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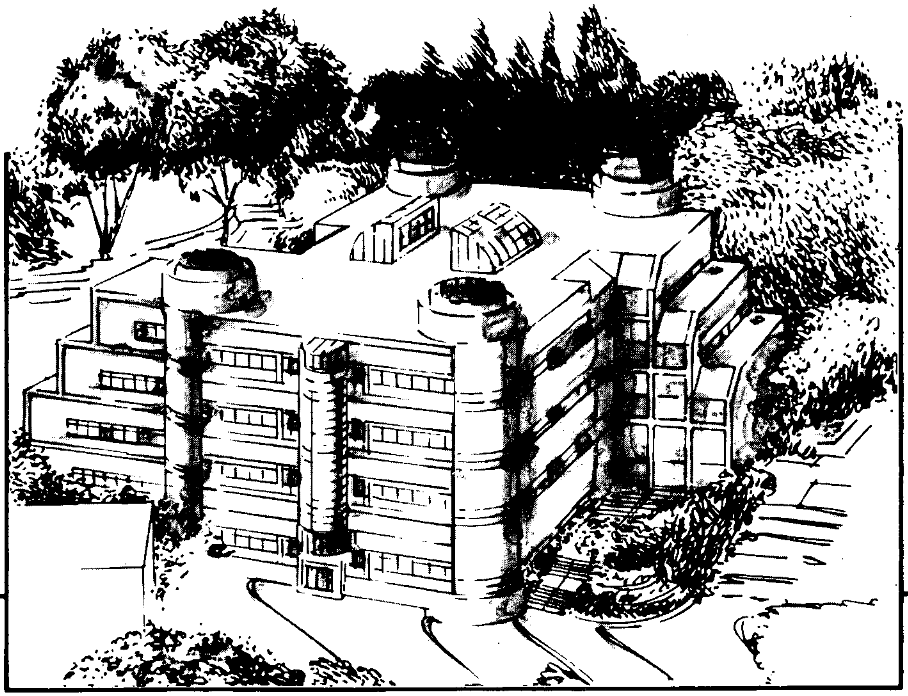

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Development of Industrial Catalysis

by

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Catalysis is involved in a very large percentage of processes leading to the production of industrial chemicals, fuels, pharmaceuticals, and to the avoidance, as well as the clear-up, of environmental pollutants. The world-wide value of fuels and chemicals produced by catalytic reactions is about \$2.4 trillion/year, or more than the Gross National Product of many nations. About 20 % of the value of all commercial products manufactured in the U.S.A. is derived from processes involving catalysis. The vast majority of industrial catalytic reactions involve heterogeneous catalysts but, over the last decade or so, homogeneously catalyzed processes have found increasing use. The value of the heterogeneous catalyst market is estimated at \$5 billion/year and is expected to grow to \$6.5 billion by the year 2000. The cost of catalysts is normally a relatively small part of processing costs and is estimated at 0.1 % of the value of fuels produced and about 0.22 % of chemicals.

Industrial catalysis has developed slowly from an art to a science and, even today, many industrial processes are based more on enlightened empiricism than on derivation from scientific knowledge. For centuries, wine and soap makers have employed catalytic agents on a know-how basis only. The lead chamber process for the manufacture of sulfuric acid using nitric acid to oxidize SO_2 to SO_3 in the presence of water was introduced in the mid-18th century and is probably the first conscious use of catalysis in industrial processing.

The lead chamber process was largely replaced, beginning in about 1900, with a heterogeneous catalytic process using platinum on acid-resisting material (asbestos or silica gel) as catalysts for the oxidation of SO_2 with air. In subsequent years, catalysts comprising V_2O_5 and K_2SO_4 on a silica support were substituted for the more easily poisoned Pt.

While other relatively small scale uses of catalytic reactions occurred in the 19th century, the first major breakthrough of modern industrial catalysis was the fixation of nitrogen by the Haber-Bosch process [1] which was commercialized in 1913.

From about 1910 on, industrial catalysis rapidly gained in importance until it dominated chemical processing by the middle of the 20th century [2]. Its growth was stimulated to a considerable extent by the industrial needs of two World Wars, and by the discovery of vast resources of petroleum, which changed the energy balance of world trade [3].

TABLE 1 presents a chronological summary of major catalytic developments of great industrial importance. It can be divided into three time periods of about 25-30 years each, during each of which about 10 breakthroughs occurred. This first period from 1910 to 1940 involved the synthesis of base chemicals (*e.g.*, ammonia, methanol, nitric acid) and the conversion of natural resources to chemical and fuel building blocks. The increasing availability of inexpensive petroleum hydrocarbons and of fuels produced from petroleum was the main stimulus for new catalytic technologies in the petroleum and petrochemical industries during the second period between about 1935 and 1965 [4].

This period was concentrated on fuels from petroleum and on monomers and polymers derived from petroleum processing. The last period from 1965 to

1990 shows a gradual, but accelerating, shift from catalytic processing of large volumes of relatively inexpensive products to more directed syntheses of smaller volume, more expensive products (such as complex fibers, specialty and pharmaceutical chemicals) and to major applications of catalysis in environmental protection. Automotive emission control [5], NO_x removal from stack gases and a wide range of chemical waste and by-products control were supplemented by new or modified processes for manufacturing chemicals with higher selectivity and fewer toxic by-products.

Another trend in catalytic processing began about 1985 with the recognition that catalysis could assist in the production of stereospecific and of chiral compounds, particularly in the pharmaceutical and fine chemicals industries. While the bulk of catalytic processing depends on solid heterogeneous catalysts, homogeneous catalysis is playing an increasing role, mostly in the pharmaceutical and fine chemical field. Zeolites, originally introduced as petroleum refining catalysts have been used in modified forms for a large variety of shape-selective reactions and have played a large role in the successful attempts to substitute heterogeneous for homogeneous catalysts, thus permitting an easier separation of catalyst from substrate.

These developments reflect a shift from an industrial economy dominated by price competitiveness alone to one in which environmental regulations may supercede the cost factor.

In the following more detailed review of the development of industrial catalysis, it is not always possible to maintain a strict chronology, since progress was often achieved by attaining a specific objective by improving previous achievements through new and better catalysts or by new engineering technology. The interplay of catalytic chemistry and process engineering is of great importance, and the transition of a concept from the laboratory to a competitive commercial product or process involves at least as much effort and ingenuity as the concept itself. Similarly, the scale-up of catalyst manufacture requires both engineering and chemistry [6, 7].

THE 1910 TO 1938 PERIOD

The Haber-Bosch synthesis of ammonia from the elements replaced dependence on guano, a rapidly diminishing resource, and on the very high temperature arc process to produce cyanamide, which was thermally inefficient. The ammonia synthesis alleviated the fear of world-wide starvation by providing fertilizers to increase crop yields in line with population increases. It also provided nitrates for military explosives. It has been said that World War I would have ended in 1916 without Germany's ability to produce gun powder from the ammonia synthesis. The military demand for nitrates also expedited commercialization in 1915 of a process originally invented by Ostwald, which permitted conversion of ammonia to nitric acid, using iron-manganese-bismuth oxide catalysts.

The ammonia synthesis using promoted iron catalysts owes its origin to the thermodynamic and kinetic studies of Fritz Haber, largely supported by grants from the chemical industry. He determined the need for high pressure and low temperature to assure reasonable yields of ammonia. His work faced serious obstacles in the development of a commercial process because of the need to build large scale high pressure equipment. Bosch and his coworkers achieved success in constructing and operating such equipment and Mittasch investigated numerous ammonia synthesis catalysts and scaled up their synthesis to commercial scale. The availability of high pressure equipment contributed greatly to the development of other catalytic processes.

During experience with the high pressure catalytic ammonia synthesis, German scientists noticed about 1913 the presence of oxygen containing compounds in the product. Further research led to the catalytic methanol synthesis from synthesis gas ($CO + H_2$) which became commercial in 1923. The catalyst employed was $ZnO\text{-}Cr_2O_3$, later replaced by CuO-ZnO catalysts. Manufacture of synthesis gas was originally based on gasification of coke from coal by means of air and steam. Only after the Second World War did production of syngas by catalytic steam reforming of natural gas or of petroleum fractions become the dominant process, using nickel-based catalysts. This process was derived from work by Mond in the late 19th century.

The oxidation of ammonia to nitric acid, first proposed by Ostwald in 1906, was commercialized in 1915, employing platinum catalysts.

Just as the military demand for gun powder had stimulated research on the ammonia synthesis, the need for a domestic supply of liquid fuels resulted in research to convert coal to automotive and lubricant fuels. In 1931, Professor Bergius in Germany demonstrated the liquefaction of coal by hydrogenation in the liquid phase, with the coal and solid catalysts being suspended in a tar oil. The hydrogen required was again derived from synthesis gas. The water gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$) using a Fe_3O_4 catalyst containing some chromia at ~350-450 °C had been discovered before 1920 and permitted the production of two moles of hydrogen per mole of carbon:

$$\begin{array}{l} C + H_2O \rightarrow CO + H_2 \\ \underline{CO + H_2O \rightarrow CO_2 + H_2} \\ C + 2H_2O \rightarrow CO_2 + 2H_2 \end{array}$$

In about 1962, a low temperature (~250 °C) shift catalyst comprising copper, zinc oxide and alumina was introduced to convert the CO remaining from the high temperature shift, which is equilibrium limited.

An alternative route to synthetic fuels from coal via synthesis gas was invented by F. Fischer and H. Tropsch and first commercialized in 1938. It is known as the Fischer-Tropsch synthesis. Hydrogenation of carbon monoxide was carried out at 400-450 °C and about 7-30 bar pressure over alkalized iron turnings as catalyst. Earlier catalysts had consisted of cobalt and of nickel or manganese oxides. Large scale plants in Germany produced about 800,000 t/year of liquid fuels during World War II, using fixed bed reactors. The products were paraffinic hydrocarbons with an appreciable amount of oxygenated compounds. After the Second World War, large scale use of the Fischer-Tropsch synthesis was centered in South Africa where, since 1955, Sasol has operated first a fixed bed reactor plant with a capacity of 250,000 t/year and later two fluid bed reactor plants with over 2,500,000 t/day capacity. Since 1993, Shell Oil Company is operating a modified Fischer-Tropsch plant in Malaysia, which uses syngas from natural gas to produce high molecular weight paraffins, which are then hydrocracked to diesel fuel. This plant appears to use a cobalt catalyst.

