

# Present status and future trends in catalysis for refining and petrochemicals

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Received 10 July 2002; accepted 16 September 2002

## Abstract

This article sets out to survey the remarkable development that has taken place in catalysis in the refining and petrochemical industries since the middle of the 20th century, and more especially since the 1970s, highlighting what appears to be the most significant progress. It then attempts to outline the energy and environmental context for the coming decades which will govern the trend in industrial catalysis in the 21st century. Although the reduction of CO<sub>2</sub> will eventually require the decarbonization of energy carriers, oil will still remain the principal source of liquid motor fuels for a long time. However, the share of gas will gradually increase and hydrogen is destined to play an important part as an energy carrier. The use of biomass will develop, but at a modest level. Within this framework, catalysis will still play a leading role in technical and economic development in the 21st century, even though it is far from being an emerging discipline.

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**Keywords:** Catalysis; Refining; Petrochemicals; Fuels; Energy; Petroleum; Gas; Coal; Biomass; Sustainable development

## 1. Introduction

Since the middle of the 20th century, catalysis has undergone remarkable development both from the point of view of fundamental knowledge and from that of its applications. At the start of the 21st century, between 80 and 90% of the products we use in our daily life have “seen” a catalyst at some point during their manufacture. What part will catalysis play in the 21st century now that new technologies are being born and developing at a faster and faster pace? It would be presumptuous to make a long-term prediction, but it is nevertheless important to try to outline the future of this discipline while limiting the scope to the field of the oil industry and to a few decades. This is the exercise that this article will undertake, after a look at the most significant progress that has marked the second half of the last century: on the one hand in the field of refining, with particular stress on fuels and motor fuels, and on the other hand in the field of the main first-generation petrochemical intermediates. Although the environment is a major factor in the background to this article, the catalysis involved in the depollution of exhaust gas from transport vehicles will not be covered. Last, an attempt will be made, insofar as

possible, to evidence the contribution of Europe to catalysis, in the past and in the coming decades.

## 2. Salient factors in the development of industrial catalysis in refining and petrochemicals in the second half of the 20th century

### 2.1. The development of refining and petrochemicals: the importance of the geopolitical context

The development of industrial catalysis in Europe in the last three decades has been especially influenced by a series of political and economic events and situations that can be summed up as follows:

- The world oil crisis of the 1970s and the realization that fossil fuel resources were limited and concentrated geographically in unstable areas of the world had the following consequences:
  - With regard to energy in general, there was a search for substitutes for fossil fuels [1] and, in areas greatly dependent on energy, such as Europe, renewed interest in alternative fuels. But oil remained a strategic

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Table 1  
Changes in European motor fuel specifications since 1994 [2]

Fuel	1994	1995	1996	2000	2005	2011
Unleaded gasoline 95/85, EN228						
Sulfur, ppm mass, max	1000	500		150	50/10	10
Benzene, vol%, max	5			1	1	
Aromatics, vol%, max				42	35	
Olefins, vol%, max				18	a	
Oxygen, vol%, max		2.7		2.7	a	
RVP (summer), kPa, max	80			60	a	
E100, vol%, min	40(s)/43(w)			46	a	
Diesel oil (standard grade), EN590						
CI, min	46			46	a	
CN, min	49			51	a	
Sulfur, ppm mass, max	2000		500	350	50/10	10
Density, kg/m <sup>3</sup> , min	820					
max	860			845	a	
T95, °C, max	370			360	a	
HPA, mass%, max				11	a	

RVP, reid vapor pressure; E100, temperature of 100% distilled; CI, cetane index; CN, cetane number; T95, temperature of 95% distilled; HPA, heavy polyaromatics.

<sup>a</sup> With the exception of sulfur, the values for 2000 specifications should be renewed in 2005.

raw material and it is still predominant where transport is concerned.

- In refining, the heavy fractions that were less and less used had to be converted into the lighter products that were in increasing demand. This led to the strong development of resid catcracking, while that of hydroconversion was much slower due to its high cost.
- The gradual realization, at the end of the 1970s, of the need to protect the environment against the noxious emissions produced by human activity had a strong impact on refining and on motor fuels in particular. The main measures taken in Europe were lead out of gasoline, which became total as of 01/01/2000, then taking sulfur out of gasoline and diesel fuel (Table 1) [2,3]. It is currently estimated that noxious gaseous emissions from transport vehicles have been lessened by a factor of around 100 compared to 1970 levels.
- In the 1990s, it was increasingly realized that the change in climate caused by greenhouse gases, such as CO<sub>2</sub>, constituted a risk. Twenty-one percent of world CO<sub>2</sub> emissions come from transport and 8% from the oil and gas industry [4]. Altogether, European refineries annually produce 100 Mt of CO<sub>2</sub>, which amounts to around 2.9 and 2.5%, respectively, of CO<sub>2</sub> production (3.5 Gt) and of all the greenhouse gases produced in Europe (4.1 Gt) [2]. The orientation of the main refinery products toward higher average levels of hydrogen and lower levels of sulfur has inevitably resulted in an increase in the CO<sub>2</sub> produced by the refinery, and this factor is all the higher, as the crude processed is heavy and consequently richer in carbon and generally in sulfur [5]. As shown in Fig. 1 [2], the reduction in sulfur content of motor fuels from 2000 specifications to 2011 specifications will lead to a 5% increase in

