oil. Typically, the FCCU is an arrangement of important item of equipment of riser reactor-disengager-regenerator, as shown in Figure 27 for modelling and simulation purposes.

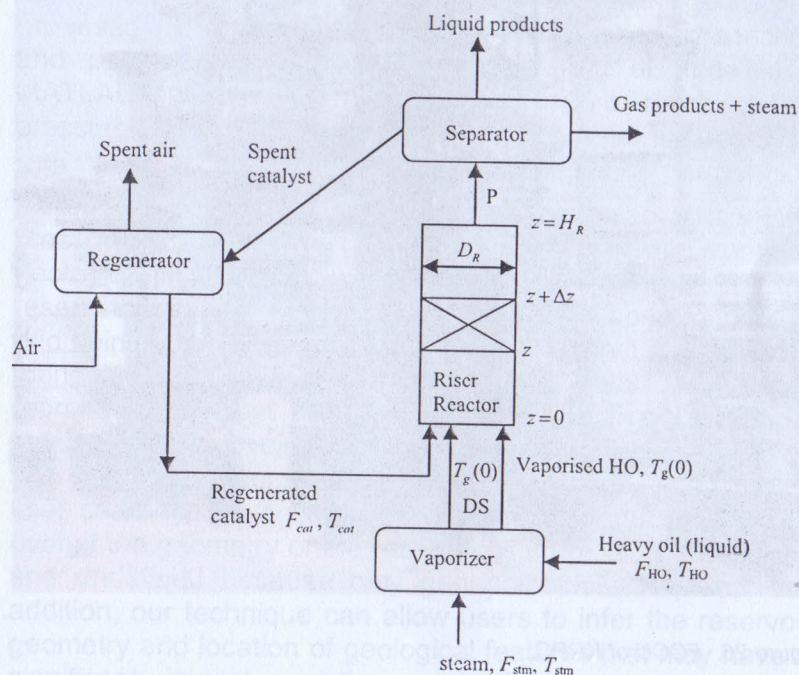


Figure 27. Block diagram of the reactor-regeneration section of a typical FCCU: DS represents dispersion steam, P represents steam +spent catalyst+cracked products from the riser reactor.

Almost all the endothermic catalytic cracking of the heavy oil and coke deposition on the catalyst occur in the riser reactor,

while in the regenerator reactor, air is used to burn off the spent coke for catalyst regeneration. The riser reactor is probably the most focussed item of equipment in an FCCU. Its modelling is very complicated for reasons of many complex reactions occurring in it, coupled with mass and heat transfer resistances between the gas and solid phases, and catalyst deactivation kinetics. Since all cracking reactions and fuel formation occur in the riser reactor, its mathematical model is a valuable tool for design modifications and/or operational changes that give higher yields and selectivity from the process. We, Olafadehan et al. (2018d; 2019c; 2019d; 2019e), developed one-dimensional adiabatic mathematical model for the riser reactor of industrial fluid catalytic cracking units, FCCUs, of KRPC in Nigeria (using five-lump kinetics of heavy oil conversion), China National Petroleum Corporation (using six-lump kinetics of vacuum gas oil conversion) and Khartoum Refinery Company in Sudan (using seven-lump kinetics of vacuum residue conversion), taking cognisance of diffusion resistances. The mechanisms of the catalytic cracking of heavy oil considered in our works are presented in Figures 28-30.

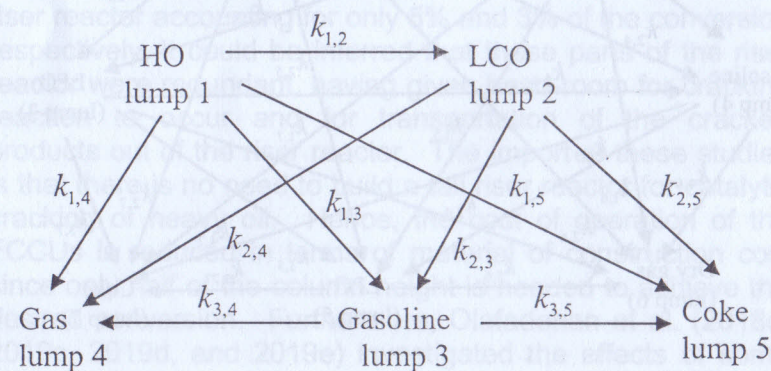


Figure 28. Five-lump model of heavy oil catalytic cracking in the riser reactor of FCCU-KRPC.

