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Review

HYDROCARBON TECHNOLOGIES

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***Abstract**. As we have moved into the 21st century, a number of important changes are taking place - in particular: hydrocarbon technologies in the oil industry tend to be evolutionary rather than revolutionary. Most research and development is oriented towards evolutionary improvement. The technologies of the oil industry tend to be more international. The technological development of the oil industry really drives economics, environment and safety. Hydrogen will become more of a focal point and a basic necessity in the industry of tomorrow. The future should bring about a gradual change in the current competition between oil and natural gas as general purpose fuels. Selective and efficient catalysts will be critical for this new trend. The importance of natural gas will rise as it becomes the fuel of choice for power generation and the feedstock for petrochemistry. LPG is both environmentally and ecologically friendly, and is considered one of the world's most important fuels. GTL technologies, the route to liquid and higher value product from natural gas, are obtained conversion via synthesis gas.*

***Key words:** petroleum, natural gas, petrochemistry, hydrogen, catalysts, alternative fuels, GTL-technologies, feedstock recycling, hydrocarbon functionalization, biorefining.*

Introduction

Hydrocarbon technologies are a branch of chemical technology based on hydrocarbon raw materials derived from petroleum and natural gas. Petroleum is perhaps the most important substance consumed in modern society. Natural gas is increasingly being recognized as a hydrocarbon raw material, the preferred chemical feedstock for the 21st century. The two major factors, that have driven petroleum technology development in recent years, have been identified as economic pressure and environmental concern. These factors impinge directly on the activities of the downstream industry, most clearly in the field of oil processing. The oil industry will be made up of very large, global, integrated companies that can produce finished or semi-finished goods from hydrocarbons. In oil products, the major impact is felt via the customer, both the direct customer, who buys a product, and the „intermediary" customer, whose product provides and the use. In fact, the term „petrochemical" may not exist as such, and petrochemicals might just be intermediates inside a more complex production module. Petrochemicals, in some form, will probably exist and be marketed globally. There will always be a need for some of the petrochemicals used in the manufacture of products that are relatively small that do not lend themselves to integrated, mass manufacture.

A relatively small portion, 250 million tonnes of oil equivalent (4.4%), of oil and natural gas is used as raw material to produce chemical products essential to our everyday life ranging from plastics to textiles to pharmaceuticals and so on. This amount provides not only raw materials for the ubiquitous plastics and other products, but also fuel for energy, industry, heating, and transportation. Petrochemistry is based on ceratin building blocks. By tonnage the petrochemical industry provides well over 90% of all organic chemicals. It grew rapidly in the 1950 and 1960s. Petroleum and natural gas products are the basic materials used for the manufacture of synthetic fibres for clothing and in plastics, paints, fertilizers, insecticides, soaps, and synthetic rubber. The uses of petroleum and natural gas as sources of raw material for manufacturing are central to functioning of modern industry.

Many new processes and products were introduced. Large economics of scale proved possible. The prices of chemicals and polymers dropped, thus becoming completitive with traditional materials. Cheerfully colored plastic house wares, highly functional packaging, and easy care garments of synthetic fibres were no longer an exciting new technology, but they became an accepted and routine part of modern life. While Germany is probably credited as starting the chemical industry, U.S. with its vast availability of natural gas and oil, is credited with founding the petrochemical industry.

By the 1970s growth was levelling off. The first and second oil shocks increased the price of crude oil and hence of its downstream products. Economies of scale ran out. The oil and petrochemical industry had matured. As its technology became better known, developing countries started their own oil and petrochemical industries, competing with developed countries, and depressing profitability. Further, the impact of the oil and petrochemical industry on the environment become evident. The downside is of course not absent from the picture: oil and politics, oil and the environment. However, for a long time yet to come oil will have a determining influence in the world and perhaps even more so in the developing countries. As such, some changes are already making themselves felt and others can be glimpsed in the distance. Oil and petrochemical industry will have to respond to increasingly stringent quality requirements, particularly with respect to environmental concerns, and has already made good progress in this area.

In the 1980s and early 1990s, new products were no longer the name of the game, in part because the 1960s and 1970s had provided an arsenal of them to attack new applications. Also, the oil and petrochemical industry became subject to strick government monitoring. Expensive toxicity was required before a new compound could be introduced.

Rather than developing bigger, better plants to manufacture novel chemicals, the oil and petrochemical industry became concerned with lessening pollution, improving processes, and developing specialty chemical formulations and niche products that could be sold at higher profit margins. Research and development became highly process oriented, in part to combat maturity and gain and edge over competition with money-saving technology.

The petrochemical industry has played part in the major events of the past 60 years. It has kept up with the great discoveries and thereby made economic development possible. Petrochemicals are manufactured from an abundant raw material with a low production cost that is easy to transport and store. Meeting the most varied requirements, they are present in our daily lives and have often become synonymous with comfort and quality of life.

