CHEMISTRY AND INDUSTRY IN NATIONAL DEVELOPMENT[1]

G. B. Ogunmola, FAS.
President, Nigerian Academy of Science
Laboratory of Biophysical Chemistry, Department of Chemistry
University of Ibadan. Ibadan, Nigeria

([1]Being text of a paper delivered at the First International Conference on Science and National Development by the President of Nigerian Academy of Science)

Since the earliest civilizations known to man there has always been in existence a manifold and important relationship between knowledge and the human society. The worlds of these civilizations became more material and rational explanations were sought in the spiritual and other levels of abstraction. Consequent on this epochal development in the history of man, the nature of the substratum of matter became a topical issue for philosophical consideration. The outcomes of these thought processes were two naturally exclusive important paradigms about the nature of matter - the atoms, of Chemistry and the genes of biology.

The past century has been so rich in discoveries and inventions, and because progress has been made across such a wide spectrum of disciplines, ranging form basic physics, chemistry and in technology but the top invention of the last century is the computer.

Many significant changes have occurred in industries and agriculture as a result of recent advances in the physical, chemical and biological sciences. The resources needed to eliminate hunger and disease and improve the human living conditions exist. Science and its application in technology are definitely the essential means of developing our creative capacities to the fullest and of meeting our material needs. There are however enormous disparities between us and other regions of the world in science and its application in technology.

Knowledge about the atoms and genes, more than any other branches of science, allows us to see and realize the uniqueness of life and the uniqueness of Man. Mankind divided today into societies representing various levels of development can become fully modern when we all realize the above uniqueness and transform that into our everyday activities. The goal of science is to augment and order our experiences, analysis of the conditions of human knowledge and improve the human condition through transformation of matter and improvement of the genetic resources must rest on considerations of the character and scope of our means of communication.

The Material Base of a Modern Society

Mankind today is heavily involved in transporting and transforming gigantic quantities of matter to provide food, shelter, clothing, transportation, communication and (to an increasing degree) recreation. Even education (which is man's method of providing continuity to civilization) is heavily involved in, and affected by, these operations.

World Outputs of Important Materials

As a result of human activity large quantities of matter are moved about the face of the earth and chemically transformed. These activities can be classified into three groups:

Mining and extractive industries (which are involved in the removal of non-living "raw materials" from the earth, including the atmosphere (e.g., O_2 and Ar) and the sea (e.g., NaCl, Mg).

Biological industries (these include agriculture, forestry and fishing).

Processing industries (these change one substance into another by non-agricultural means. This activity includes what is commonly called "chemical industry," but other very important industries also depend on chemical reactions and will be included in this category: the metals industries (which produce Fe, Al, Zn, Cu, etc., from their ores), the cement industry, the petroleum industry, the glass and ceramic industry and the pulp and paper industry).

In addition to these three "materials industries", many people are involved in shaping things and putting them together - such as building houses, making automobiles, making radios and TV sets, weaving cloth, making clothing, printing books, and so on. What we can call this activity manufacturing or fabrication, but the borderline between manufacturing and chemical processing is sometimes hard to draw (for instance, the making of wood pulp out of wood involves a chemical process whereas the making of paper out of pulp is really a fabrication process, yet both are generally considered to be a single industry - the pulp and paper industry - because the same factory usually performs both operations).

Total coal reserves	World	8100000	MMT
Total petroleum reserves	World	75500	MMT
Total mass of earth's atmosphere		5,200,000,000	MMT
Total mass of oceans		1,400,000,000,000	MMT
Total mass of earth		6,000,000,000,000,000	MMT

The table contains many interesting items that are food for thought. Palm oil is used for soap, and also as cooking oil in many countries); where does all of that gypsum go? The main points to be noted are: (1) predominance of energy (↑6000MMT). (2) Construction (sand, gravel, rock, logs, cement, brick, and gypsum) also involves many thousands of MMT. (3) Foods come to ↑2000MMT altogether, with wheat, rice corn, potatoes ↑3000MMT each. (4) Clothing (cotton wool) a small item in tons ↑ 20MMT). (5) Metals (= processed raw materials other than metals): wood pulp, sulphuric acid, probably around ↑ 50MMT. NaOH and HNO_3 ↑ 25MMT each; all other "chemicals" probably come to 50MMT altogether.