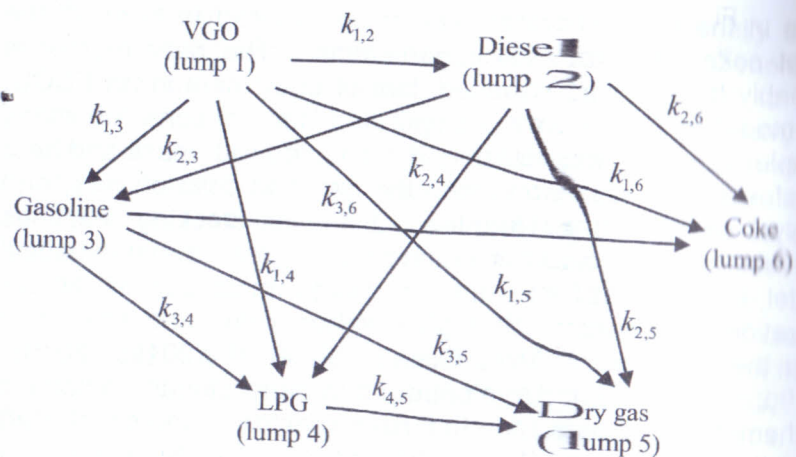


Figure 29. Six-lump model of vacuum gas oil catalytic cracking in the riser reactor of FCCU-China National Petroleum Corporation.

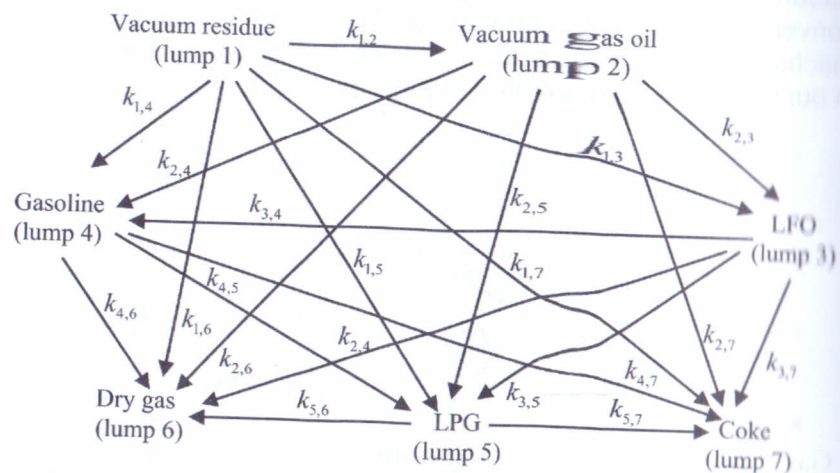


Figure 30. Seven-lump model of vacuum residue catalytic cracking in the riser reactor of Residue Fluid Catalytic Cracking Unit (RFCCU) of Khartoum Refinery Company (KRC).

FOCU of Figure 26 was simplified to the one shown in Figure 27, in which the control-relevant dynamics of the riser reactor-regenerator section of the Refineries' FCCUs investigated was described by modelling the plant as four subsystems. The mathematical model of the riser-type FCCU contained the following components, taking cognisance of diffusion resistances: model for the vaporizer subsystem, kinetic model of the catalytic cracking of heavy oil, catalyst deactivation model, hydrodynamic model of the riser reactor, continuity equation of components in the riser reactor, force balance, and the energy balance. Excellent agreements were achieved between these Refineries' FCCU plant data and our simulated results for instantaneous vaporisation of feedstock with average (or mean) absolute deviation (AAD) being $< \pm 5\%$ in all cases investigated. Also, optimal yields of the cracked products needed to meet market demands and ensuring profit were achieved. Interestingly, it was revealed in our studies that most of the cracking reactions occurred towards the inlet of the riser reactor, with 90% of the final conversion occurring in the first 5m, 95% and 97% of the conversion occurring in the one-third and a half of the riser reactor respectively. With the other two-thirds and half of the riser reactor accounting for only 5% and 3% of the conversion respectively, it could be inferred that these parts of the riser reactor were redundant, having given head-room for cracking reaction to occur and for transportation of the cracked products out of the riser reactor. The import of these studies is that there is no need to build a tall riser reactor for catalytic cracking of heavy oil. Hence, the cost of operation of the FCCUs is reduced in terms of material of construction cost since only half of the column height is needed to achieve the desired conversion. Furthermore, Olafadehan et al. (2018d, 2019c, 2019d, and 2019e) investigated the effects of some process variables on the Refineries' FCCU risers. The analysis provided detailed information on catalyst management and losses minimisation. Normally, for industrial applications, the main goal of FCCU-riser reactor simulations is to predict, for a particular set of operating conditions, the mass fraction of each component (gasoline, LGO, LPG, dry gas, and so on) at the riser reactor outlet, so that the set of input parameters may be changed, aiming to