Actual Problems

The major sources, petroleum and natural gas, provide some basic chemicals or chemical groups from which most petrochemicals are made. The basic building blocks comprise olefins – ethylene, propylene, butadiene, isobutene, 1- and 2-butenes, isoprene, cyclopentadiene; aromatics– benzene, toluene, xylenes, styrene, C_9–C_{10} aromatics; synthesis gas– methanol and hydrogen manufacture. Whereas acetylene was very important fifty years ago, its significance has been steadily decreased by newer chemistry based on ethylene and propylene. Chemistry of methane, a relatively unreactive molecule, which, nonetheless, is the source of synthesis gas. A small amount of chemistry is based on alkanes other than methane.

In Western Europe, demand for petrochemicals remains strong, in contrast to stagnant oil requirements. Under these conditions, refiners have new opportunities not only as manufacturers but also as a petrochemical feedstock suppliers. Tighter gasoline specifications are rejecting olefins and aromatics from local gasoline pools. Thus, refiners can recover propylene and xylenes from processing streams for sale or feedstock purposes. These two petrochemicals have very strong consumption demands.

Between 1990-1995, the petrochemical demand in Western Europe grew annually by 2,45%. This trend is expected to continue, although at a gradually slower pace, during 1995-2010 at almost 2,4%. To be provocative, the regional petrochemical market by 2010 is projected at more than 61 million tonnes (MMton) and will almost match the combined gasoline markets of France, Germany, and the UK.

Since over one–half of all manufactured petrochemicals ends up in polymers, we concentrated on polymerization processes and polymer properties. We have also expanded new processes scope to include many apparently less important reactions that are significant because they rise the more profitable specialty chemicals. So–called “Fine Chemicals”, such as ingredients for pharmaceutical and pesticides, dyestuffs, and food additives, make a large contribution to the chemical industry added value than they do its shipments. They tend to be high-priced products with specialized markets, and their manufacture is less capital and more labour intensive than the manufacture of the run-of-the mill general chemicals. Their importance to the petrochemistry is best represented by the value added figure, which for example, emphasizes, the importance of the pharmaceutical sector.

The relative amounts of usable fractions obtainable from crude oil do not coincide with commercial needs. Also, the qualities of the fractions obtained directly by distillation of crude oil also seldom meet required specifications. Hydrocarbon feeds of the refining operation are further converted or upgraded to needed products. Major hydrocarbon refining and conversion processes include cracking, dehydrogenation (reforming), alkylation, isomerization, addition, substitution, oxidation-oxygenation, hydrogenation, metathesis, oligomerization and polymerization. The chemistry of the high temperature conversion and transformation processes of hydrocarbons is based on homolytic processes. Thermal cracking, oxidation, hydrogenation-dehydrogenation, cyclization, and so on, proceed through free radicals.

Low molecular mass olefins, such as ethylene and propylene, are very rare or even absent in hydrocarbon sources. The high demand for these olefins required their preparation from readily available petroleum sources. Cracking is the process in which high-molecular-mass hydrocarbons, olefinic or alifatic, are converted to more useful low-molecular-mass materials through carbon-carbon bond fission. Cracking is affected by one of three general methods: thermal cracking, catalytic cracking, or hydrocracking. Each process has its own characteristics concerning operating conditions and product composition. Because of different chemistry of cracking processes their products have different composition. The major industrial source of ethylene and propylene is pyrolysis (steam cracking) of hydrocarbons. Ethane, butane, and naphtha are the most useful feeds in steam cracking. Because of their ready availability, natural-gas liquids are used in the manufacture of ethylene and propylene in the United States. In Europe and Japan the main feedstock is naphtha. Dehydrogenation of saturated compounds also takes places during refining processes and is practiced in petrochemical synthesis of olefins and dienes. Several industrial processes have been developed for olefin production through catalytic dehydrogenation of C_4-alkanes. The currently high and increasing demand for oxygenates, especially MTBE in new gasoline formulations calls for a substantial increase in the capacity of isobutylene production. The higher olefin processes are commonly used to manufacture detergent-range (C_{10}–C_{14}) olefins via dehydrogenation of corresponding alkanes. All commercial processes use the catalytic dehydrogenation of ethylbenzene for manufacture of styrene.

A demand for olefins will account for the largest part of regional petrochemical demand and is also expected to show high growth. Its share represents about 75% of the total petrochemical demand by 2010, up from 70% in 1990. These trends are supported by strong growth in production of polyolefins, that represent more than half of the consumption for ethylene and propylene. These commodity petrochemicals represent the bulk of olefins consumption. By the year 2010, polyethylenes (PEs) will account for 62% of the ethylene demand, up from 57% in 1995. Accordingly, polypropylene (PP) share of propylene will increase from 48% in 1995 to an estimated 52% in 2010. The other important point affecting olefin requirements is the faster growth of propylene demand relative to ethylene. The recent and forecast development in the propylene/ethylene demand ratio, which reached 67,5% in 1995, is expected to increase to 76,5% by 2010.