There has been an abundance of publications during the last 50 years to cover various scientific and/or technological aspects of the Fischer-Tropsch synthesis, including mechanisms as well as the effect of various catalyst metals, *e.g.*, ruthenium, on product distribution.

In 1902, Sabatier had demonstrated the catalytic hydrogenation of ethylene using nickel catalysts. With the availability of high pressure equipment, M. Pier and his coworkers in the 1920s and 1930s extended catalytic hydrogenation to several important processes, such as olefin saturation, hydrocracking and aromatic saturation, using metal sulfides as catalysts.

From the 1930s on, there has been a continuous stream of process and catalysts improvements, in addition to novel processes.

THE 1938-1965 PERIOD

The Second World War stimulated the rapid development of three major processes which had been invented during the 1933-45 period: catalytic cracking provided much of the high-octane gasoline for the Allied air and land forces; catalytic alkylation was a source of close to 100 octane number gasoline which, blended with catalytically cracked gasoline, provided a superior aviation fuel, and catalytic dehydrogenation of methylcyclohexane in petroleum naphtha resulted in a supply of toluene for further nitration to trinitrotoluene (TNT). Based in part on these developments and further inventions, numerous other industrial applications of catalysis occurred between 1945 and 1965.

Catalytic Cracking

Gasoline comprises only 15-25 % of natural petroleum. Its chemical components consist primarily of relatively low octane number paraffins. Since motor and aviation fuel gasoline was (and still is) the most desirable petroleum fraction, methods to convert higher molecular weight (C_{12}^{+}) hydrocarbons to large volumes of gasoline of high octane number were attractive. This required not only breaking of carbon-carbon bonds, but also structural rearrangement of hydrocarbons by isomerization, dehydrogenation and aromatization. All these reactions can be catalyzed by acidic catalysts. Eugene J. Houdry based the first large scale application of catalytic cracking on the earlier recognition that acidic clays were good cracking catalysts, and he overcame several severe engineering problems, particularly heat balancing the reactor design for an endothermic reaction and regenerating a catalyst which was continuously being deactivated by coke deposition. The first Houdry units, which came into operation shortly before World War II, had fixed bed tubular reactors surrounded by a molten salt bed acting as a heat transfer medium. A group of three reactor units was operated in a cyclic mode with one reactor on stream, one being purged by inert gas, and the third being regenerated with air. A schematic drawing is in FIG. 1 and indicates the complex valving required.

Numerous commercial units were built all over the world during and after World War II and, at its peak, catalytic cracking units in the U.S.A. alone produced over 250 million tons of gasoline per year. Quite early in the development of large scale catalytic cracking, major modifications of both unit design and catalyst composition occurred. The cumbersome design of the fixed bed units was replaced by units having separate reactors and regenerators with the catalyst being moved from one to the other and back. In one mode, this was accomplished in a moving bed unit, in which spent pelleted catalyst was continuously withdrawn from the reactor and lifted either by elevators or pneumatically to the regenerator, from which regenerated catalyst was, by gravity flow, re-introduced to the reactor. In the other, ultimately more successful mode, both reactor and regenerator operated in a fluid bed mode with small catalyst particles suspended in a gas stream (FIGS. 2a, 2b, 2c). Fluid bed operation also permits good temperature control by heat transfer and has found wide application in other exothermic or endothermic reactions, *e.g.*, in the partial oxidation of hydrocarbons.

Catalyst improvements progressed steadily from the inception of catalytic cracking to the present. Acid treated clays were replaced by synthetic silica-alumina catalysts—first in pelleted, later in bead form. Pore structure was adjusted for minimal diffusion limitations. Resistance of the catalysts to abrasion and erosion was important for moving bed operations. A new set of parameters was required for fluid bed catalysts (such as particle size distribution and burning characteristics during regeneration).

A major breakthrough occurred in 1964 at Mobil Oil Co. with the finding that zeolites and particularly zeolite X and Y (faujasite) catalysts showed tremendous improvements in gasoline yield and octane number, while coke deposition was reduced. An example is given in TABLE 2, presenting a comparison of a silica-alumina with rare earth containing Y zeolite (REHY) for cracking a heavy gas oil at constant conversion. Results will, of course, vary with oil composition and conversion. The zeolite is used with a silica-alumina matrix.

At the present time, almost all catalytic cracking units in the world operate with zeolite catalysts. Depending on local refinery requirements, feed stock variation and government regulations, modifications of zeolite containing catalysts are being used, which give different yields and octane numbers. These differences are relatively small, compared to the difference between SiO_2-Al_2O_3 and REHY.

Catalytic Alkylation

Alkylation refers essentially to three reactions:

(a) the reaction of C_3 to C_5 olefins with isobutane to produce C_7 to C_9 isoparaffins of high octane number. This process is catalyzed by strong acids, usually H_2SO_4 or anhydrous HF.

(b) the reaction of aromatic hydrocarbons with olefins to produce alkyl aromatics. This process is also acid-catalyzed.

(c) the reaction of olefins with alcohols, *e.g.*, methanol, to produce ethers, such as methyl tertiary butyl ether (MTBE), as high octane components of gasoline. Relatively mild acids, such as ion exchange resins, are catalysts.

The olefin-isobutane reaction was invented by V. Ipatieff and was rapidly commercialized during the Second World War in the U.S.A. to provide a very high octane number blending stock with catalytically cracked gasoline for aviation fuel. The process has been used to utilize excess amounts of olefins and has gained renewed importance in the early 1990s as a component in "reformulated" gasoline, a hydrocarbon blend rich in isomeric paraffins that meets environmental restrictions. The use of sulfuric or hydrofluoric acid, however, creates other environmental and toxic concerns. For almost 40 years, there has been a search for a solid non-toxic catalyst for this reaction. No commercial process using such a catalyst is in operation as of 1994.

Aromatics alkylation is important for ethylbenzene production (a precursor of styrene) and for the detergent industry. For many years, anhydrous aluminum chloride was the preferred catalyst for this reaction until disposal problems made it undesirable. It has been largely displaced by zeolites of the HZSM-5 type, which are strong enough solid acids and pose no disposal problems.

Catalytic dehydrogenation and catalytic reforming

The demand for toluene as a precursor for TNT during the Second World War was greater than could be supplied from straight-run gasoline. A process for the catalytic dehydrogenation of methylcyclohexane contained in the naphtha fraction of petroleum was instituted. This process used molybdena catalysts, usually supported on alumina or on bauxite. To avoid rapid deactivation of the catalyst by coke deposits, the reaction was carried out in the presence of external hydrogen (at about 15 bar). Reactors were mostly of the fixed bed type, but one plant was constructed as a moving bed unit, the first such unit to operate at elevated pressure.

It was soon recognized that it would be desirable to complement the dehydrogenation reaction with an acid-catalyzed reaction, which would permit isomerization, cracking and aromatization to proceed. Three processes, Platforming, Catforming and Houdryforming, were almost simultaneously introduced in the early 1950s, all of which employed platinum as a metal dehydrogenation and alumina or silica-alumina as acid catalysts. A network of hydrogenation-dehydrogenation and isomerization reactions (FIG. 3) allowed conversion of C_5 and C_6 cycloparaffins to aromatics and by-product hydrogen. Catalysts doing this job were called dual-functional. They formed the basis for catalytic naphtha reforming, the second largest refinery process. Many catalyst and process improvements and modifications were introduced over the years. The original processes operated at 30-40 bar pressure in the presence of hydrogen and in a fixed bed mode. Catalyst life was 0.5-3 years without regeneration. It was obvious that from a thermodynamic point of view, lower pressure would improve the volume yield of reformate (TABLE 3). Introduction of bimetallic catalysts by Chevron in 1967 accomplished this, lowering operating pressure by 14-17 bar. The bimetallic catalysts contained rhenium, in addition to platinum and acidic alumina. Alternatively, pressure could be lowered in exchange for more frequent regeneration. In a severe example of this, a moving catalyst bed operation was introduced. Since dehydrogenation and reforming are strongly endothermic, a reforming unit usually consists of at least three reactors in series with interstage heaters. This complicates engineering design for regenerative operation.

Reforming processes have been a major source of hydrogen for other processes for many years. In the early 1990s, with the introduction of "reformulated gasoline", there has been a reduction in the daily volume of reformate, since benzene was considered toxic and aromatics content of gasoline was restricted. This in turn has led to a shortage of hydrogen in some refineries.

The alkylation of benzene with ethylene has been mentioned earlier. Dehydrogenation of ethylbenzene to styrene (a major monomer) has been, since 1951, a catalytic process. Iron oxide catalysts containing Cr_2O_3 and KOH or K_2CO_3 are used, and heat for the endothermic reaction is supplied by means of superheated steam.

HYDROGENATION AND HYDRODESULFURIZATION

Sulfide catalysts are probably the oldest class of catalytic materials used in the production of liquid transportation fuels. Developed after World War I for the hydrogenation of coal tar liquids, the sulfide catalysts are currently used in virtually every refinery in the world (FIG. 4). They are employed to remove sulfur and/or nitrogen compounds from hydrocarbons and to hydrogenate petroleum, tar or coal fuels. They may be used before another catalytic process, such as reforming or catalytic cracking, to hydrogenate aromatics to cycloparaffins which are easier to crack and to remove sulfur compounds which may poison noble metal or zeolite catalysts. They may also be used after a catalytic reaction to finish the product and meet final product specifications.

Modern sulfide catalysts are usually molybdenum- or tungsten-based and supported on alumina, some of which are promoted with cobalt and/or nickel. This generation of sulfide catalysts has proven to be very successful in meeting past sulfur removal from fuel goals. However, they may not be sufficient to meet the constantly increasing specifications for sulfur and nitrogen removal from hydrocarbon liquids and for saturation of complex aromatics.

Hydrocracking of heavy petroleum fractions or residua has gained increasing importance as more dependence on heavier oils developed. While tungsten and molybdenum oxides or sulfides supported on an acidic compound, such as alumina or faujasite-type zeolites, are the preferred catalysts for hydrocracking, precious metals on these supports are also used. The catalyst must have a proper balance of hydrogenation and of acidic cracking function, which can be different for different feedstocks.

While most hydrocracking units operate in the fixed or trickle bed mode, resid hydrocracking may require a solid catalyst suspended in a heavy liquid, using a slurry bed in several stages. Such a unit has been built by Amoco.