H_2SO_4 Raw Materials:
(1) Elemental sulphur obtained by melting with superheated steam from deep salt domes (the Frasch process)
(2) By-product is obtained in natural gas and high sulphur crude oils.
By-product SO_2 forms the smelting of sulphide ores.
Uses: 60 - 70% used in making phosphate fertilizer (by treating phosphate rock with H_2SO_4).
The rest is used in many chemical processes, to make other things.

CaO (Lime) Raw Materials: Limestone ($CaCO_3$).
Uses: 40% in making steel (as a flux to remove SiO_2, Al_2O_3 phosphorous and sulphur impurities; it forms a low-melting slag which floats on top of the molten iron and is easily separated as "slag").
15% in water treatment (pollution control)
8% in making refractory brick for high temperature furnaces, etc.
7% in the pulp and paper industry.

NH_3 Raw materials: Air (N_2) and H_2 (from natural gas, CH_4)
Uses: 75% as fertilizer (NH_4NO_3, urea, ammonium phosphate)
10% for plastics, fibres and resins
A lot is used to make HNO_3, the basic substance of the explosives industry

O_2 (Liquid) Raw material: air
Uses: 65% in metal refining
15% in chemical processing
7% in metal fabrication (e.g., welding)

C_2H_4 (Ethylene) Raw material: Cracking of petroleum hydrocarbons.
Uses: 45% to make polyethylene polymer
20% to make ethylene oxide and glycol (used in antifreeze, polyester fibres, solvents and other polymers)
10% to make styrene (polyvinyl chloride polymer, used in synthetic rubber, automobile tyres, etc.)

N_2 (liquid) Raw material; air.
Uses: 30% as blanketing atmosphere in metals and electronics industries

7% as a freezing agent

NaOH Raw materials: electrolysis of NaCl solutions

Uses: 50% in diverse chemical processes.

15% in pulp and paper making.

5% in aluminium industry (dissolving $Al_2H_2O_3$ from bauxite - the chief Al ore).

5% in the petroleum industry

5% in the textile industry

Cl_2 Raw material: electrolysis of NaCl, also by recovery from by-product HCl (Parsons process: $O_2 + HCl \rightarrow Cl_2 + H_2O$).

Uses: 40% in diverse chemical processes

15% for solvents (dry-cleaning, etc.)

15% as a bleaching agent in pulp and paper making (mainly at ClO_2)

5% in treatment of domestic water

H_3PO_4 Raw material: Phosphate rock

Uses: 80% as fertilizer

10% in detergents and water softening

HNO_3 Raw materials: NH_3 ($NH_3 + 2O_2 \rightarrow HNO_3 + H_2O$; platinum catalyst - the Ostwald process)

Na_2CO_3 Raw material: Dry lakebeds ("trona"), synthetically from NaCl, $CaCO_3$ (Solvay process)

Uses: 55% glass industry

25% diverse chemicals

5% pulp and paper

C_6H_6 (benzene): Raw material: Petroleum reforming; coal tar.

Uses: 50% styrene polymers (through ethyl benzene to polystyrene – see ethylene, above)

20% cyclohexane ($\rightarrow$ adipic acid $\rightarrow$ nylon)

20% other polymers

NH_2-CO-NH_2 (Urea) Raw material: NH_3 + CO_2

Uses: 75% fertilizer

15% urea-formaldehyde polymer (a plywood adhesive and foam insulator- "polyurethane")

10% animal feed - a good source of nitrogen.

$(CH_3)_2\ C_6SH_4$ Raw material: Petroleum reforming

Xylene, ortho and parts Uses: p-xylene:95% polyester fibre (used in clothin, p-xylene $+O_2 \rightarrow$ terephthalic acid $\rightarrow$ (with ethylene glycol) polyester polymer)

o-xylene: mostly oxidized to ophthalmic acid (with ethylene glycol) alkyl resin, plasticizer for polyvinyl chloride plastics

CH_3OH (methanol) Raw material: natural gas (CH_4) $\rightarrow$ CO + 2 $H_2 \rightarrow$ methanol.