CO<sub>2</sub> production by European refineries in the case of diesel fuel and to an increase of over 7% in the case of gasoline. But this will not have a positive impact on the earth's atmosphere unless the excess CO<sub>2</sub> emitted is more than offset by commensurate gains in the consumption of refinery products, particularly where transport is concerned.

The European petrochemical industry, which came into its own in the 1960s, is now well established and complementary to the refining industry. Steam crackers mainly process liquid feedstocks (particularly naphtha) and produce most of the raw materials required by the chemical industry (ethylene, propylene, butenes, butadiene, and aromatics in particular) [6]. Around 23% of propylene is currently produced by refinery units: the rate of propylene recovery in FCC was only 29% in 1980 but today it is in the region of 80% [6]. Regarding aromatics, petrochemicals cover 79% of benzene requirements, 41% in the case of toluene but

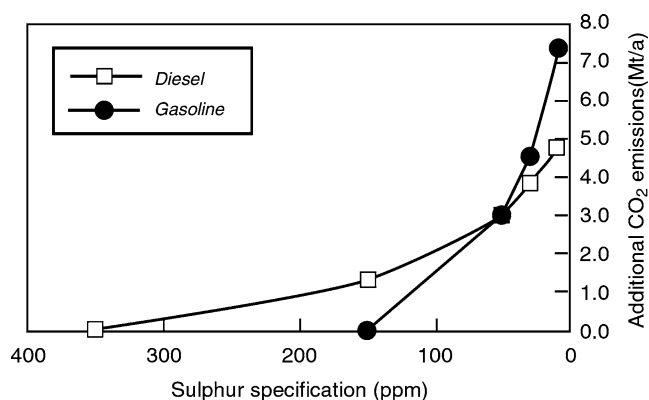


Fig. 1. Increase in CO<sub>2</sub> emissions by European refineries as a function of the reduction in the sulfur content of motor fuels.