Coal liquefaction by direct hydrogenation is derived from the old Bergius process. Coal and heavy tar hydrogenation differs from residual oil conversion only in the fact that they are hydrogen poorer feedstocks and require more severe operating conditions. The catalysts used are largely the same as in resid hydrogenation.

Heavy oils and tars often contain organically-bound metals, particularly vanadium and nickel, which tend to poison and also block the catalyst pores. While catalysts poisoned by coke deposits can be regenerated by oxidation, conventional regeneration does not remove metals from the catalyst. Catalysts used in this service must be physically robust and also relatively inexpensive. Their ultimate disposal can create environmental problems because of the toxic nature of heavy metals.

There are several industrial catalytic hydrogenation processes of small overall volume. Among them are: the selective hydrogenation of olefins and diolefins in pyrolysis gasoline to allow extraction of aromatics; the selective hydrogenation of diolefins in C_3 and C_4 streams prior to polymerization, involving precious metal catalysis in liquid phase; and the saturation of fats.

Dehydrogenation

As mentioned earlier, the military and civilian requirements of World War II resulted in the rapid commercialization of a number of catalytic processes. Among them were two dehydrogenation processes which, with some modification, are still in use 50 years later. The Houdry dehydrogenation process produced butenes and butadiene for "Buna" rubber from n-butane, employing a chromia-alumina catalyst. There is appreciable coke deposition on the catalyst and swing reactors are being used with alternate reactors being on stream and on regeneration. Heat for the highly endothermic reaction is provided by burning of the coke. Another method using oxidative dehydrogenation over bismuth molybdate or over perovskite catalysts was operated for a while. It did not have to deal with temperature swings, but had the disadvantage of not producing hydrogen, which instead was burned to water.

The Houdry dehydrogenation process has seen a revival in the 1980s and 1990s, this time with isobutane as feed stock and the aim to provide isobutene for alkylation with methanol in the production of MTBE, used in as large as 5 % by volume as gasoline additive. British Petroleum and U.O.P. have developed a propane or butane dehydrogenation process using a supported precious metal catalyst and a process design involving a continuous moving bed. Commercial units have come on stream in the early 1990s.

The need for a substitute for natural rubber during the Second World War also stimulated a process to dehydrogenate ethylbenzene to styrene. Alkali promoted iron catalysts have been used and this reaction, as well as the butene to butadiene process, is carried out in the presence of steam to reduce polymerization of the desired product. In recent years, large polystyrene demand has kept the process alive.

Isomerization

During World War II, there developed a need to isomerize n-butane to isobutane for alkylation with C_3 and C_4 olefins. This required a strong acid catalyst and anhydrous aluminum chloride was used in the presence of traces of water, either suspended in heavy oils or supported on bauxite. Release of HCl and high corrosivity of the early process were reduced with introduction of the U.O.P. and Shell processes employing Pt-alumina or Pt-mordenite catalysts, respectively. Isomerization of C_5 and C_6 fractions has been practiced, although the equilibrium concentration of the desirable highly branched isomers is relatively low at the kinetically required temperatures.

Isomerization of alkyl aromatics and particularly of xylenes became necessary to produce the para-isomer, a monomer for synthetic fibers. $AlCl_3$ was again the catalyst in early operation to be replaced with ZSM-5 zeolite as a noncorrosive catalyst with no disposal problems. Xylene isomerization gives an equilibrium mixture of the isomers, which have to be separated to recover the desired para-xylene. Recently, shape-selective isomerization on ZSM-5 has permitted higher than equilibrium yields of p-xylene.

Oxidation [8]

The oxidation of aromatics, *e.g.*, of naphthalene to phthalic anhydride is an old art. Xylene has been commercially converted to phthalic anhydride since 1946. Vanadium oxide is the preferred catalyst, although molybdena catalysts have also been used. The process was greatly improved when fluid bed technology was introduced and permitted better temperature control of the highly exothermic reaction. The same technology is used for oxidation of benzene to maleic acid.

Direct partial oxidation of lower molecular weight olefins, particularly ethylene and propylene is carried out in a variety of catalytic processes to produce ethylene oxide, glycol and propylene oxide. Silver is the almost exclusive catalyst for ethylene oxide production and it is promoted with alkali and with small amounts of halides. Propylene oxide is today manufactured in a homogeneous reaction by oxidizing propylene in the presence of soluble molybdenum compounds with t-butyl hydroperoxide, which, in turn, is obtained by air oxidation of isobutane. Tertiary-butyl alcohol is a by-product.

Propylene is also the feed for oxidation to acrolein over cuprous oxide and later over bismuth molybdate catalysts. Acrylonitrile, an important monomer, is manufactured from propylene, ammonia and air in a fluid bed over catalysts such as uranium antimonate or tin antimony mixed oxides.

Partial oxidation of methane to synthesis gas ($CO + H_2$) is an alternate route to steam reforming, but is not a catalytic process. In the early 1990s, experiments for catalytic partial oxidation of methane have been described in the literature, but no commercial process is yet operating.

Oxidation of HCl to chlorine is important since all chlorination reactions produce stoichiometric amounts of HCl. The Deacon process, reacting HCl with oxygen over copper chloride was discovered as early as 1860. There have been several attempts to operate large scale "Deacon" plants using cupric chloride catalysts, but all failed because of corrosion problems. The "Kelchlor" process developed by the M.W. Kellogg Co. operated successfully in a DuPont plant for many years in the 1970s and 1980s. It involves a homogeneous reaction of air or oxygen with HCl, using nitrogen oxide catalysts. The reaction is carried out in sulfuric acid, which absorbs the water produced and thus reduces corrosivity and also drives the equilibrium to higher yields.

In another partially homogeneous reaction, ethylene is oxidized to acetaldehyde (which, in turn, can be oxidized to acetic acid) with palladium chloride in the presence of water. Reduced Pd metal is oxidized back to $PdCl_2$ with cupric chloride and the reduced cuprous chloride is reoxidized with HCl and oxygen. This "Wacker process" has operated in numerous plants and a similar reaction is used to make vinyl acetate.

Acetic acid, a large scale chemical, is produced by oxidation of acetaldehyde and and, since 1977, largely by the Monsanto process, involving reaction of CO with methanol in a homogeneous process promoted by a rhodium catalyst.

Hydroformylation, the reaction of olefins with CO and hydrogen, was discovered by Roelen in the early 1940s and the resulting "Oxo Process" still produces propionaldelyde from ethylene and butyraldehyde from propylene.

Polymerization

The need for high octane gasoline during World War II led to efforts to dimerize and trimerize ethylene and propylene, and the development of the solid phosphoric acid process (phosphoric acid on kieselguhr). The previously mentioned monomers, butadiene, isoprene and styrene, were co-polymerized to synthetic rubbers.

In the 1950s polyethylene and nylon and its derivatives became the first products of the plastics and synthetic fiber industry. The early processes were of the high pressure free radical type. In 1955 Ziegler disclosed a "low pressure" polyethylene process employing an aluminum alkyl and titanium tetrachloride catalyst. Natta, at about the same time, produced polypropylene by catalytic polymerization. While the original Ziegler catalyst was used in solution, later catalysts employed were solids, such as supported chromia or molybdena, used with promoters.

The polymer industry uses a wide spectrum of catalysts, many of which are proprietary. An early and very successful catalyst was "Dabco" (triethylene diamine), introduced in 1959 for the production of urethane foams from isocyanates and alcohols. Dabco is still in use today. A more recent example of catalytically produced polymer chains are rigid polymers of great strength and light weight. "Kevlar" has a tensile strength higher than that of a steel fiber of the same dimensions, weighing only one-fifth as much. It is produced employing eight catalytic steps, using a combination of acid, hydrogenation and oxidation catalysts. Polymers like Kevlar are likely to replace steel as a structural material in many applications.

Zeolites

While the use of zeolites as catalysts has been discussed in several of the preceding sections, the importance of zeolite chemistry to catalytic processing and engineering deserves special attention as one of the major breakthroughs of the 1960s. The first announcement of the ability of faujasites to catalyze an acid dependent reaction (isomerization) was made by Rabo of Union Carbide Corp. in

1960. This was followed by Mobil Oil Co. introduction of zeolite cracking catalysts. Prior to about 1960 there had been a general belief that crystalline materials possessed poor catalytic properties and there also were relatively few natural zeolites available. The synthesis and the blending of zeolites with clays and aluminas provided the stepping stones required for large-scale applications.

Early processes used synthetic X- and Y-zeolites and, in a few cases, natural erionite. In the mid-1960s the synthesis of ZSM-5, a medium pore size zeolite, was described by Mobil Oil Co. workers. The pore size of ZSM-5 permitted controlled molecular diffusion or shape selectivity to supplement acidic properties. This material then found broad applications, *e.g.*, in methanol conversion to gasoline, aromatics processing and in cracking. Numerous other zeolites have since then been synthesized and found use in a wide variety of reactions. Incorporation of metal functions into the pores of ZSM-5 resulted in new hydrocracking and in new isomerization catalysts. Changes in the silica-alumina ratio of zeolites permitted control of the acid function.

THE 1965-1990 PERIOD

While some major specific catalytic process accomplishments are discussed below, this time period is characterized by a large number of new processes and process modifications relating to smaller size chemical processes and to the production of fine chemicals. Three recent review papers [11] have analyzed this trend in the U.S.A., Japan and Europe. In Europe alone, there have been over 100 new developments between 1980 and 1990, which obviously cannot be discussed in detail within the present framework, but which are of undoubted value for obtaining specific products. Lists of these developments are presented in the reference papers.

Shape Selectivity

Shape selectivity of zeolites was discovered in the mid-1960s, has since found many applications and its importance continues to grow. It is based on the concept that the pores of certain zeolites in which chemical reactions are catalyzed are of the same order of size as the molecular dimensions of the reacting molecules. Depending on the size and shape of reacting molecules, they may or may not diffuse into the zeolite and some potential reaction products can, for steric reasons, not form in the zeolite pores. Early applications of shape-selective reactions were "Selectoforming" and "M-forming", which permitted the selective cracking of normal or of slightly branched paraffins of low octane number, but not of more highly branched, high octane number parraffins. Shape-selective isomerization of xylenes has already been mentioned earlier. Distillate dewaxing with either ZSM-5 or mordenite catalysts became commercial in the early 1970s. Toluene disproportionation to benzene and xylene is being practiced on an appreciable scale. In 1982, the MTG (methanol to gasoline) process was commercialized in New Zealand with construction of a 750,000 t/year plant to convert natural gas to gasoline *via* methanol. The process uses the shape selective properties of ZSM-5.