Aromatic compounds are the most widely used and are structured of the most important classes of petrochemicals. As excellent solvents they constitute an important component of synthetic rubbers and fibres. Catalytic reforming has become the most important process for preparation of aromatics. The two major transformations that lead to aromatics are dehydrogenation of cyclohexanes and dehydrocyclization of alkanes. Additionally, isomerization of other cycloalkanes followed by dehydrogenation (dehydroisomerisation) also contributes to formation of aromatics. BTX processing, the major source of these important chemicals, is connected to catalytic cracking and catalytic reforming. In the United States steam cracking is the major source of aromatics. In Europe and Japan the major process for production of aromatics is catalytic reforming. The cracking process, the dealkylation of alkylbenzenes became an established industrial synthesis to produce aromatics. Several technologies for both catalytic hydrodealkylation and thermal dealkylation are operated industrially. Dealkylation, isomerization, disproportionation and transalkylation processes are used in the manufacture of benzene and xylenes.

Naphtha remains the most important petrochemical feedstock. However, future shortage will force petrochemical manufacturers to seek alternative raw material sources. Operators in olefins are considering other sources such as heavy condensates, middle distillates, ethane and refinery gas. Flexible olefin cracking operations and integration with a refinery will affect future alternative feedstock usage. Increased processing of heavy condensates by dedicated splitters may entice some Western European refineries to participate in the local merchant petrochemical feedstock markets. Continued, strong petrochemical demand can open revenue opportunities for refiners.

Benzene share in consumption of aromatics is about 56% in 1995, with little change expected. Similar to ethylene and propylene, benzene is the single important derivative in the structure of demand for aromatics. While styrene represents about half of the benzene usage with a minor change during the period analyzed, demand for xylene is primarily structured for paraxylene, whose importance is growing continuously. Paraxylene share, accounted for 61% of the xylene requirements in the 1995, is expected to increase steadily to more than 72% by 2010.

Methane and carbon monoxide are the two materials of practical importance in C_1 hydrocarbon chemistry. As to the present industrial practice allows, natural gas (methane) can be converted to a mixture of carbon monoxide and hydrogen, called synthesis gas. Hydrocarbon can be produced from synthesis gas via the Fischer-Tropsch synthesis. As to the technological modification, Fischer-Tropsch synthesis in the liquid phase may be used to produce light alkenes under appropriate conditions in a very efficient and economical way. The favourable surface composition of the catalyst suppresses secondary transformation, thus ensuring selective á-olefin formation. The transformation of synthesis gas to methanol is a process of major industrial importance. The conversion of methanol to alkenes, cycloalkanes, or mixture of alkanes and aromatics requires the elimination of oxygen. In general, medium-pore zeolites (ZSM-5 and ZSM-11) are the best catalyst to produce hydrocarbons from methanol. Hydroformylation has gained substantial industrial importance in the manufacture of *n*-butyraldehyd and certain alcohols. Hydroformylation is the metal-catalyzed transformation of alkenes with carbon monoxide and hydrogen to form aldehydes.

All these processes exist and are already being implemented. However, since they are due to take on ever more importance, their performance will have to be improved by developing more sophisticated, active and selective catalysts to allow less demanding operating conditions (pressure, velocity, etc.). A large segment of modern oil and petrochemical industry is based on catalytic processes. Technology in the petrochemical industry tends to be evolutionary rather than revolutionary. Rarely does a researcher in the oil industry and petrochemistry come up with an entirely new product or a process which will open up a completely new market application for fuels and petrochemicals or which will give us entirely new route to the production of a product. Most research and development is orientated towards evolutionary improvement. The common questions are: how can we achieve better yields from an existing process, how can we improve the quality of exploration data, or how can we produce our products to new quality standards that meet ever higher expectations of regulators and customer.

Technological development in the oil and petrochemical industry also derives predominantly from applied technology rather than pure "blue sky" science. If we look at the major technological developments in offshore engineering, the story is the same. The material scientists and the computing specialists have developed stronger, lighter materials and more advanced CAD together with structural analysis tools which the oil and petrochemical industry has successfully applied to the design of safer, cheaper and more reliable structures as its operations move into deeper waters.

What then really drives the technological development of the oil and petrochemical industry? Is it an industry whose operational ethos tends to be risk-averse and frequently conservative in applying new technology? The answer lies in three words – **economics, safety** and **environment** – the three principal preoccupations of oil and petrochemical industry management at the beginning of the twenty first century.

In modern oil and petrochemical industry most of the available technologies are considered "mature", and even considerable research effort is not expected to yield significant improvements. However, as profit margins can sometimes be increased by improving selectivities by one percentage point or less, it is still desirable to invest in improving catalyst performance. Moreover, the polymer chemistry continues to demand monomers that are not only less expensive but also increasingly pure.

Petrochemistry is based in large part on the conversion of alkenes because of the ease and economy with which they can be obtained from petroleum, and as they are easily functionalized, they are considered versatile raw materials. However, petrochemical industry is moving toward the direct use alkanes, which can be obtained from both petroleum and natural gas, and are even more economical. One of the most important applications of selective oxidation catalysis is the functionalization of hydrocarbons. Of selective oxidation processes, only the oxidation of *n*-butane maleic anhydride has been commercialized.