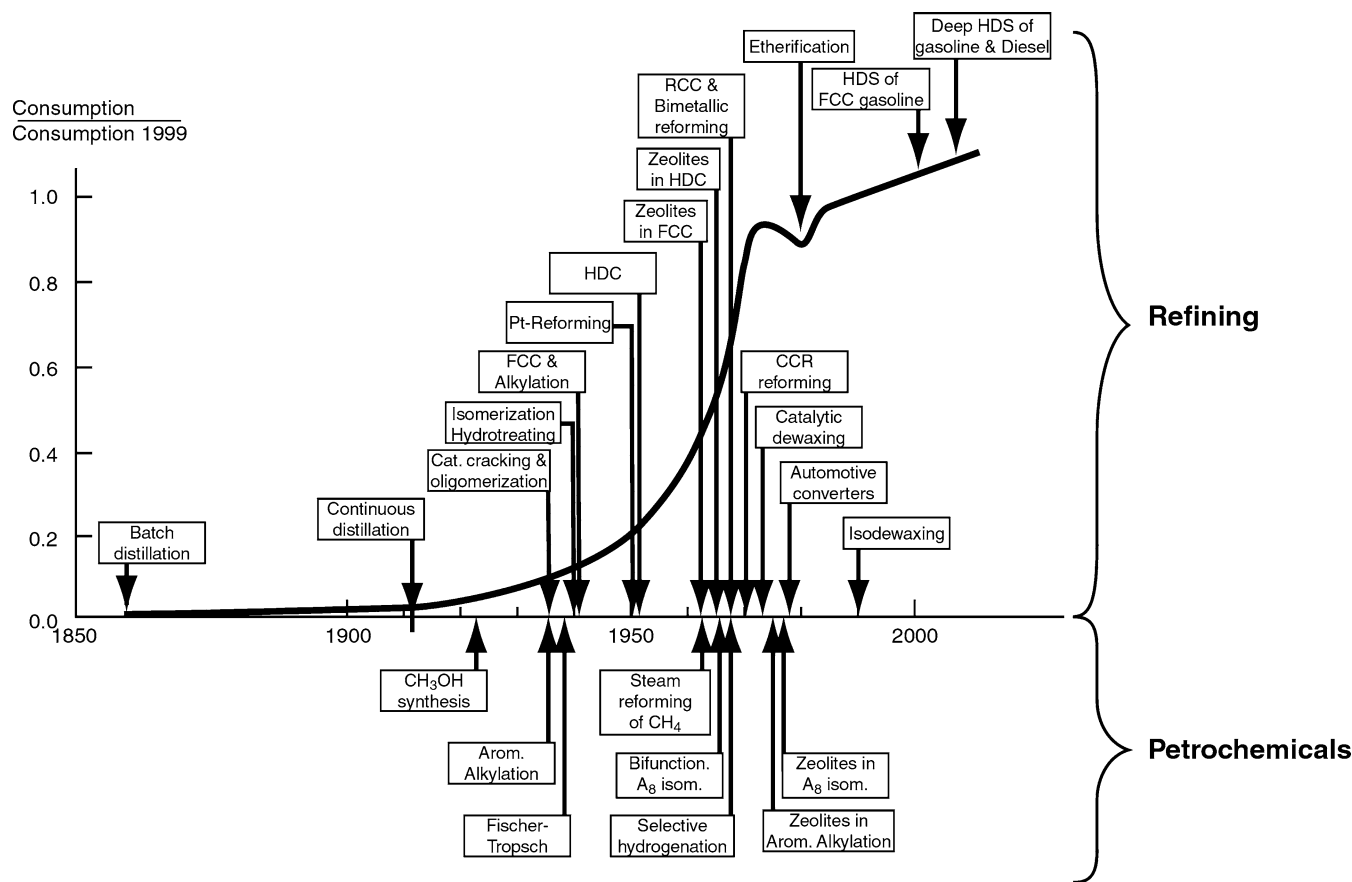


Fig. 2. Some important dates in the development of the refining and petrochemical industries (Alkyl, alkylation; Ag, C<sub>8</sub> aromatics; Arom., aromatics; Bifunct., bifunctional; CCR, continuous catalyst regeneration; FCC, fluid catalytic cracking; HDC, hydrocracking; HDS, hydrosulfurisation; RCC, resid catalytic cracking).

only 25% where xylenes are concerned; the complement is mainly provided by refining [6]. The demand for olefins is increasing regularly (2.2 and 2.9% per year on average for ethylene and propylene, respectively). With regard to aromatics, demand is also increasing but in the near future it may not be able to absorb the large amounts that could be delivered to the market by a massive reformulation of fuels.

## 2.2. Developments in catalysis in refining and petrochemicals

Catalysis undoubtedly played a very important part during the second half of the 20th century in the development of the refining and petrochemical industries. Fig. 2 [7–9] indicates some of the important dates that marked their history. With the exception of steam cracking, which has always played a leading role in petrochemicals, the importance of the purely thermal processes has declined steadily over more than 40 years, in favor of the higher performance catalytic processes. Apart from base catalysis, which is not much used, the refining and petrochemical industries currently use almost all the main categories of catalysts, and the latter are often indebted to these two industries for their initial applications and the significant progress achieved over half a cen-

tury. The main categories of catalysts mostly belong to heterogeneous catalysis, which involves acid, metal, sulfur, and bifunctional catalysts and, to a lesser degree, oxide phases (other than supports). Nevertheless, some important applications belong to homogeneous catalysis, particularly where olefin conversion is concerned. This development in catalysis in refining and petrochemicals will be briefly examined by main types of processes, starting with the conventional processes used before 1970.

### 2.2.1. Development of the conventional catalytic refining processes [7,10,11]

In refining, one of the oldest processes, and one that is still among the most important, is catalytic cracking. Since this process was first used toward the end of the 1930s, the catalyst has evolved considerably, particularly with the use, at the beginning of the 1960s, of the Y zeolite containing rare earths, which greatly increased gasoline yield. In the 1980s, gains in octane number were obtained with the ultrastable Y (USY), then by the use of the ZSM-5 zeolite as an octane booster. The development of metal and SO<sub>x</sub> traps and the progress achieved with regard to the acidity and the pore architecture of the matrix of FCC catalysts has extended their use to resid feedstocks. Since the 1990s, the ZSM-

5 zeolite has also been increasingly used to produce an additional amount of olefins, especially propylene.