In 1982, crystalline aluminophosphates were introduced, which exhibit shape selectivity similar to zeolites but at lower acidity and are used in a number of fine chemicals syntheses.

The concept of shape selectivity, while originating in the petroleum refining industry, is finding increasing applications in the synthesis of polymers and of pharmaceutical, agricultural and enzymatic syntheses.

Environmental Catalysis [9]

The first impact of environmental concerns occurred in the early 1960s with the recognition that automobile emissions provided a serious health hazard as did the use of tetraethyl lead as a gasoline additive. While there had been scientific work on the conversion of carbon monoxide and of nitrogen oxides, large scale application was expected to be expensive and not commercially attractive. It was due to government regulations in the United States, which set standards for CO and NO_x emissions from automobiles, that a major effort was made by various automobile and petroleum companies operating individually and in combination to come up with catalytic technology to meet the required standards. The success of this effort is shown in TABLE 4. The history of the development of automotive emission control catalysts is an interesting one. It is also interesting to note that early work under the pressure of compliance with regulation deadlines was concentrated on non-precious metal catalysts which could give about 90 % reduction of CO content but not the 98+ % reduction required by law. Similarly, the requirement that the catalysts were to perform for at least 50,000 miles of a car's operation shifted the commercial development to precious metal catalysts even though they were appreciably more expensive than non-precious metals or metal oxides.

Increasing consciousness by the public of the health hazards of many toxic materials emitted into the air and into the water during chemical manufacturing and other processing techniques as well as the problem of disposal of non-biodegradable products has led to a rapid increase in efforts to ameliorate toxic effects and environmental damage. Economics will shift to enviro-economics as a driving force. Most of the processes developed thus far involve catalysis. There are three driving forces: (1) society's increasing environmental awareness, concern and expectations; (2) corporate responsiveness and action; and (3) legislation and regulation.

Consumer demands focus on clean air, water and land to safeguard the biosphere and these concerns were clearly expressed in the International Conference in Rio de Janeiro in June 1992. Among the items that seem to predominate in consumers' minds are the destruction of the ozone layer, recycling programs, environmentally friendly packaging and product labeling that reflects environmental considerations. The political pressure exercised by these concerns is clearly demonstrated by the Green Parties in Europe and the Sierra Club in the United States. The cost-risk factor has to be considered but will not be easy to explain to the public. Environmental costs will increasingly become an integral part of process economics.

Automobile exhaust emissions are determined by fuel composition, engine design and operation, and by catalytic converters located in the exhaust system. Exhaust gases from spark-ignition automobiles contain harmful CO, NO_x and hydrocarbons (incompletely combusted fuel constituents). Automotive converters using oxidation catalysts were introduced in the U.S. in 1975, converting CO and unreacted hydrocarbons to CO_2 and H_2O. Three-way automotive converters catalyze these oxidative reactions and also simultaneously reduce nitrogen oxides (FIG. 5). They have been widely adopted to meet federal NO_x standards, beginning in 1981.

Catalysts for automotive emissions are now well developed and in general are capable of meeting presently mandated U.S. standards for CO, NO_x and HC emissions from auto exhaust gases. New cars today emit only a few percent of the exhaust pollutants in cars built 25 years ago, before emissions control. Modern three-way converter catalysts control CO and hydrocarbons by oxidation. Simultaneously, NO_x is removed by reduction according to the equations:

(1) $2CO + 2NO \rightarrow 2CO_2 + N_2$, and

(2) $HC + 2NO \rightarrow CO_2 + \frac{1}{2}H_2 + N_2$.

The generic converter catalyst structure was invented in the early 1950s. Catalytic materials in automobile converters are generally supported on a ceramic honeycomb monolith. The honeycomb, made of cordierite

($2MgO.2Al_2O_3.5SiO_2$), contains 30-60 square channels per square centimeter, is coated with an activated alumina layer called the wash coat. Catalytic Pt, Pd and Rh are highly dispersed on the high area wash coat. Rh metal displays high activity for the removal of CO, HCs and NO_x and is particularly important for reduction of NO_x. Fresh Pd is more active than Pt in most cases for CO, NO_x and hydrocarbon conversion, but is more susceptible to poisons such as lead and sulfur and sinters rather easily in a reducing atmosphere. Ceria may be added at a loading of 2-30 wt.-% to the wash coat of three-way catalysts to store oxygen, to promote the water-gas shift reaction and to stabilize the noble metals against thermal damage. Nickel can be added to scavenge H_2S.

Automobile pollution control necessarily interrelates fuels composition, engine combustion performance and catalytic converter remediation systems. FIG. 5 describes the effectiveness of NO_x, CO and HC control by the Pt/Rh catalyst as a function of the optimal stoichiometric air/fuel ratio (equivalence ratio, λ). In addition, fuel economy and maximum power vary considerably with air/fuel ratio. Major steps have been taken by auto manufacturers to accommodate the requirements for efficient operation of converter catalysts.

Although it is estimated that 96 % of the exhaust HC and CO and 76 % of the NO_x can be eliminated by the use of catalytic converters, there are needs and opportunities for improvements. Three-way catalysts operate near the stoichiometric air/fuel combustion ratio and exhaust temperatures are normally 400-600 °C. However, today's catalytic converters do not reach minimum operating temperatures until about 100 seconds after the cold start of an automobile. During this warm-up period, more than 50 % of hydrocarbons and CO emissions pass unreacted. The problem of cold-start pollution must be addressed by seeking to provide special procedures and catalytic apparatus.

There are two major modes of pollution control: (1) *primary prevention* such as preemptive pollution or avoidance, and (2) *secondary prevention* such as waste or pollution cleanup.

Primary prevention eliminates toxic by-products by increased selectivity. An example of this is the Dow Chemical cumene process, which permits the highly selective alkylation of benzene with propylene using a 3-DDM (3-dimensional dealuminated mordenite) catalyst. Cumene is preferentially formed and the production of disubstituted benzene is inhibited.

Some other examples are shown in FIGS. 6 and 7. Other typical cases are removal of phosgene from the production of methylenediphenyldiisocyanate; the removal of hydrofluoric acid from olefin-paraffin alkylation; avoidance of sulfuric acid use in the production of methyl methacrylate; finding substitutes for chlorofluorohydrocarbons as propellants and refrigerants; avoiding production of $AlCl_3$ sludges by using ZSM-5 zeolite for the production of ethylbenzene from benzene and ethylene. In all these cases, catalytic steps have been found or are being investigated to play a major role. A particularly interesting case is catalytic alkylation. The requirement for clean-burning gasoline of relatively little volatility has resulted in the need to reduce the aromatics and butane content of gasoline. To maintain octane requirement, additional alkylation capacity is required. Replacement of hydrofluoric and sulfuric acid, with solid acid catalysts would reduce hazard and operating costs. Clean-burning gasoline also will increasingly demand inclusions of oxygenated hydrocarbons in the gasoline such as MTBE. MTBE in turn demands both more methanol production and more isobutene than are currently available. This has led to emphasis on improved or new routes of catalytic dehydrogenation of butanes, as mentioned earlier.

Elimination of toxic waste streams and by-products

A few examples here are elimination of sulfonating agents in the production of resorcinol and substituting aromatic alkylation and oxidation; the

Wacker process for the production of acetaldehyde gives aqueous solutions of, as well as volatile, chloro-organics. Other catalysts and processes can be substituted (often at some cost) to minimize or eliminate the undesirable by-products.

Elimination of toxic emissions

Catalytic combustion appears to be one way of avoiding the production of large quantities of NO_X. NO_X is formed in a kinetically controlled reaction in the high temperature of the flame (FIG. 8). At temperatures below 1600 °C, relatively little NO_X is formed, while at 1700 °C, almost three times as much and, at 1800 °C, eight times as much NO_X is formed. Gas turbine power generation is becoming increasingly attractive, particularly in areas where natural gas is available, which, of course, is an environmentally more attractive material than coal. Turbine efficiency increases with combustion temperature. By catalytic combustion, high temperature homogeneous flames are eliminated without losing efficiency. In this connection, it is interesting to note a combination of catalytic processes which has been proposed to increase turbine efficiency. The chemically recuperated gas turbine involves both catalytic combustion and catalytic steam reforming.

Examples of secondary prevention are: (1) automotive emission control; (2) NO_X control from stationary exhausts; and (3) waste stream purification. The contribution of catalysis to the decrease in air pollution can be shown for the 1966-1986 period by 90 % reduction in carbon monoxide emissions, 30 % reduction in SO_2 emissions, 70 % reduction in NO emissions, and 10 % reduction in surface ozone production. However, there are novel ways of NO_X decomposition or reduction, such as the already large-scale use of the reaction of ammonia with NO_X over titania/vanadia catalysts, and proposed novel methods of NO decomposition, using, for instance, copper/ZSM-5 catalysts.

Other Industrial Applications of Catalysis [10]

Throughout the last 50 years, there have been numerous cases of catalytic processing in the fine chemicals area, which involved high-price, relatively low-volume products. During the last 20 years, the emphasis on catalytic steps in the synthesis of pharmaceuticals and of agrochemicals, as well as food additives, has sharply increased. Major progress in novel catalytic reactions has, to some extent, shifted from hydrocarbon conversions and fuels to environmental control and to organic (and, to a lesser extent, inorganic) chemical synthesis. Important among biochemicals is "chirality", the "handedness" or optical rotation of the molecule, which determines its bioactivity. One of the chiral isomers can be very effective, while the other may be ineffective or even harmful. A typical example is the case of thalidomide, which is a sedative for pregnant women in its R-form, but is a potent teratogen in its S-form, causing children to be born with deformed limbs. Another example is aspartame, which, in one isomeric form is sweet, in other is bitter (FIG. 9). It is obvious that isomer separation and, if possible, selective synthesis of the desired isomer are essential. Ibuprofen, a widely-used pain-relieving drug, is more effective in its S-form than its R, S-form. FIG. 10 shows the common synthesis to the R, S-form involving two catalytic steps and improved technology, also involving catalysis. In the latter case, it is shown how R, S-ibuprofen can be converted to S-ibuprofen by means of enzyme catalysis. The U.S. market for chiral compounds is expected to grow from $0.5 billion in 1990 to $3 billion in 2000.