Uses: 45% $\rightarrow$ formaldehyde $\rightarrow$ polymers

20% to make other polymers

10% as solvent

H_2CO (formaldehyde) Raw material: Residue of natural gas used for NH_3 production; natural wells.

Uses: 40% refrigeration (food, 30%, industrial. 10%)

35% beverage carbonation

In this survey of materials used by man, it is interesting to look at the overall abundances of the elements, both cosmically and on the land surfaces of the earth, cosmically and in the igneous rocks of the upper continental crust. You will see that there are some parallels, but also some wide differences. You will also note, in many instances, a marked lack of correlation between the costs of some of the elements we use most and their abundance on the earth's crust (for example, Zn, Cu and Pb).

Petroleum in our National Economy

Petroleum use has increased steeply, worldwide: as much petroleum was taken from the ground between the last ten years as was produced in the preceding 110 years. The significant of the increase is accentuated by the complex chemical processing required to convert the raw natural product into chemical forms that meet the demands of modern, high-compression engines. Refinement of the crude oil begins with distillation for separation by boiling range. Hydro treating may be needed to upgrade feedstock product quality. By catalytic cracking, the large molecules are fragmented into lower boiling molecules. Alternative, catalytic reforming can convert the molecular structures to higher-octane forms.

Chemical catalysis has made this miracle of process engineering possible. Table 1 lists four important catalytic processes recently introduced during a period when environmental concerns dictated the reduction of noxious by-products and development

Table 1: Heterogeneous Catalysis in the Petroleum Industry

Feedstocks	Catalyst	Product	Used for
C_{16}-C_{24} oils	Zoolite Molecular sieves (aluminosilicates)	C_y-C_9 alkanes, alkenes	"Cracking" to high-(al octane fuels)
C_7 - C_9 unbranched Hydrocarbons	Platinum-rhenium Platinum-rhenium	Aromatics, other Hydrocarbons	"Reforming" to high-octane fuels
CO, NO, NO_2	Platinum/Palladium /rhodium	CO_2, N_2 C_y-C_9 branched Hydrocarbon,	Auto exhaust cleanup
CH_3OH	Molecular sieves (aluminosilicates)	aromatics	Gasoline production

of high-octane, lead-free gasoline. The need for new discoveries is even greater today as the world turns to lower grade petroleum feedstock with higher sulphur content, with higher molecular weights and with catalyst-poisoning constituents (e.g., vanadium and nickel in California off-shore oils). Not everybody is lucky to produce the Nigeria Bonny Crude - sweet oil in international market with low sulphur content.

Challenging opportunities await chemists and chemical engineers in such key areas as recovery (getting more oil from the known deposits), refining (converting the crude oil into the most useful chemical form), and *combustion* (getting the most energy from the finished fuel).

Recovery

About 4000 billions of barrels of oil have been discovered, worldwide, with Nigeria ranking as the sixth major world producer. Most of that oil, however, is not recoverable by presently known extraction methods. Primary recovery, based upon natural pressure, typically can recover no more than 10 to 30 percent of the oil from its natural reservoir, a complex structure of porous rock. Secondary recovery, in which water, gas, or steam injection is used to revitalize the deposit, can raise the recovery efficiency; but even then, only about 35 percent of the known U.S. oil deposits are classified as recoverable.

Tertiary recovery requires new chemistry and new methods to gain access to the rest of this valuable resource. Surfactants (detergents) and solution polymers can be used to lower interfacial tension between oil band water and reduce capillary pressure. Micellar-polymer, caustic, and micro-emulsion flooding are some of the enhanced oil recovery methods under development or on the drawing boards. Fundamental questions of transport phenomena, phase behaviour, viscosity, interfacial tension, and influence of electrolytes on surfactants must be better understood. There are difficult problems to be faced; but if recovery could be made feasible, it would have enormous economic significance because it would permit us to tap the remaining barrels of oil already discovered but currently beyond economic reach.