Catalytic reforming of naphtha is another important refining process. It has for a long time made use of the metal–acid bifunctional catalyst [12]: the first use of a platinum catalyst supported on chlorinated alumina dates back to 1949 and was carried out by UOP. Significant improvements in selectivity and stability were achieved by the introduction of an additional metal at the end of the 1960s: germanium (UOP), tin (Total), rhenium (Chevron), or iridium (Exxon) [8,13,14]. The most frequently used bimetallic catalysts today are Pt–Re and Pt–Sn. Knowledge of the nature of metal associations is far from complete [13]. There is always interaction between the second metal and the platinum [13,14], but the actual nature of the interaction and the manner in which it modifies the catalytic process are still not very clear [13,14]. Moreover, the second metal often also interacts with the support at a degree of oxidation different from 0 [13,15].

Hydrotreating is a process widely used in refineries to purify a large number of different petroleum cuts. Hydroprocessing operations use sulfur metal-type catalysts that associate metals from groups VI (Mo, W) with metals from group VIII (Co, Ni). The first industrial use of Mo-based hydrotreatment catalysts appears to date from after the first world war [10]. For decades the basic metals engaged in the active sulfur phase have remained unchanged in spite of numerous efforts to replace them by more active or less costly elements. Nevertheless, their performance has been greatly improved by the optimization of the synthesis of the support, by the addition of various adjuvant elements, such as F, B, and Si, and by the development of new methods of preparation [16–18]. Thanks to the considerable fundamental research carried out since 1980, in which Europe has taken a very active part, much knowledge has been gained of the intimate nature of the catalyst site, of its mode of operation, and of the mechanisms of the different reactions involved [19], and current models allow a satisfactory description of them [20]. Hydrocracking is a process for the hydroconversion of heavy feedstocks such as VGO, which in Europe is almost entirely oriented to the production of middle distillates and, to a lesser extent, that of lube oils. The bifunctional catalyst associates a hydro–dehydrogenating function, which is a metal sulfide phase of the same type as the previous ones, with an acid function. Regarding the latter, the replacement of the amorphous silica–aluminas by the Y zeolite exchanged with alkaline earth ions at the start, then in the ultrastable Y form, has significantly increased the activity and stability of catalyst performance but, on the other hand, has resulted in decreased selectivity with respect to middle distillates, especially gas oil. Although not perfect, understanding of the reaction process is satisfactory and is based on carbocation chemistry. A number of other important refining processes use acid or noble metal–acid-bifunctional catalysts. The isomerization of light C<sub>5</sub>–C<sub>6</sub> paraffins requires a very strong acid function in order to

operate at temperatures as low as possible and thus benefits from more favorable thermodynamic conditions. The Brønsted superacid monofunctional catalyst HAlCl<sub>4</sub> was the first to be used industrially [21]. It was rapidly replaced in the 1960s and 1970s by bifunctional catalysts that are more stable but much less active. The two bifunctional catalysts currently the most widely used are Pt based, supported either on highly chlorinated alumina or on dealuminated mordenite. The first is more active than the second but is also more difficult to use, corrodes the installations, and is less environmentally friendly. Considerable work has been devoted to replacing the acid functions of these two catalysts by a support with an acidity that is the same as or close to that of chlorinated alumina and as easy to use as the zeolite.

The difficult isobutane–butene alkylation reaction into high-octane paraffinic gasoline is, like isomerization, thermodynamically promoted by low temperatures and therefore requires highly acid catalysts. Today the liquid catalysts H<sub>2</sub>SO<sub>4</sub> and HF [22,23] that were first used industrially in the 1940s are still to be found in the alkylation units of refineries, in spite of the considerable research carried out in the 1990s to replace them by solid catalysts. The solid acid catalysts proposed include acid zeolites (Shell, Akzo), the triflic superacid deposited on a porous silica (Topsoe), and an undisclosed solid acid (UOP). Compared to conventional liquid acid catalysts, they are less dangerous to use and more environmentally friendly but they do not perform better and require frequent rejuvenation and/or regeneration procedures. These catalysts are therefore unlikely to replace the liquid catalysts unless the latter are prohibited by the authorities.

There has been considerable development over the last 30 years of the oligomerization of olefins into petroleum cuts to be used as gasoline. The original process, which is still the most widely used, the UOP Catpoly process oriented to gasoline production, uses phosphoric acid supported on silica (SPA) and dates from the 1930s. This catalyst has been gradually replaced since the 1970s by other acid catalysts of the amorphous silica–alumina type that are easier to use and more environmentally friendly, such as the IFP Polynaphtha process [24–26]. Since the 1980s, two main categories of catalyst have developed: solid catalysts and organometallic complexes. The first category includes the organized silico–aluminates: the zeolite ZSM-5 of Mobil's MOGD process [27,28], the Ni–mordenite of Shell's SGPK process [28–30], and the mesoporous silica–alumina developed by EniTechnologie [31–34] that allows the process to be oriented toward the production of gasoline or middle distillates. Recently, Snamprogetti [35] and Fortum [36] have developed a process for the dimerization of isobutene probably on an acid resin whose selectivity is controlled by the addition of water.