Optimization of the catalytic performance in terms of reactant conversion, yield, productivity, and selectivity to the desirable product, is related not only to a thorough knowledge of the nature of the catalyst and surface-active phases, reaction mechanism, thermodynamics, and kinetics but also to the development and use of suitable reactor configuration, where all features can be successfully exploited. Catalytic distillation is a unique unit operation which utilises a solid heterogeneous catalyst and mass transfer single column, thus providing a simultaneous reaction and distillation. Catalytic distillation is being applied to various production processes and promises to play a major role in the refining and petrochemical industries. The first catalytic distillation started up the production of methyl *tertiary* butyl ether (MTBE), later CD was applied for the production of ETBE, TAME, and TAEE.

Significant development has been achieved in recent years in the membrane reactor technology, in which the capability of membrane reactor processes in the selective permeation of particular components in a mixture is combined with reactive application. The selective transport of oxygen or hydrogen in membranes can be used in oxidation and dehydrogenation processes.

In any case, hydrogen will become more and more of a focal point and a basic necessity in the industry tomorrow. Hydrogen production potential resides in hydrocarbons whose H/C ratio is greater than motor fuel requirements, i.e. the alkanic C_1 to C_4 fractions have specific uses. Two compounds will be critical for this new trend. Hydrogen is the first of them, as even regenerative reformers will no longer suffice. Partial oxidation, in particular of gases or heavy residues by stream, be needed to supplement production. The second compound are selective, efficient catalysts that will limit severity of operating conditions.

The evolution of tomorrow's refinery will not be strictly confined to petroleum processes. Energy production, whether electricity or steam, is an important item in plant cost and reliability. The major consequence will be a much more environmentally friendly product quality. These problems are solved in refinery of the future, the refinery beyond 2000 with the arrival of deep conversion processing, such as residue hydrocracking, carbon rejection and gasification processes which can lead to the elimination of heavy fuel production, if need be, supplementary processes for deep treatment of distillates coming from conversion or deep conversion, and synthesis of compounds from light ends of the same conversion processes which led to advanced flow schemes themselves. This type of refinery approaches that of a petrochemical complex, capable of supplying the traditional refined products, but also meeting much more severe specifications, and petrochemical intermediates such as olefins, aromatics, hydrogen and methanol.

This brief description of past and present refining developments leads to a certain number of important remarks. First of all, we are observing a gradual, continuous evolution. It could hardly be otherwise, considering the large time factors – it takes several years to build a refinery – the capital investments, and the tightness of the product specification. Moreover, refining evolves around successive modification to basic flow scheme containing a limited number of processes. These processes have been greatly improved over the past twenty years from the technological point of view and, for catalytic processes, the level of performance of the catalysts in service. On other hand, very few new processes have appeared: as early as 1970 one could almost have built the refinery of the year 2005 but with much lower performance with regard to energy, economics, and product quality. Among the truly new processes, one can name selective oligomerization, light olefin etherification very low pressure reforming with continuous catalyst regeneration and petrochemical FCC (DCC).

In many cases, considerable effort has been directed toward improving performance in all stages of the system, from pretreatment of reagents to storage of the product. Such research is generally toward maximizing operating flexibility, increasing efficiency in the use of raw materials utilities, and minimizing waste. Catalysts have been improved, computer simulations have been developed to optimize parameters, and catalyst beds have been redesigned using a single bed with a catalyst of varying activity (structured reactors). Almost all oxidation plants have been renovated along these lines, and it is not unusual for actual productivities to be two to three times or even more times higher than the original productivity in a plant. Thus, although innovation requires improvements in the sense of a radical change in production, much industrial research effort is still being devoted to incremental improvements, which requires thorough knowledge of the basics of the catalytic reaction and a catalyst/reactor system. Reducing the number of steps in a chemical transformation is advantageous not only in terms of reduced capital cost, but it is advantageous especially to: (i) avoid storage of possibly dangerous products, (ii) reduce the risks and the cost of environmental control in complex plants, and (iii) increase process flexibility. Sometimes, a simplification of a process involves just elimination of a purification step, so that the product of one reactor goes straight into another without isolation of an intermediate. We should therefore conclude that refining will witness a very important evolution without revolution that will affect both the processes and procedures utilized. The objective will be to produce “clean” products in a „clean” energy-efficient manner.

Characteristics

The chemical and allied product industries have certain well-defined characteristics that govern their attitudes and performance.

Maturity. Maturity, highly prized in a individual, is feared in an industry. No company could operate in the chemical industry unless it fully understood all the ramifications of maturity, which express them selves in overcapacity, intense competition, low prices, and low profitability. Ultimately, they lead to restructuring. All of these things have happened in the chemical industry particularly with commodity chemicals.

Maturity occurs because of market saturation, wide diffusion of technology and low barriers to entry to the industry. In oil and petrochemical industry, most of the available technologies are considered mature. Technological innovations in catalytic processes are thus expected from introducing substantial modification in technology. New raw materials and catalysts are being used, and new process technologies, new machinery, and new equipment are developed. There is a pressure for fine-tuning of existing processes. Work continues on optimizing all the process components, eliminating bottlenecks, and revamping existing plants. Producers try to comply with new requirements and regulations. Processes are being developed that have a less severe environmental impact, which translates into lower pollutant emissions, less waste, and greater safety. There is also an increasing demand for purer products for the production of high-quality polymers.