Refining

The oil most easily removed by primary and secondary recovery also has the most desirable composition. As these best fractions become depleted, we must learn to refine heavier crude oils (higher molecular weights) with lower hydrogen content and more undesirable contaminants, such as sulfur, nitrogen, and organometallic compounds. A new generation of catalysts may be needed to escape the poisoning effects of some of these contaminants. Thus vanadium seems to be carried by porphyrin complexes into molecular sieve-zeolite-catalysts where it clogs catalyst pores and blocks catalytic sites. In contrast, nickel contaminants have their own undesired dehydrogenation catalytic activity, which increases the amount of coke, again clogging catalyst pores.

It is likely that future-refining techniques will differ markedly from those currently used. Petroleum refining technology is already undergoing an evolution as refineries are being adapted to lower quality feedstocks. Some of the heavier components are being converted through catalytic hydroprocessing and coke-forming operations. Future developments may be based upon combustion of the low-hydrogen and coke components to fuel energy-consuming processes. The least desirable crude components may be gasified to generate hydrogen, a useful reactant in catalytic hydroprocessing. More dramatic departures are to be expected, though their development will follow from new research discoveries in separation techniques, molecular characterization of heavy crudes, high temperature chemistry, and catalysis. We are not facing that problem as of now as we produce abundant light crude oil for which we have currently import heavy crude blend to make them perform effectively in the present finery set up.

Combustion

There is much remaining to be learned about this chemistry, one of the oldest technologies of mankind dating back to the discovery of fire. The need for more knowledge stems from ever increasing dependence on combustion, from changing fuel compositions, and most important, from the sudden awareness and concern about the environmental impacts of combustion. Society has recognized and begun to grapple with the undesired side effects of profligate and careless combustion of fossil fuels. These side effects include smog from nitrogen oxides, acid rain from sulphur impurities, dioxins from inefficient burning of chlorinated compounds, and the almost imponderable long-range problem of the effect of accumulating CO_2 on the global climate.

The combustion process is a tightly coupled system involving fluid flow, transport processes, energy transfer, and chemical kinetics. This complexity is epitomized in the methane-oxygen flame.

Fortunately there is no sub-area of chemistry offering greater promise than that of chemical kinetics. Such optimism derives from an array of new, sophisticated instrumental techniques that permits us to address and clarify the fundamental behaviours at work. Such advances as they occur, will be quickly taken up by chemical engineers and translated into higher combustion efficiencies and decreased environmental pollution. As one index of its importance, an increase of only 5 percent in the efficiency with which we combust oil and gas would reduce environmental pollution and an immeasurable additional value if it is accompanied by reduction in the growing problems of smog and acid rain over our cities. Port-Harcourt is a city to watch and protect from environmental assault.

Natural Gas

Natural gas is a mixture of low-molecular-weight hydrocarbons, mostly methane the rest, ethane, propane, and butane in varying percentages). While it contains some sulfur- and nitrogen-containing impurities, they are removable to produce a clean-burning fuel and a versatile chemical feedstock. The ethane and propane can be catalytically converted to ethylene, propylene and acetylene, all valuable precursors to products needed by our society. This is the basis of our petrochemical plant.

Its ease of transport via pipelines and its desirable qualities for application make natural gas an important resource.

The Nigeria natural gas reserves are comparable to our petroleum reserves, perhaps somewhat larger. However, again like petroleum, natural gas is limited in amount both worldwide and domestically.

Coal

Coal is equally an abundant of the fossil fuel energy sources. Estimates of recoverable supplies worldwide indicate 20 to 40 times mare coal than crude oil. There can be no doubt that dependence on coal would continue to increase as petroleum reserves are depleted. Fortunately, this predictable chronology gives us time for th basic research needed to use this valuable resource efficiently and cleanly.