The second category includes two IFP processes. They use a Ni-based catalyst in the liquid phase: the dimersol G process (gasoline) commercialized in 1977 [37] and the more recent difasol process in which the catalyst is retained in a liquid salt that constitutes one of the phases of a nonaqueous biphasic medium [38–40].

### 2.2.2. The more recent refining processes

Since the 1970s, a number of new processes have appeared. Some of them have not yet been developed industrially, for economical reasons or because the refiner is not yet ready to risk investing in a process that is not industrially proven.

The process that has probably been the most successful industrially is the Claus process, which recovers sulfur from the stack gas streams [41] of hydrotreatment and FCC units. The most commonly used catalysts are alumina based (bauxite or promoted alumina). The most effective catalyst is titanium oxide based and was developed in Europe [42]. The consumption of the Claus catalyst is particularly high (in the region of  $25 \times 10^3$  t/year).

In the early 1970s the use of zeolites made it possible to replace the solvent dewaxing of petroleum cuts by a simpler catalytic operation that consists of removing the least branched paraffins by cracking. The first bifunctional catalyst of this type, Pt/H–mordenite developed by BP [43], was rapidly replaced by a monofunctional catalyst developed by Mobil, based on the more effective ZSM-5 and used for middle distillates and lube oils [27]. Other zeolitic catalysts were proposed: a silicalite-based catalyst by Fina [44] and a ferrierite based catalyst by Shell [45]. More recently, in the 1990s, a new category of more selective catalysts gradually became established. These catalysts perform a dewaxing operation through hydroisomerization, known as isodewaxing, effected by zeolites which slightly isomerize the long straight paraffinic chains and at the same time strictly limit cracking [46,47], as in the case of Chevron's SAPO-11 [46]. The conversion of methanol into hydrocarbons for gasoline production (MTG process) or olefin production (MTO) is one of the innovations of the last 30 years. It provides good selectivity due to the use of new zeolites with intermediate pore sizes, such as the ZSM-5 [48–52], followed more recently by the SAPO-34 [53–56].

The aromatization of alkanes by different catalytic reforming processes is another innovation of this period. Various catalysts and processes have been developed. They include processes involving acid catalysis such as Mobil's M2-Forming using a ZSM-5 zeolite [27], or the aromatization of light alkanes using Ga/ZSM-5 [57,58], and those involving monofunctional metal catalysis, such as the very selective aromatization of  $C_{6+}$  alkanes, using a Pt/K–L zeolite [14,59]. The last two catalysts were discovered in Europe: the Ga/ZSM-5 catalyst was developed by BP [57,58], and the Pt/K–L catalyst by Elf [59].

The remarkable selectivity of ferrierite in isomerizing butenes into isobutene, an olefin used for the synthesis of MTBE and ETBE ethers, was identified by Shell [60,61]. The isobutene required for the synthesis of MTBE can also be produced by the dehydrogenation of the isobutane produced by FCC, for example with catalysts of the Pt–Sn/ $Al_2O_3$  type [62–64], whose acidity is neutralized by alkaline elements.

The synthesis of MTBE by etherification of isobutene by methanol uses a very active and selective acid catalyst discovered in 1949 by the Atlantic Refining Company [65] and implemented industrially for the first time by Anic/Snamprogetti in 1973 [65,66]. It is composed of sulfonic resin and its only disadvantage is its nonregenerability. A recent process developed by Snamprogetti makes it possible to selectively orient the production of the MTBE unit, using the same type of catalyst, to ether or diisobutylene [67].

Other recent interesting developments concern catalysts designed to improve motor fuel quality. Some of them allow the desulfurization of FCC gasoline with minimum octane loss, such as the IFP Prime G+ process [68] and the BP OAT process [69]. Others are designed to remove aromatics from gas oil cuts. This operation can be performed by hydrogenation in the presence of limited amounts of sulfur compounds with the help of noble metals deposited on an acid support. This is the case of the sulfur-resistant bimetallic catalysts in which the metals (Pt–Pd) are deposited either on the Y zeolite [70,71] or on a halogenated alumina [72]. On the other hand, the bifunctional catalyst for hydrodeacyclizing the aromatics of an FCC LCO, patented by Exxon–Mobil at the end of the 1990s [73] and composed of Ir deposited on a slightly acid Y zeolite, would require prior intensive hydrotreatment.