All life processes depend on the biological catalysts called enzymes. An enzyme is essentially a protein molecule, although it may have other atoms or molecules attached. A protein molecule is a long chain, made up of hundreds or thousands of amino acid molecules, assembled in very specific order. When dissolved in water, this chain naturally kinks and knots up. The sequence of amino acids making up the protein determines the shape that the protein knots itself into and it is this shape that allows the protein to catalyze reactions. The molecules that participate in the reaction fit into crevices in the protein like a key in a lock, causing shape selectivity. Once inside the crevice, the molecules are held in just the right relative orientation for the reaction to proceed.

Enzymes have been industrially used for centuries, *e.g.*, in wine-making. While this use was originally without any scientific understanding, a large industry has developed in the last two decades which uses enzymes on the basis of scientific knowledge. The conversion of cornstarch into corn syrup by the enzymes alpha- and gluco-amylase generates corn sweeteners for soft drinks and other uses. The enzymatic conversion of acrylonitrile to acrylamide has been commercialized in Japan. The stereospecificity of enzyme-catalyzed reactions has been used to advantage in polymer synthesis as well. Workers at ICI have developed a combined enzymatic chemical process for the synthesis of polyphenylene from benzene.

A major difference between enzymatic and heterogeneous catalytic approaches is the fact that enzymes work well in dilute aqueous solutions and at moderate temperature, pressure and pH. The reactions catalyzed by these systems are typically environmentally friendly in that few byproducts or waste products are generated. The catalysts and the materials that they synthesize are as a rule biodegradable and therefore do not persist in the environment. The reactions are typically selective with extremely high yields, and enzymes can be used to catalyze a whole sequence of reactions in a single reactor, resulting in vastly improved overall yields with high potential specificity.

Considerable work is being done and has been done on immobilized enzymes. This refers to a technology in which the active part of the protein molecule is chemically attached to an inert, inorganic substance such as a silica, alumina or a zeolite. This then permits these immobilized enzymes to be used like heterogeneous catalysts in reactors in which the liquid or gaseous substrate is passed over a solid material. Advantages of such techniques lie in easier separation of the catalysts from the reactants.

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FIGURE CAPTIONS

Figure 1.	Schematic drawing of Houdry fixed bed catalytic cracking unit.
Figure 2a.	Schematic of FCC unit (UOP design).
Figure 2b.	FCC reactor.
Figure 2c.	FCC regenerator.
Figure 3.	Reaction network for reforming of C6 hydrocarbons.
Figure 4.	Simplified diagram of a hydrodesulfurization process.
Figure 5.	The effect of exhaust gas stoichiometry on the conversion efficiency of an automobile catalyst.
Figure 6.	Specific examples of primary prevention.
Figure 7.	Specific examples of primary prevention.
Figure 8.	NO_x formation.
Figure 9.	Physiological effects of chirality: Aspartame.
Figure 10.	Technology to R,S- and to S-Ibuprofen.

TABLE 1. Major Catalytic Inventions

Year of First Commercialization	Process	Products
~1850	Lead chamber process	H_2SO_4
~1900	Air oxidation of SO_2	H_2SO_4
1913	Ammonia from $N_2 + H_2$	NH_3
1915	Ammonia oxidation	HNO_3
~1920	Water gas shift	$CO_2 + H_2$
1923	Methanol synthesis	CH_3OH
1931	Bergius coal hydrogenation	Liquid fuels
1936	Catalytic cracking	Gasoline
1938	Fischer-Tropsch	Fuels
1941	Fluid bed technology	Fuels and chemicals
1942	Paraffin alkylation	Gasoline
1950	Naphtha reforming	Gasoline
1951	Hydrocracking	Fuels
1955	Ziegler-Natta polymerization	Plastics
1960	Ethylene oxidation	Acetaldehyde
1962	Steam reforming of CH_4	Syngas
1963	Low pressure ammonia synthesis	NH_3
1963	Ammoxidation	Nitriles
1964	Zeolite catalysts	Fuels and chemicals
1964	Oxychlorination	Chlorohydrocarbons plus chlorine
1966	Olefin disproportionation	Higher olefins

TABLE 1 (cont'd)

1967	Bimetallic reforming catalysts	Fuels
1968	Shape selective catalysis	Chemicals
1970	Low pressure methanol synthesis	CH_3OH
1976	Emission control catalysts	Environmental control
1978	Methanol to gasoline	Synfuels
1982	Crystalline aluminophosphates	Chemicals
~1986	Stereospecific synthesis	Pharmaceuticals
~1986	$NO_x + NH_3 \rightarrow N_2 + 2H_2O$	Environmental control
1990	Combustion catalysts	Environmental control

TABLE 2. Catalytic Cracking of Gas Oil

	SiO_2-Al_2O_3	REHY
Conversion, %	42.5	42.5
C_{5+} gasoline, vol.-%	24.5	30.6
Total C_4, vol.-%	9.4	8.2
Dry Gas, wt.-%	6.5	4.7
Coke, wt.-%	8.7	4.9
Gasoline Octane No. F-1	85.6	90.7

TABLE 3. Yield-Octane Relationship for Reforming C_6-360 °C Naphtha at Constant Temperature

Pressure, bar	Yield, C_{5+}, vol.-%	Octane No. C_{5+} (R+O) [12]
100	90	92
100	83	99
200	87	92
200	80	99
250	82	92
250	76	99
500	88	92

TABLE 4. Average Emissions from Gasoline Cars [13]

			<-------------Hydrocarbons------------->		
Model Year	CO	NO_x	Exhaust	Evaporative	Total
Zero Miles					
1966	78	3.4	7.2	4.5	11.7
1986	1	0.5	0.2	0.6	0.8
Reduction, %	98	84	97	88	93
50,000 Miles					
1966	89	3.4	8.1	4.5	12.6
1986	13	1.3	1.0	0.6	1.6
Reduction, %	85	62	88	87	87

Gram/mile over EPA federal test procedure

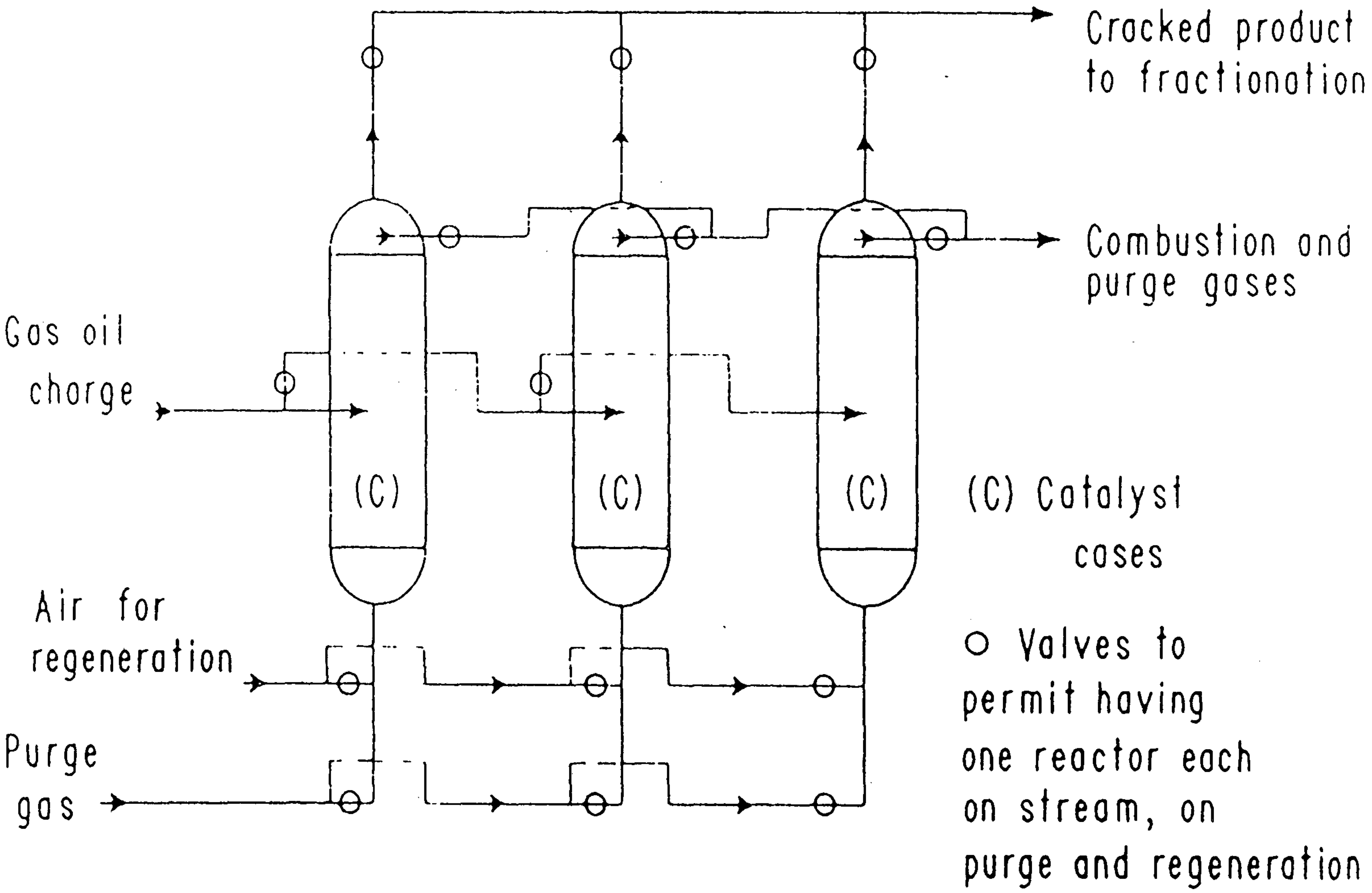

Cracked product
to fractionation
Combustion and
purge gases
Gas oil
charge
(C)
(C)
(C)
(C) Catalyst
cases
Air for
regeneration
○ Valves to
permit having
one reactor each
on stream, on
purge and regeneration
Purge
gas