It must be noted, too, that petroleum is not only a fuel, it also provides us with many important fin chemicals and chemical feedstocks. In fact, some people contend that petroleum as a source of other chemical ought to be classified as "too valuable to burn". Insofar as coal can be economically converted on a massiv scale into combustible fuels, we gain the option to "save" petroleum for more sophisticated uses. Then, furthe ahead, we can foresee that with creative advances in chemistry, coal itself can provide its own array of valuabl feedstocks, including some now derived from petroleum.

Solar Energy

By far the most important natural process for use of solar energy is photosynthesis - the process by which green plants use the energy of sunlight to synthesize organic (carbon) compounds from carbon dioxide and water, with the concomitant evolution of molecular oxygen. To be able to replicate this process in the laboratory would clearly be a major triumph with dramatic implications. Despite much progress in understanding photosynthesis, we are still far from this goal.

The basic path from carbon dioxide to carbohydrate has been well worked out, chemistry and further insight has been gained, particularly into the initial events in photosynthesis.

The solar spectrum that drives photosynthesis places about two-thirds of the radiant energy in the red and near-infrared spectral regions. Understanding the way nature manages to carry out photochemistry with these low-energy photons in one of the keys to understanding (and mimicking) photosynthesis. Current-day explanations are generally based upon the energy of which near-infrared photon initiates in a series of electron transfer reactions (oxidation-reduction steps). The urgency of the problem lies in the initiation of preparations for changing the basic organic supply structure.

Organic Materials

Organic materials and products are so pervasive that people generally take their presence for granted. Indeed, it would be difficult to imagine a world in which organic substances were absence, or even substantially reduced. A world without synthetic fibres, plastics, drug and rubber would be very different forms the present. Automobiles produced today often have hundreds of pounds of organic materials in addition to tyres. And the wheels of the world are mostly polymer-clad. Many household articles and material of construction are partly or wholly organic. The wood in a home is supplemented by paints, flooring insulation, furniture; counter tops, roofing, and other petrochemically produced organic materials. Much of clothing today is produced from synthetic fibres; all are organic.

Industry uses enormous quantities of organic materials. Organic materials are replacing metals in many applications. Structural and electrical uses consume large amounts. Wire, cable, films, packaging, piping, and a variety of applications make organic materials essential for modern industry. Industry could simply not operate in anything like present form without the large volume of organic materials now available.

Petroleum is an important precursor of much of the world's fertilizer and, as such, is responsible for the earth's capability to support its large and growing population. Depletion of petroleum thus carries a grim notice for everyone, but particularly we in the developing nations. Few people realize the extent to which agricultural productivity depends upon fertilizers, and consequently, petroleum.

Energy uses account for most of the consumption of organic materials. Burning of petroleum goes on at an ever-increasing pace, and the future crisis of supply is directly related to this fact. Throughout much of the world people have come to take petroleum-derived heat and transpiration for granted.

Organic materials form the basis of industries of great size. Facilities for organic manufacture and conversion influence the lives of people virtually everywhere. The employment of a substantial fraction of the world's work force depends on the supply of organic materials, directly or indirectly.

The future of organic raw materials for chemical synthesis can't be divorced from the much larger demand for energy sources. The questions that concern us thus fall into a broad domain of national and international policy, where the governments of the world have much more of a say-so than do scientists, academicians or industrialists. Decisions on resources are based as much on political and social concerns as on the technical and economic facts.

Everyone knows that technology must help the world meet its future resource needs. Steps can be taken to advance such technology. What I want to suggest is that there are also steps to be taken in the realm of government and economic policy. Unless these too are successful, the technology may not come into being or flourish. My conclusions are these:

1. We need a closer coupling among industrial organizations, academic institutions, and the national government, with much more attention to the long pull and less preoccupation with momentary issues.
2. We need a broader and better public understanding of the resource problems and prospects, to build support for appropriate political action.
3. We need an economic and political climate that encourages development of alternative energy sources, and at the same time places priority value on the assignment of oil and gas to the uses of greatest importance.
4. We need to expand the support for research, with special emphasis on long-range studies that might not pay out until well into the future, after the year 2004. There is a definite role for the universities in this.