### 2.2.3. Development of petrochemical processes

These processes mainly concern the hydrogenation and transformation of olefins and the interconversion of alky-monoaromatics.

**2.2.3.1. Hydrogenation [74]** The extremely selective hydrogenation of various petroleum cuts was achieved in the 1960s with the use of either very active metals in the absence of sulfur compounds or metal sulfides when the cuts contained sulfur impurities.

The most widely used catalysts are Pd for selective hydrogenation of diolefins and alkynes in the  $C_2$  to  $C_5$  olefinic cuts or the hydrogenation of olefins in a sulfur-free aromatic cut, the sulfide Ni–Mo or Ni–W associations for hydrogenating olefins in an aromatic cut containing sulfur and passivated Ni for selective hydrogenation of polyunsaturated molecules in olefinic and aromatic steam-cracked gasoline containing sulfur. The use of other metals is much less common: for example Ru is used for the selective hydrogenation of benzene into cyclohexene. The addition of a second metal (Ag, Au in particular) to the principal metal (palladium in particular) in the 1980s significantly improved performance, especially selectivity [75].

For total hydrogenation of aromatics, Ni can be used for sulfur-free feedstocks, as in the IFP process of benzene hydrogenation into cyclohexane with a soluble catalyst in homogeneous phase [74]. Pt is substituted for Ni if the feedstock contains traces of sulfur. For sulfur-containing feedstocks, catalysts are based on sulfide of metal associations.

**2.2.3.2. The transformation of olefins** The main use of ethylene is polymerization, with the use of increasingly sophisticated catalysts. The old Ziegler–Natta catalysts are now being replaced by single-site, metallocene or constrained geometry catalysts [76] and the postmetallocene catalysts [77]. These last-generation catalysts produce new grades of polymers whose properties are more and more precisely controlled. The light alpha olefins produced by oligomerization of ethylene are used in copolymers (LLDPE) with ethylene. The oligomerization processes of CPChem (Al–alkyl catalyst), of BP (Al catalyst), and of Shell (SHOP process, two-phase catalysis with a Ni complex) produce a wide range of alpha olefins (from C<sub>4</sub> to C<sub>40</sub>) [78]. The recent IFP Alphaselect process [79] produces mostly C<sub>4</sub>–C<sub>8</sub> alpha olefins used in LLDPE. The trend is the selective production of a single product. The IFP Alphabutol process (Ti catalyst), for example, very selectively produces high-purity 1-butene by dimerization of ethylene [79,80]. It is also possible now to selectively produce 1-hexene by trimerization of ethylene (Phillips, Cr catalyst) [81].

The concern with improving the flexibility of the ethylene/propylene ratio of the steam cracker and making best use of olefins as a whole has led to the development of several transformation processes. With the metathesis processes of Lummus (WO<sub>3</sub>/SiO<sub>2</sub> catalyst) [82] and IFP (Re<sub>2</sub>O<sub>7</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst) [83] it is possible to produce more propylene by reaction between the ethylene and the butenes. The Dimersol (homogeneous catalysis, Ni) and Difasol (biphasic catalysis, Ni) processes of IFP [79,80] dimerize the butenes into isooctenes used in the synthesis of PVC plasticizers.

**2.2.3.3. The interconversion of alkylmonoaromatics** The isomerization of xylenes to maximize paraxylene production has been performed industrially since the end of the 1960s. Significant advances were first made in the 1970s with the replacement of the amorphous acid supports by the much more active mordenite, and then in the 1980s with the use of the ZSM-5 catalyst. In the space of 20 years, several types of process succeeded each other, using only these two zeolite structures. At present a distinction is made between two main categories of industrial process, based on their bifunctional catalyst composed of a noble metal associated with one or other of these two zeolites: both of them isomerize the three xylenes, but whereas mordenite isomerizes ethylbenzene into xylenes, the ZSM-5 dealkylates it into benzene [27,84]. Very recently, considerable gains in selectivity have been obtained by isomerizing xylenes and ethylbenzene with the use of new zeolites (Table 2) like that of the IFP Oparis process [85,86].

The same two zeolites, mordenite and ZSM-5, are used in the industrial operations of the disproportionation of toluene into benzene and xylenes, and transalkylation between toluene and C<sub>9</sub>+ polymethylbenzenes [87]. Great progress has been made by using zeolites for these applications because they promote bimolecular reactions better than any other solid. The reduced pore apertures retain the ZSM-5 in the disproportionation of toluene but can orient this reaction toward the selective production of paraxylene [27,87]. Mordenite has larger pore apertures and can perform either of the two reactions but offers no paraselectivity.