Fig. 1

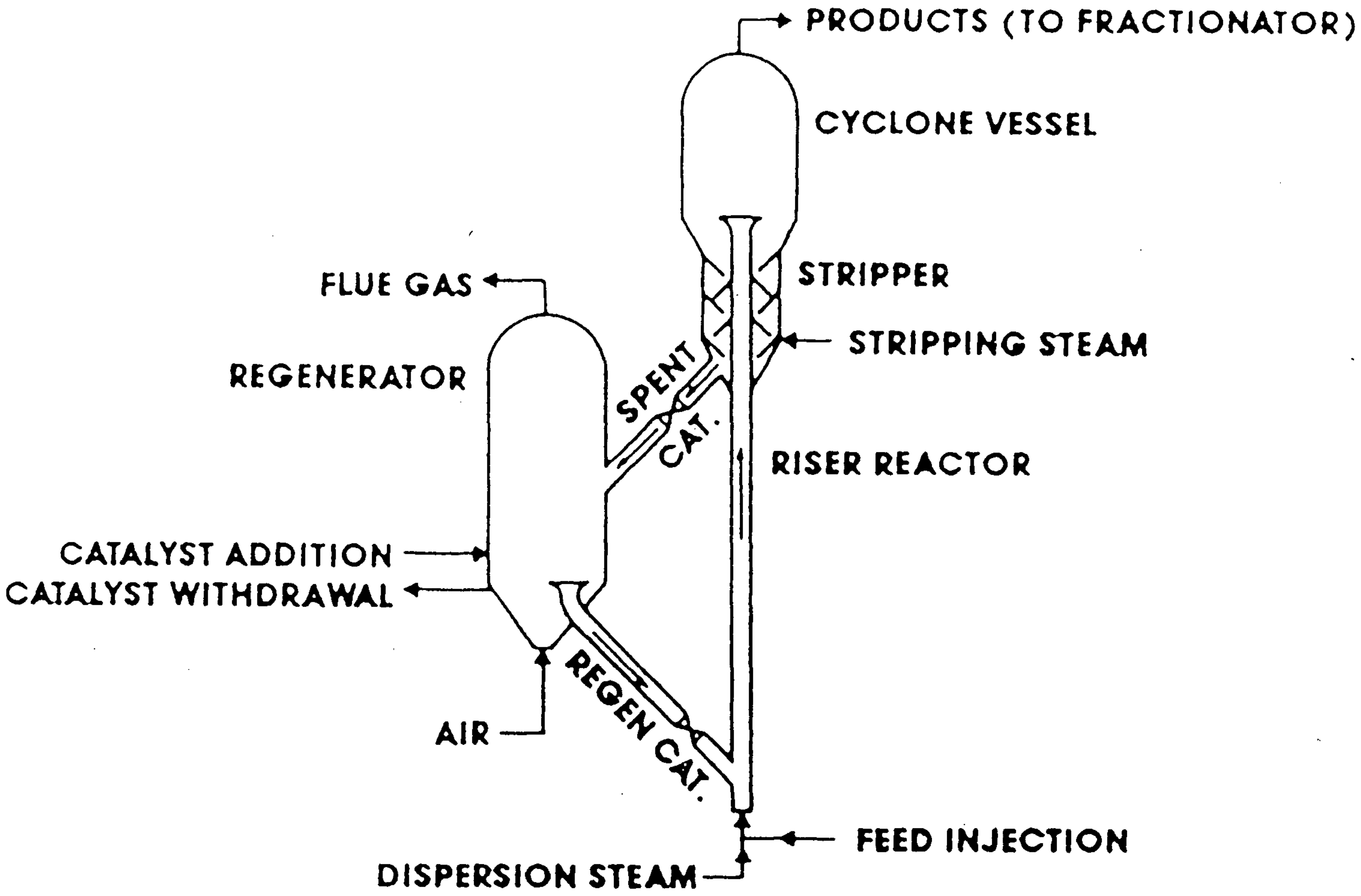

PRODUCTS (TO FRACTIONATOR)
CYCLONE VESSEL
STRIPPER
FLUE GAS
STRIPPING STEAM
REGENERATOR
SPENT CAT.
RISER REACTOR
CATALYST ADDITION
CATALYST WITHDRAWAL
REGEN CAT.
AIR
FEED INJECTION
DISPERSION STEAM

Fig. 2a

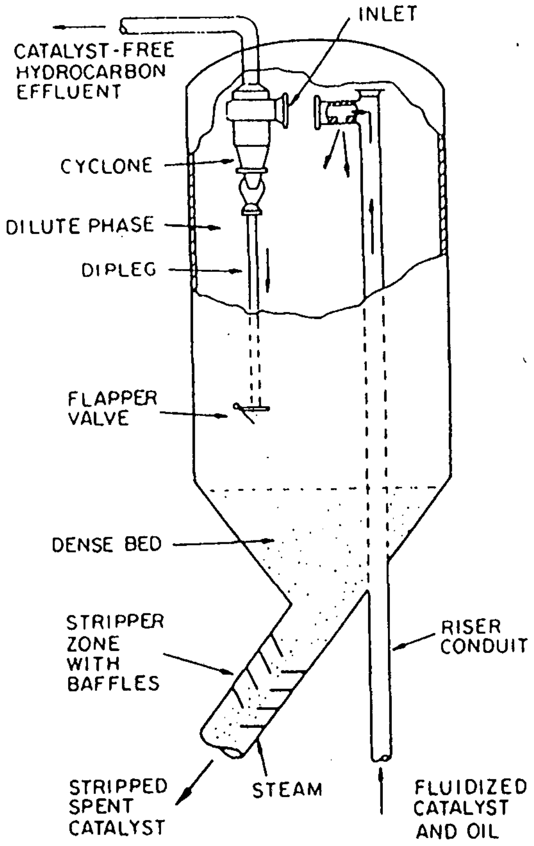

INLET
CATALYST-FREE HYDROCARBON EFFLUENT
CYCLONE
DILUTE PHASE
DIPLEG
FLAPPER VALVE
DENSE BED
STRIPPER ZONE WITH BAFFLES
RISER CONDUIT
STRIPPED SPENT CATALYST
STEAM
FLUIDIZED CATALYST AND OIL

Fig. 2b

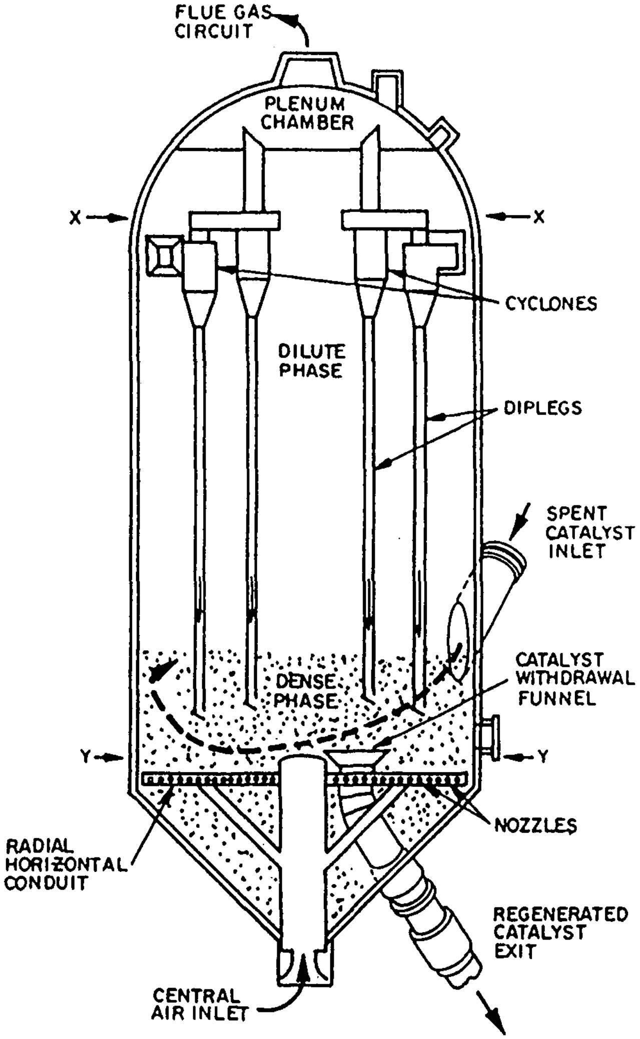

FLUE GAS CIRCUIT
PLENUM CHAMBER
X
X
CYCLONES
DILUTE PHASE
DIPLEGS
SPENT CATALYST INLET
DENSE PHASE
CATALYST WITHDRAWAL FUNNEL
Y
Y
NOZZLES
RADIAL HORIZONTAL CONDUIT
REGENERATED CATALYST EXIT
CENTRAL AIR INLET