Participation in international trade. The technology of the oil and petrochemical industry tend to be very international. To a great extent, there are the same petrochemical companies and the same international service companies that are found in most areas of the world and, not surprisingly, the technology that they employ is broadly the same in whichever country they operate. Fierce economic competition has been one of the key characteristics of international petrochemical industry since its earliest days, and this characteristic has been strengthened over the past 20 years by the global trends towards deregulation, competition and privatization, creating a more pluralistic industry that consists of many ´players´ in each segment of the industry and more transparent transfer of prices between them.

Competition from Developing Countries. Natural gas has been discovered in many places in the world and, of course, many countries have petroleum. Many of them are eager to enter the chemical business because it promises greater value added than it is possible to obtain when the gas or oil is used for energy. Thus, an awesome list of countries has built or is building chemical industries. The United States, Western Europe, and Japan have long-standing chemical industries. Newcomers include Saudi Arabia and other Gulf states, Canada, Mexico, Venezuela, Brazil, Argentina, and other Latin American countries, including Trinidad and Chile, the former members of the USSR and other Eastern European countries, as well as Taiwan, Korea, China, Thailand, Indonesia, Malaysia, Phillipines, and Singapore. Many of these countries enter the chemical business to provide for their own needs. Taiwan and Thailand indicate that they will not be major exporters because they can consume locally most of their own production. Korea, Saudi Arabia and Canada and most other countries will, however, become formidable competitors in the international trade arena.

Capital Intensity and Economies of Scale. The chemical industry is capital intensive. It produces huge quantities of homogeneous materials, frequently liquids or gases, which can be manufactured, processed, and shipped most economically on a large scale. This was less so through the nineteenth century until the World War II. The early chemical industry used general-purpose equipment and operated batch processes that required little capital investment but had high labour costs.

The petroleum refining industry was the first to convert to continuous operation on a large scale. The engineering development for the petroleum industry was applied to the petrochemical industry. Plant sizes escalated as dramatic economies of scale became possible. The capacity of a typical ethylene steam cracker unit rose from 32.000 tonnes/year in 1951 to 450.000 tonnes in 1972. In the early 2002s plants with 1,3 million tonnes/year capacity were built (E3, Joffre, Alta., joint Nova Chemicals Corp.-Calgary a Union Carbide Canada Inc.). Currently, there are few batch processors of any size in operation for commodity chemicals, and substantial economies of scale have become a characteristic of the modern petrochemical industry.

Criticality and Pervasiveness. Any chemical industry is critical to the economy of a developed country. In the nineteenth and the first half of the twentieth century, the industrial development of a nation could be gauged from its production of sulphuric acid as the grandfather of economic indicators. Today one uses ethylene production as a yardstick for industrial sophistication. An advanced economy cannot exist without a chemical industry; neither can a chemical industry exist without an advanced economy to support it and provide the educated labour force it requires.

Freedom of Market Entry. Another characteristic of the chemical industry is freedom of market entry. Anyone who wants to manufacture bulk petrochemicals may do so by buying so-called “turnkey” plants from chemical engineering contracting companies. Such companies have processes for preparation of virtually any common chemical and will build a plant guaranteed to operate for anyone who wishes to invest the money. This was the way how many of the petroleum companies gained entry to the petrochemical business and also the way how many of the developing countries are laying the foundations of their own chemical industries.

Strong Regulation. The chemical industry is one of the most highly regulated of all industries. The regulations are intended to protect and improve the worker’s and the nation’s health, safety, and environment. The Chemical Manufacture Association (CMA) has documented the vigorous response of the industry to the need for pollution abatement. Of all the regulations, the stringent requirements of the Clean Air Act will have the most far-reaching economic impact on the industry, with a cost projected at $25 billion/year.

High Research and Development Expenditures. The chemical industry is research intensive. It hires many graduates, over 15% of all scientist and engineers in the United States and most of them work in research and development laboratories. The proportion of the chemical industry of the total almost doubled from 1970 to 1992.

In the mid-1960s, however, the concept changed to “demand pull.” What problems are there in the marketplace that require technical solutions? Market research to answer such questions became a discipline and, for the past 25 years, the industry has talked of “market orientation.” Examples of technology push include television, sulfonamides, and lasers. Examples of demand-pull include hard water compatible detergents, jumbo jets, and automobiles with low-exhaust emission. A catalytic cracking catalyst that gives increased amounts of isobutene and propene is an obvious example of the result of a market-oriented research project, isobutylene being required for the production of methyl tert-butyl ether for unleaded gasoline. Both kinds of research should be part of the game plan in any large company, although there has been a marked trend to de-emphasise the “blue-skies” research that leads to truly novel discoveries.