Table 2  
Zeolites in oil industry catalytic processes

Zeolite structures	Zeolites	Pore apertures (Å)	Principal accepted molecules	Principal unaccepted or barely accepted molecules	Applications
FAU	Y	7.4	P, N, monoarom	Polyalkylnaphthenoarom, polyalkylpolyarom	Cracking (FCC) & hydrocracking of VGO, alkylation of aromatics
BEA	Beta	7.6 × 6.4	P, N, monoarom	Polyalkylnaphthenoarom, polyalkylpolyarom	EB & cumene synthesis
LTL	K–L	7.1	P, N, monoarom	Polyalkylnaphthenoarom, polyalkylpolyarom	Aromatization
MOR	Mordenite	7.0 × 6.5	P, N, xylenes, TMB	Trialkylmonoarom	Hydroisomerization of <i>n</i> -P, Ag isomerization, transalkylation of aromatics, cumene synthesis
MFI	ZSM-5	5.3 × 5.6	<i>n</i> -P, MBP, xylenes	Gem-DMP	FCC, dewaxing, aromatization, xylene isomerization, toluene disproportionation, ethylene-benzene alkylation
	Silicalite	5.1 × 5.5			Methanol to fuels or light olefins
AEL	SAPO-11	3.9 × 6.3	<i>n</i> -P, slightly BP (MBP)	Gem-DMP	Isodewaxing
TON	ZSM-22	4.4 × 5.5	<i>n</i> -P, slightly BP (MBP)	Gem-DMP	Isodewaxing
MWW	MCM-22	5.5 × 4	Cumene	?	EB and cumene synthesis
FER	Ferrierite	4.2 × 5.4 3.5 × 4.8	MBP	Gem-DMP	Butene isomerization
CHA	SAPO-34	3.8 × 3.8	<i>n</i> -P and <i>n</i> -O	<i>i</i> -P, <i>i</i> -O, monoarom	Methanol to light olefins
Undisclosed		–	Xylenes	TMB	Ag isomerization

P, paraffins; O, olefins; N, naphthenes; A or arom, aromatics; *n*, normal or linear; *i*, iso; BP, branched paraffins; MBP, monobranched paraffins; DMP, dimethylparaffins; TMC<sub>5</sub>, trimethylpentanes; EB, ethylbenzene; TMB, trimethylbenzenes; DIPB, diisopropylbenzenes.

In the alkylation of benzene by ethylene or propylene the zeolites used since the 1970s have greatly improved operation and performance compared to the former catalysts. Since their shape selectivity is not a decisive advantage in these two applications, several zeolites with very different apertures are used: ZSM-5, MCM-22, beta, and Y for ethylene; MCM-22, mordenite, beta, and Y for propylene [88].

Processes for syngas production and methanol or Fischer–Tropsch syntheses will be briefly described in the following section.

### 2.3. The technical factors of progress

On the whole, the significant advances made in catalysis for refining and petrochemicals during the last 50 years are chiefly the result of the research work carried out in different disciplines.

#### 2.3.1. Materials

A class of materials that has played an important part is zeolites. The number of known structures has increased considerably in just over 40 years, from fewer than 30 at the end of the 1950s to over 125 in 2001. However, as shown in Table 2, only around a dozen of them are currently used in industrial catalytic processes [89–91].

Metals form another class of materials that has greatly contributed to progress in catalysis, particularly the multi-metallic associations currently used in various applications, such as hydrogenation or reforming. Table 3 lists the principal metals found in modern monofunctional or bifunctional catalysts used in refining and petrochemicals.

In the field of hydrotreatment, although the chemical nature of the active sulfide phase has remained virtually the same for several decades, the quality of the alumina support has been significantly optimized and its pore structure in particular has been adapted to the molecular weight of the feedstocks processed, especially where very heavy feeds are concerned [92,93].

#### 2.3.2. Catalyst preparation

Modern methods of industrial catalyst preparation are increasingly being designed to monitor and control the state of the active phase or its precursor throughout all the elementary stages of manufacture. This rigorous procedure has led to great improvement during the last few decades with respect to catalysts apparently simple to manufacture. Moreover, during the last two or three decades, new, much more sophisticated methods have been adopted and they have also had their share in the progress made: implementation of new active-phase precursors, judicious use of the varied interactions between the precursors and the inorganic support [94] or an initial metal phase [95], or adjustment of the gaseous atmosphere to the nature of the active phase during thermal treatments.