Fig. 2c

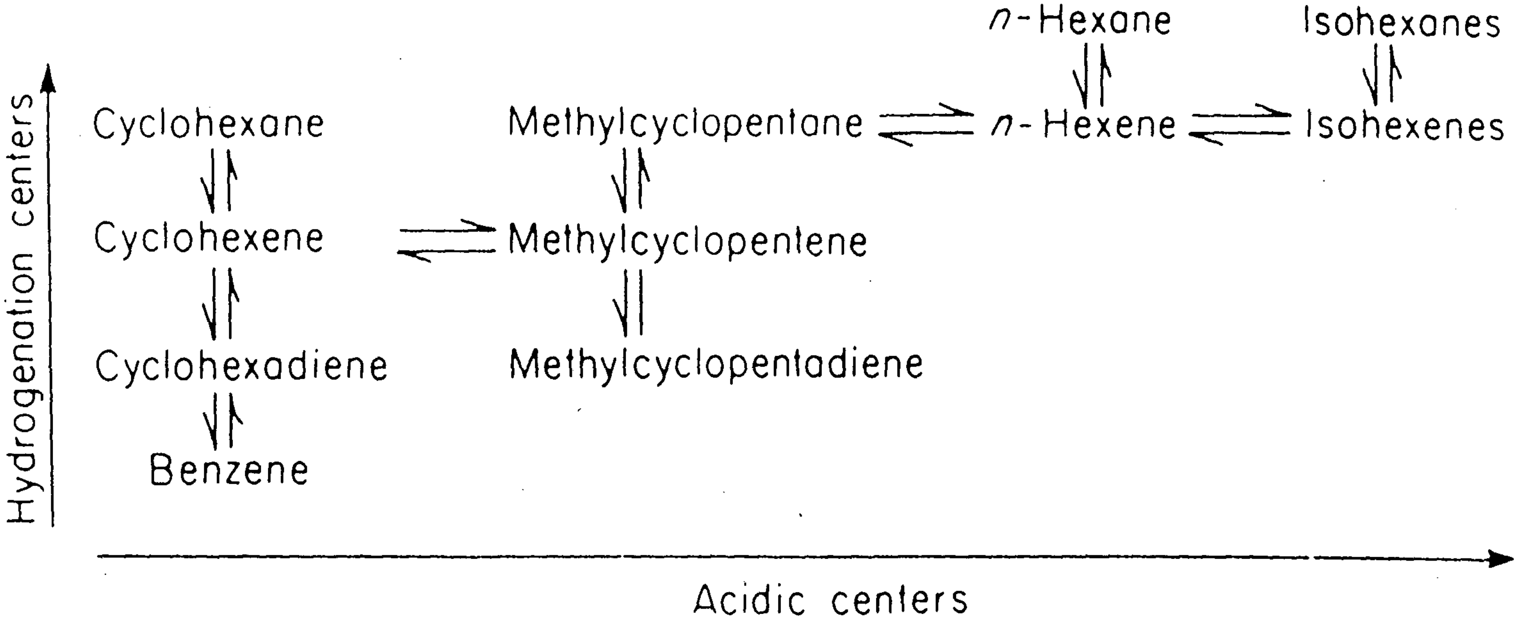

n-Hexane
Isohexanes
Cyclohexane
Methylcyclopentane
n-Hexene
Isohexenes
Cyclohexene
Methylcyclopentene
Cyclohexadiene
Methylcyclopentadiene
Benzene
Hydrogenation centers
Acidic centers

Fig. 3

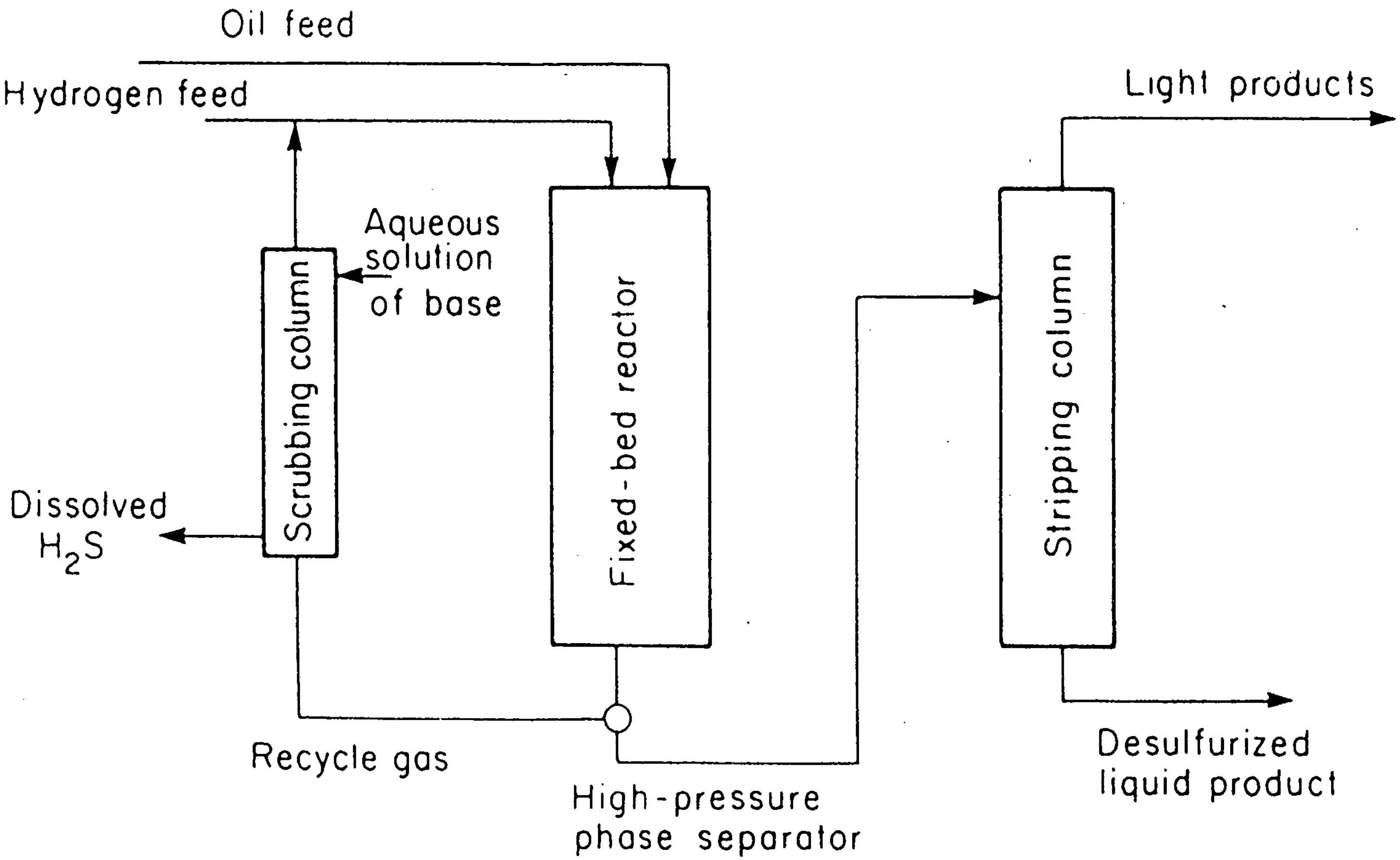

Oil feed
Hydrogen feed
Light products
Aqueous solution of base
Scrubbing column
Fixed-bed reactor
Stripping column
Dissolved H_2S
Recycle gas
High-pressure phase separator
Desulfurized liquid product

Fig. 4

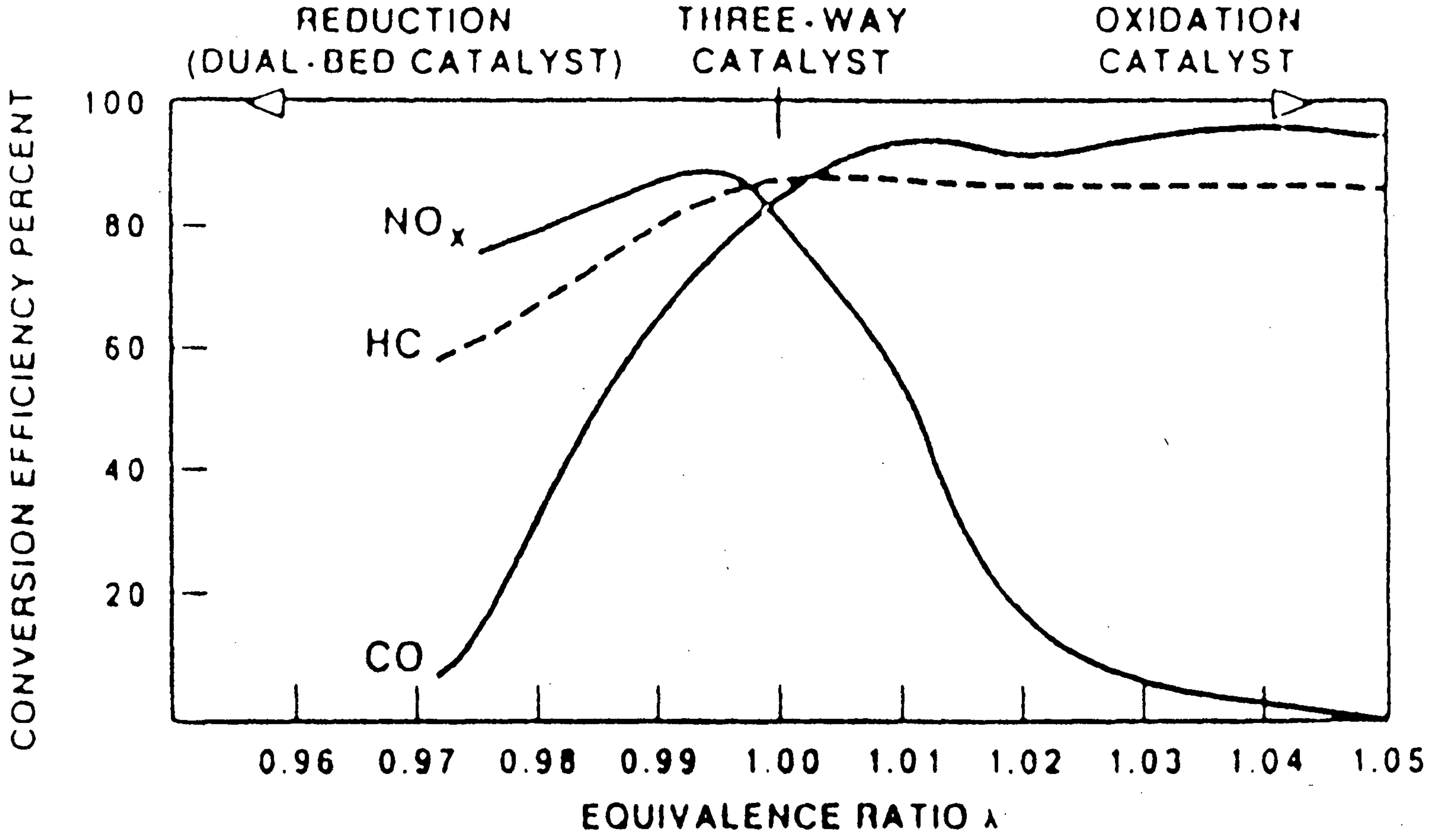

REDUCTION
(DUAL-BED CATALYST)
THREE-WAY
CATALYST
OXIDATION
CATALYST
CONVERSION EFFICIENCY PERCENT
100
80
60
40
20
NO_x
HC
CO
0.96
0.97
0.98
0.99
1.00
1.01
1.02
1.03
1.04
1.05
EQUIVALENCE RATIO λ