A major area for research in today’s world is monitoring and reducing pollution. One-fifth of new capital expenditure in the

1990s was for pollution abatement and control; approximately the same amount of the R&D budget of a large company is likely to be spent on ecologically oriented projects. Thus, first-generation research was "blue-skies" research. It required little participation by management, and researchers were generally regarded as a group of people difficult to communicate with. It was only when a project reached the development and marketing stages that management was required.

Today there is a third generation of research managers who recognize that research should be a part of the organization not apart from it. Research and development should figure in corporate objectives and should take directions from these objectives in exactly the same way as any other business function. They should thus help the organization to achieve its overall goal. Indeed, they should even help to set goals by managing technology as opposed only to inventing and applying it.

Thus the R&D department has to determinate which technologies may by developed internally, which may be obtained trough licensing, and which may be obtained through strategic alliances. This is very much like a "make-or-buy" decision in manufacturing. It was obviously better for many companies to license BPs ammoxidation technology than to try to work out an acrylonitrile process on their own. Similarly, when Himont wanted to develop highly sophisticated catalysts for propylene polymerization, it joined forces with Mitsui, for both companies had strong background in catalyst development, and jointly they could bring these to bear on the objective. Du Pont decided to develop a superior maleic acid process, since this presented an important raw material for a new process, they invented to prepare Spandex, their most profitable product, in the late 1980s and early 1990s.

A sensible R&D strategy avoids duplication, but a large amount of duplication takes place in the research laboratories all over the world. The patent literature discloses

twenty-five processes for the manufacture of 1,4-butanediol and similar number for propylene oxide. At last recently fifteen companies have worked on the homologation of methanol to higher alcohols, a process that none has commercialized. There are many other examples.

The bulk of R&D dollars is spent on development. This includes work on new and improved processes, finding new uses for existing products, solving ecological problems, and pursuing the analytical activities on which a modern laboratory depends.

Dislocations. An important concept in chemical industry today is the ever-present possibility for dislocations. This is particularly important for planners who, all too often, find their scenarios askew because of a dislocation. Dislocations are defined as events over which a given company has no control but which markedly affect that company's business. In planning, one cannot forecast what a dislocation might be. Indeed, if it could be forecast, it would not be a dislocation. But what must be anticipated in planning is that there will be dislocations either for good or for ill.

The Future

Catalysts. The catalyst can play a significant role in the production of higher quality fuel as required by standards which step-by-step are going to be introduced all over the world due to growing consciousness of the damage to human health and environment from existing products. Fuel reformulation has been seeded by the growing consciousness of the potential damages mankind was causing to the ecosystem and to itself. Fuel reformulation means that fuels are defined on chemical composition the basis of their with additional engine-technology related standards rather than on pure performance bases. These standards, which are getting more and more stringent, can be met by different leverages, mainly catalyst and process operating conditions.

Huge improvements towards the development of environmentally friendly processes have been achieved in the alkylations of aromatics with olefins during the last four or five decades. Particularly, many efforts have been devoted to the research of solid catalysts adequate to substitute mineral or Lewis acids and free bases traditionally employed as catalysts in the acid or base catalyzed alkylations. Various solid catalysts based on different zeolites have been developed for the production of EB and cumene up to the industrial scale.

An alkylate defines a mixture of C_8 isomers, mainly trimethylpentane, with minor amounts of higher components obtained via acid catalyzed addition of isobutane to linear butenes. Today two families of alkylation technologies are available: the H_2SO_4 based and the HF-based, proposed by UPO and Phillips. Both of them suffer from a severe environmental impact.

Therefore, the high potential for reformulated gasoline faces severe constraints in the production cycle which, in turn, generates a strong impulse to searching for solid alkylation catalysts. Many materials have been tested starting with zeolites in the late 1960s. However, catalysts that have reached the stage of pilot unit are not based on zeolites, instead, they are composites of mixed oxides. UPO (alkylene process) proposed $AlCl_3/Al_2O_3$ with a small amount of noble metal (Pt); Catalytica/Neste Oy/Conoco selected a boron trifluoride on Al_2O_3, while CD Tech/Chevron developed SbF_5/acid-washed silica. All of them are supported strong Lewis acids. H. Thopsoe AS proposed the most innovative approach: a supported or anchored trifluorsomethansulfonic acid (triflic acid F_3CSO_3H) on silica.

As in other countries, cleaner or more environmentally friendly production of materials and chemical energies is becoming more and more important. Examples are the changes to solid acid from liquid acid catalysts, to catalytic oxidation from stoichiometric chemical oxidation, etc. Catalytic processes, which make use of less expensive and more abundant raw materials in a smaller number of reaction steps, are always highly desired. Recently, this has been stressed particularly in the syntheses of fine chemicals, although the search for new functional compounds is also of great concern in this field.

After recent development of two processes using heteropolyacids (2), Asahi Chemicals have industrialized the production of cyclohexanol from benzene via partial hydrogenation and subsequent hydration. The two-steps are catalyzed by Ru and a zeolite, respectively. The new process is superior to the conventional two-steps oxidation process in several respects: selectivity, safety, corrosion, and energy-consumption.