Mr. Vice Chancellor, Sir, further works are ongoing in the application of our developed models to Indian Oil Corporation and the New Port-Harcourt Refining and Petrochemical Company. For modelling and simulation studies, the gigantic

increase (or maximise) the conversion of a specific product. The procedure can be conducted with just a few model experimental validation tests in the unity. Then, with the experimentally validated model, precise numerical results are expected to be obtained for any other operating and geometric conditions, for similar feedstock. Therefore, many other tests could then be accurately simulated with a computer code, allowing fast, simple, and low-cost adjustment (or maximisation) of unit production, following market fluctuations. Conclusively, the models presented in our works and the numerical results obtained demonstrated that they are very useful for the design of new units and for optimum system control and optimisation of operating conditions of FCCU riser reactors, combining accuracy with low computational time to obtain real-time solutions when simulating actual FCCU riser reactor operation.

CONCLUSION

Chemical engineers, as well as other Engineers and Scientists, work in a very diverse set of industries and many of these industries rely on modelling and simulation (M&S) of their operations. M&S is one of the ever-growing range of tools that can be used to meet the challenges of fierce competition among process industries, and the strong need to protect the available market, human wellbeing and the environment. The advent of fast computers has made its application in process engineering very interesting and rewarding. Process modelling and simulation is like a torch in the hands of a chemical engineer guiding him to the best engineering solution. Modelling and simulation of a process is giving us a message: there is almost no discipline that cannot afford to tap into the untapped or under-tapped golden potential of modelling and simulation. It is the inevitable part of chemical engineering in particular and engineering in general, for process design, research and development, production planning, optimisation, training and education to decision-making, which makes it one of the most important disciplines of engineering. The use of models makes the running of costly, effort- and time-consuming experiments

unnecessary. Thus, modelling saves costs and compensates for time and effort used in developing and simulating models. However, the art and practice of modelling and simulation cannot be learned overnight: the mathematical/computational intuition and sound judgement necessary to apply theory to practice will come only from practical experience. In conclusion, the value of a good model is often priceless!

RECOMMENDATIONS

Mr. Vice Chancellor, Sir, in the light of the foregoing discourse, I do hereby proffer the following recommendations:

1. Judging from the promising results of our studies, Nigeria should harness agricultural, plant and fishery wastes to produce efficient and high-quality adsorbents (especially activated carbon and chitosan) for remediation of industrial wastewater and groundwater. This would reduce reliance on biosorbents importation, save millions of dollars in foreign exchange and thus provide significant economic succour in form of job opportunities, and create wealth from waste. In addition, it will sanitise the environment, resolve some health challenges resulting from consumption of water contaminated with heavy metals, and preserve the scarce fresh water bodies.

2. Government agencies, at both states and federal levels, should ensure strict compliance of environmental regulations by industries, otherwise, their licenses of operations should be revoked.

3. Nigeria, with a population of almost 200 million people, has a total energy production capacity of about five Gigawatts, which is quite below the estimated energy demand of 100 GW required for national transformation. She cannot continue to rely on fossil fuel energy resources to drive her economic wellbeing. Immediate action on implementing bioenergy alternatives to improve the ailing energy sector and to reduce its carbon footprint should be vigorously pursued: countries like Brazil and the USA currently utilising cellulosic substrates to produce bio-ethanol and butanol; Iceland, Norway and Singapore generate 100% of their electricity from

renewable resources. Moreover, the Nigeria government should encourage as many players as possible to operate in the field of renewable electricity as much improvement has not been recorded in the generation and distribution by GENCOs and DISCOs respectively.

4. In spite of our economic downturn, insecurity challenges and other social vices plaguing the land, we should never give up on our dear country, Nigeria, as the country is endowed with numerous natural and human resources and our collective geniuses can be used to turn things around positively if properly accessed. With no personal agenda playing a part, soon we will be good as any industrialised and developed nation in the world. There is always light at the end of the tunnel! Surely, we will get there.