Fig. 5

Some Specific Examples of Primary Prevention

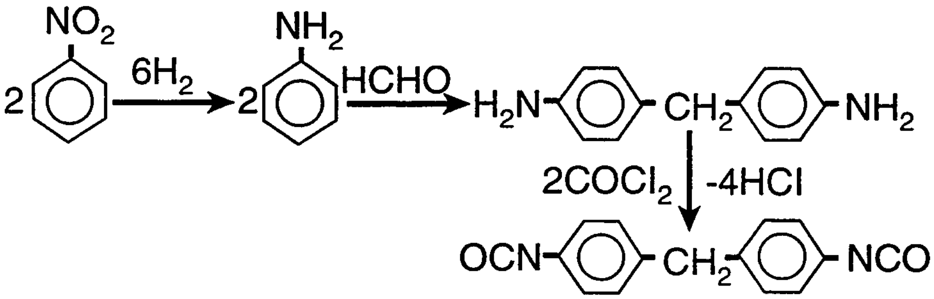
- Elimination of toxic reagents and intermediates
  - Methylene diphenyl diisocyanate (MDI)
  - Gasoline alkylation
  - Methyl methacrylate
  - Elimination of chlorofluorohydrocarbons
- Elimination of toxic waste streams and by-products
  - Resorcinol
  - Acetaldehyde
  - Bioactive molecules
- Elimination of toxic emissions
  - Catalytic combustion (NO)

Fig. 6

Primary Prevention

Elimination of Toxic Reagents and Intermediates: MDI

- Current technology



- Emerging technology

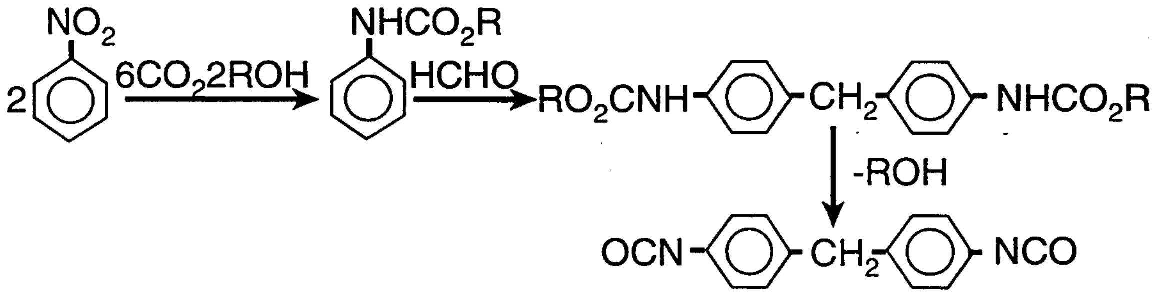


Fig. 7

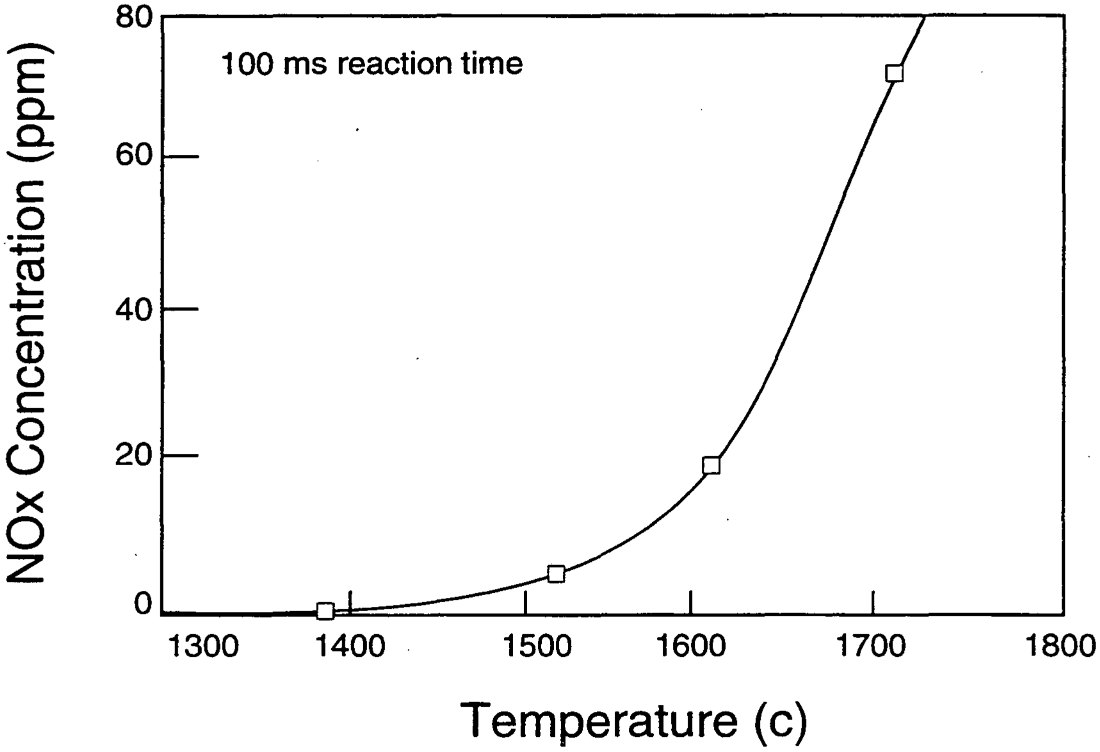
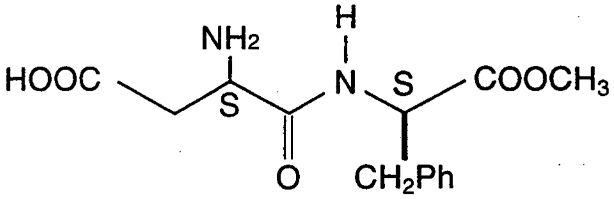
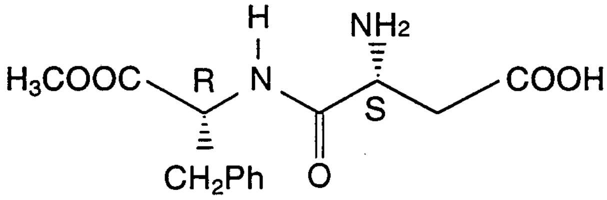

80
60
40
20
0
100 ms reaction time
NOx Concentration (ppm)
1300
1400
1500
1600
1700
1800
Temperature (c)

Fig. 8

Physiological Effects of Chirality: Aspartame



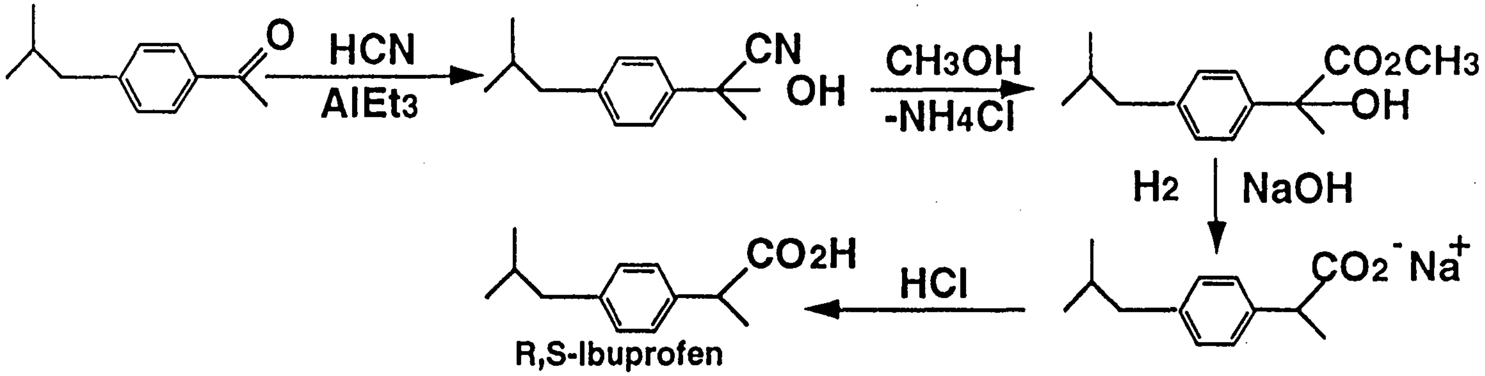
(S$_1$S)
Sweet



(R$_1$S)
Bitter

Fig. 9

Current Technology to R,S-Ibuprofen



Emerging Technology to S-Ibuprofen

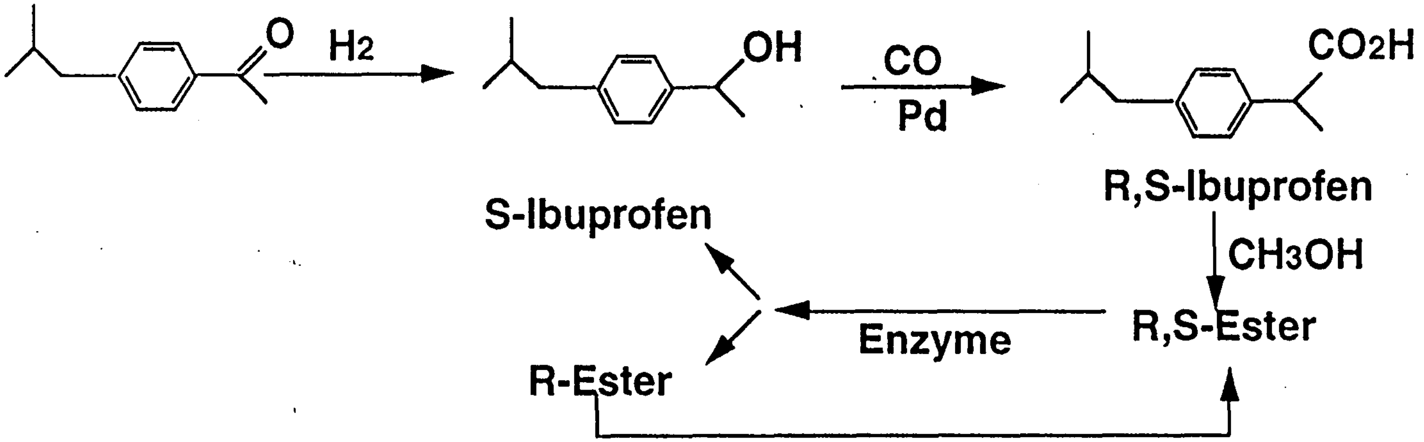


Fig. 10

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1 CYCLOTRON ROAD
BERKELEY, CALIFORNIA 94720