In gas-phase Beckmann rearrangement of cyclohexanone oxime and synthesis of pyridine derivates have been many attempts to replace the conventional process, which utilizes fuming sulfuric acid by a gas-phase solid acid process. This long-term wish is about to be fulfilled by using a silicalite-type catalyst, that is almost non-acidic, in the presence of methanol in the feed.

Other promising routes in acid catalysis can be mentioned, such as MCM-41/Nafion composite prepared from a sol-gel preparation of nanostructured silica in the presence of cethyltrimethylammonium and Nafion gel in monophasic conditions. This novel material was applied in the dimerization of á-methylstyrene to produce selectively the corresponding acyclic dimer.

When these modified materials were used to catalyze the condensation reaction between phenol and acetone, highest selectivity in *p,p´*-bis phenol A isomer (I) versus *o,p´*-bis phenol A isomer (II) was obtained as the reaction occurs inside the pores.

Hydrogen. Historically, refinery hydrogen consumption has increased as refiners increase the degree of conversion and process heavier and sourer crudes. However, increases in hydrogen use are being accelerated by recently enacted environmental regulations that require refiners to produce cleaner burning transportation fuels.

As refineries are reconfigured to produce clean fuels, there will be an increase in hydrogen demand and refiners will be required to find new sources of hydrogen. Off-gas sources within refineries may provide a portion of these requirements but more hydrogen will be needed than can be economically recovered. Expansions of existing steam reformers must be considered during any evaluation because of the potential for obtaining hydrogen at attractive incremental costs. The ultimate solution, however, may be a new on-purpose capacity, using traditional steam reforming technology or, in specific situations, partial oxidation (POX) technology, also well-proven in plant operations. When new hydrogen demand is combined with bottom-of-the-barrel destruction, POX technology may have some very compelling synergies but must still provide hydrogen product at competitive costs to be considered viable. The term "Dry or CO_2 reforming" as used in this presentation is short for CO_2 reforming of natural gas. In contrast to steam reforming of natural gas, addition of CO_2 permits optimization of the synthesis gas composition for methanol production.

Development and utilization of more efficient energy conversion devices are necessary for sustainable and environmentally friendly development in the 21st century. Fuel cells are fundamentally much more energy-efficient, and can achieve as high as 70-80% system efficiency in integrated units including heat utilization, because fuel cells are not limited by the maximum efficiency of heat engines or IC engines dictated by the Carnot cycle.

Hydrogen would be an ideal fuel for fuel cells but due to the lack of infrastructure for distribution and storage, processing of fuels is necessary for producing H_2 on-site for stationary applications or on-board for mobile applications. Hydrocarbons and alcohols can both be used as fuels for reforming on-site or on-board. Hydrocarbon fuels have the advantages of existing infrastructure of production and distribution, while alcohol fuels can be reformed at substantially lower temperatures. Further research and development are necessary on fuel processing for improved energy efficiency and size reduction, and on electrode catalysis related to fuel processing, such as tolerance to CO and sulfur components in reformate.

Alternative Fuels. Alternative fuels are often classified as fuels to replace conventional gasoline and diesel fuels or fuels to extend conventional fuels with environmentally favourable reformulations.

Possibilities:

✖ Replacements for gasoline and/or diesel fuel
- Methanol
- Ethanol
- Compressed natural gas
- Liquefied petroleum gas
- Electricity

✖ Gasoline and diesel fuel reformulation
- Varied gasoline volatility, T90, aromatic and olefinic hydrocarbon, sulfur, and oxygen content
- Varied diesel sulfur and aromatic hydrocarbon content, natural cetane number, and cetane improver

GTL Technologies. The huge and continuously growing reserves of natural gas have stimulated its exploitation in terms of liquid fuels because of its intrinsic characteristic: high energy content, absence of heteroatoms, high hydrogen-to-carbon ratio in the raw material, geographical availability, and growing cost of reinjection and flaring (when dealing with oil-associated gas).

GTL or Gas-To-Liquid technology has unfortunately become synonymous with Fischer Tropsch technology. It is up to all of us in the gas conversion community to continue to point out the many business options and the rich chemistry in the conversion of natural gas to liquid fuels, fuel additives and chemical feedstocks. Today, the route to liquid (or even solid), higher value products from gas is through conversion via synthesis gas (syngas). Two basic types of liquid products can be manufactured, namely hydrocarbons via Fischer-Tropsch Synthesis (FT) and oxygenates such as methanol and dimethyl ether (DME). The GTL is nowadays targeted to diesel because of the linearity of chains in the product mixture, which leads to good cetane number.

The importance of these GTL technologies is the raw material: a liquid fuel is derived from natural gas instead of oil. It opens opportunities for natural resource exploitation, which will influence our future. Conversion olefin to diesel (COD process) is in some way bridging the oligomerization with the GTLs technologies aimed to produce a high quality fuel from natural gas or, in a more imaginative prospects, to open the doors to a „methane-based refinery".