ACKNOWLEDGEMENTS

Mr. Vice Chancellor sir, I wish to express my sincerest appreciation and gratitude to all who have in one way or the other contributed in making me what I am today or have assisted to make my life a happier one. First and foremost, to God be the glory for preserving my life and lifting me to the position I occupy today, in spite of all odds and travails.

I remember in a very special way my late father, Pa Tewogboye Akanbi Olulaja Olafadehan (of Baale Aguodo Compound, Ogbomoso), teacher of teachers, who meticulously laid for me the strong mathematical foundation, which was very easy to build on. To my mum (of Apena Compound, Isale Emere, Abeokuta), I say thank you for being a wonderful mother. My parents' contributions toward my achievements in life will always remain indelible in my memory. I love you unconditionally, thanks for being the world's greatest parents and for all that you have done for me. I am very fortunate to have Mama Olaosebikan as my mother. Thanks for all your love, kindness, discipline and prayer. May God bless, guide, protect, and grant you divine health, long life and prosperity. I call you blessing IJMN. I appreciate my elder brothers (Mr. Olugbenro Olafadehan, Mr. Biodun Olajuwon Olafadehan), younger brothers (Pastor

Oyetokunbo Folarin Solomon Olafadehan, Professor Olurotimi Ayobami Olafadehan, Mr. Oludare Olafadehan, Mr. Oluwagbenleke Olafadehan and Mr. Ayoola Olafadehan) and my only sister (Mrs. Ikeoluwa Abimbola).

My coming to academics is not accidental. Great men and women influenced my chosen career in teaching/lecturing and attainment of Professorial appointment. As the adage goes: Every successful person started as an amateur. Firstly, I appreciate all those dedicated men and women who brought me up from primary to secondary schools, and who enabled me to take teaching/lecturing/research a hobby and a pastime.

My profound gratitude goes to my academic father and career mentor, the teacher of teachers, the lecturer of lecturers, Professor of Professors, the amiable, enigmatic and indefatigable first Professor Emeritus of Chemical Engineering, University of Lagos. He is no other person than the outstanding academic scholar with over 200 publications in erstwhile international journals, Emeritus Professor Alfred Akpoveta Susu, FAEng, NNOM, whom I refer to as one of the fathers of the Department of Chemical Engineering. He wants everybody to succeed, and who apart from giving me "fish", equally taught me how to "fish" in a competitive academic environment. I considered myself fortunate to have done my PhD under his supervision/tutelage. I am one of more than 25 PhD students he has supervised. His immense contributions to the field of Engineering in the areas of Research and Human Capacity Development (of which I am proud to be a product) stands him out. He has indeed impacted my life (and lives of countless others) through his academic and administrative sagacity and prowess. I stand as indelible proofs of his enduring contributions to Engineering. May God in His infinite mercy uphold you sir and your family in His righteous hand of glory, Amen. May He grant you longevity in good health to see your biological and academic children, grandchildren and great-grandchildren attain lofty heights, in the mighty name of Jesus, Amen. If I dedicate more pages to let the whole world know the significant role you played, you are still playing, in

my life and many others, it is not sufficient. I can but say thank you, sir. I doff my hat!!!

I also appreciate another academic father in the person of Professor Ayodele Francis Ogunye, *FAEng, DSC*, the first Professor of Chemical Engineering in the University of Lagos at the age of 36 and the first inaugural lecturer in Chemical Engineering in Nigeria on April 24, 1980, whom I always refer to as the "father of the Department". He founded the Department of Chemical Engineering, University of Lagos in 1973. His unparalleled magnanimity was demonstrated by giving me the opportunity to use a Computer System, for the first time, for my final year Research and Design Projects in Chemical Engineering: he solely acquired more than a dozen Computer Systems for Chemical Engineering students in 1988, and gave us easy access to both his home on campus and office at any hour of the day. We turned "BABA's" (as he was fondly called, and is still being called) office to our hostel to enjoy the cool breeze of the air conditioner and the rug for relaxation. Words cannot adequately express my gratitude to you, sir. Thank you, sir.

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**DO NOT FEEL BAD IF SOMEONE REJECTED YOU
BECAUSE PEOPLE USUALLY REJECT EXPENSIVE
THINGS WHEN THEY CANNOT AFFORD THEM!!!**

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