Feedstock Recycling. The production of environmentally friendly materials and chemical energies (clean fuels) as well as environmentally friendly disposal and recycling systems are the targets of current research. Although economically acceptable recycling is now very limited in quantity, the importance of recycling or waste treatment will grow rapidly. This particularly applies for polymer and plastics manufacturers. Improvements of quality are also needed for transportation fuels; in order to meet the new stringent regulations, this will necessitate significant alternations in the oil refinery processes.

The severe limitations on the mechanical recycling of plastic wastes highlight the interest and potential of feedstock recycling, also called chemical or tertiary recycling. It is based on the decomposition of polymers by means of heat, chemical agents and catalysts to yield a variety of products ranging from the starting monomers to mixtures of compounds, mainly hydrocarbons, with possible applications as a source of chemicals or fuels. The products derived from the plastic decomposition exhibit properties and quality similar to those of their counterparts prepared by conventional methods. A wide variety of procedures and treatment have been investigated for the feedstock recycling of plastic and rubber wastes. These methods have been classified into the following categories:

- chemical depolymerization by reaction with certain agents to yield starring monomers,
- gasification with oxygen and/or steam to produce synthesis gas,
- thermal decomposition of polymers by heating in an inert atmosphere,
- catalytic cracking and reforming. The polymer chains are broken down by the effect of a catalyst, which promotes cleavage reactions,
- hydrogenation. The polymer is degraded by combined actions of heat, hydrogen and in many catalysts.

Functionalization of Hydrocarbons. Early research on the functionalization of methane yielded only marginal results. On the basics of these efforts, it was easy to predict that chemistry would never be discovered to make methane the basic building block for chemical industry. The 1980s, however, saw major advances in catalysis. Methane functionalization attracted intense research in the 1980s, which accelerated in the 1990s. Data are accumulating so rapidly that we can do little more here than provide some insights into the approach. Three reactions provide the goals. These are the direct oxidation of methane to methanol and/or formaldehyde; the dimerization of methane to ethane, ethylene, or higher hydrocarbons; and the aromatization of methane.

The primary existing and under developed alkane selective oxidation processes are: (i) methane to formaldehyde or ethene, (ii) methane to vinyl chloride in the presence of HCl, (iii) ethane to 1,2-dichloroethane in the presence of HCl, (iv) ethane to acetic acid, (v) propane to acrylic acid, (vi) propane to acrylonitrile in the presence of ammonia, (vii) *n*-butane to maleic anhydride, (viii) isobutane to methacrylic acid, (ix) *n*-pentane to phthalic anhydride, (x) isobutane to *tert*-butyl alcohol, and (xi) cyclohexane to cyclohexanone and cyclohexanol. Some of this alkanes e.g. *n*-butane and *n*-pentane, will be more available in the near future as environmental regulations impose increasingly stringent limits on the light-alkane content of gasoline. In addition, the increasing demand for chemicals such as methyl *tert*-butyl ether (MTBE) favours the development of new synthetic routes. For example, the conversion of

n-butane to isobutane and the conversion of isobutane to *tert*-butyl alcohol by direct monoxygenation might be of considerable industrial interest (*tert*-butyl alcohol is an intermediate in MTBE synthesis).

Out of the process listed above, only the oxidation of *n*-butane to maleic anhydride has been commercialized. Butane is a particularly attractive material for this process because of its low cost, ready availability, and low toxicity. The fact of this commercialization refutes the commonly held notion that alkanes cannot by used as raw materials because of their low reactivity, which generally translates into low selectivity.

Biorefining. Until now, the major applications of biotechnology in the petroleum industry have been limited to the microbiologically enhanced oil recovery, the production of single-cell protein, the treatment of waste streams (waste waters or gases) and the bioremediation of soils contaminated during the recovery, processing and distribution of petroleum. There are no reports concerning the application of biorefining processes at the industrial scale yet.

Even if most of the efforts in research and development have been directed to biodesulfurization (BDS), other research projects have been initiated for removing other contaminants from petroleum such as nitrogen and heavy metals. Projects concerning the transformation of heavy crudes into light crudes have also been reported. Depolymerization of asphaltenes is also envisaged. However, the most advanced area is BDS for which pilot plants were announced, while the other areas of application in biorefining are still at the level of basic research. It appears that in the distant future, the use of biotechnology could also be extended to other areas of petroleum refining, making possible hydrocarbon cracking, isomerization, polymerization or alkylation by biological catalysts. The introduction of biocatalysis in petrochemistry is also expected. The success of biocatalysis will depend on the ability to enhance biocatalyst activity (i.e. rate and range of substrates) and stability under the conditions found in the petroleum refining industry using genetic engineering strategies. In all cases, the development of commercial biorefining processes will depend on significant improvements in the cheap and abundant production of highly active and stable biocatalysts adapted to the extreme conditions encountered in petroleum refining. Important improvements will also have to be realized in the design of bioreactors and phase contact and separation systems. Until now, BDS is the most advanced field of biorefining but no commercial application has been announced yet. The results obtained for BDS may be generally applicable to other areas of biorefining. The interdisciplinary participation of experts in biotechnology, biochemistry, refining processes and engineering will be essential.

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