#### 2.3.3. Technology

The second half of the 20th century has brought a number of technological breakthroughs, and the most salient are probably the fluidized bed in FCC at the beginning of the 1940s, continuous catalyst regeneration or CCR in reforming in the 1970s, the catalytic distillation column during the 1980s for etherification and alkylation of benzene,

Table 3  
Principle metals used, or of potential use, in catalysis in the refining and petroleum industries

Catalyst	Metals	Industrial use
Monometallic	Al, Ti, Ni, Zr	Oligomerization (homogeneous catalysis)
	Cr	Selective trimerization of ethylene (homogeneous catalysis)
	Fe, Co	Fischer–Tropsch
	Ni	Oligomerization (heterogeneous), steam reforming, selective hydrogenation, disproportionation–transalkylation of aromatics
	Cu	Selective hydrogenation
	Ga, Zn <sup>a</sup>	Aromatization of light alkanes
	Mo, W	Metathesis of olefins
	Ru	Selective hydrogenation, metathesis of olefins <sup>b</sup>
	Pd	Hydrocracking, selective hydrogenation
	Ir <sup>b</sup>	Hydrodecyclization (dearomatization)
	Pt	Reforming, C <sub>4</sub> –C <sub>6</sub> isomerization, isodewaxing, dehydrogenation, Hydrogenation, A <sub>8</sub> isomerization
	Re <sup>a</sup>	Metathesis of olefins, disproportionation–transalkylation of aromatics
Association of metals	Fe or Co with Ru	Fischer–Tropsch
	Fe or Co with Pd (Pt)	Fischer–Tropsch (Pd or Pt = promotor of reduction)
	Mo (W) with Co (Ni)	Hydrotreatments (including hydrocracking)
	Pd with Ag or Au	Selective hydrogenation
	Pt with Ge, Sn, Re or Ir	Reforming
	Pt with Sn	Dehydrogenation
	Pt–Pd	Hydrogenation of aromatics in presence of sulfur

Ag, C<sub>8</sub> aromatics.

<sup>a</sup> Also present in the form of oxide.

<sup>b</sup> Possible catalyst.

ebullating bed reactors used for resid hydrotreatment, and circulating slurry reactors. The last type of reactor had been used in 1964 for hydrogenating benzene into cyclohexane [96] and was used on a larger scale by Sasol in 1993 for Fischer–Tropsch synthesis.

#### 2.3.4. Reactions

The main refining and petrochemical reactions were already virtually known in the 1950s or 1960s [7,10]. Since 1970, a few new reactions have been discovered. They include the direct conversion of methanol into hydrocarbons in the 1970s by Mobil, and the aromatization of light alkanes ( $C_3$ – $C_4$ ) into aromatics in the 1980s by BP.

Some reactions, whose initial applications occurred after 1970 but which are in fact simply improved variations of long-known reactions, are also worth mentioning: the etherification of isobutene by methanol into MTBE (Snamprogetti), the selective alkylation of toluene by methanol (Mobil), the aromatization of paraffins into  $C_{6+}$  on Pt/K–L-based catalysts (Elf), the selective dimerization and trimerization of straight-chain olefins in homogeneous phase (IFP, Phillips), metathesis (IFP, Lummus), the hydrogenation of benzene into cyclohexane in homogeneous phase (IFP), the cyclodimerization and cyclotrimerization of butadiene, respectively, into cyclooctadiene (Dow, DSM, and Shell) and into cyclododecatriene (Shell).

#### 2.3.5. Cooperation between the different disciplines

Several major refining processes are the fruit of cooperation between specialists in catalysis and experts in chemical engineering and technology, for example FCC, especially all riser cracking, and CCR reforming. One of the greatest successes attained in catalysis during the last 25 years in environmental protection is the development of automotive post-combustion catalysts, which is largely due to cooperation between specialists in catalysis and automotive engineers.

#### 2.4. Development of knowledge

The progress made in knowledge is marked by the discovery and exploitation of several major concepts that have enabled us to better understand and rationalize catalyst behaviour. Among these concepts, some of which have been established for half a century, the following may be noted.

- The concept of bifunctional catalysis was applied in 1949 in a catalytic reforming unit, defined by Weisz [97,98], then further developed by Weitkamp [99], and has since been immensely successful in a great variety of applications.
- The distinction between demanding (structure sensitive) and nondemanding reactions in metal catalysis was made by Boudart et al. and Burch toward the end of the 1960s [100,101]. The reason for the demanding character is not yet very clear, although the size of the particle seems to be a major parameter: Does it

require the presence of ensembles of sites on the metal particle [102,103] or of highly energetic sites (steps, kinks, vacancies) [104]?

- Hydrogen spillover was identified in the 1960s [105–107].
- The concept of the reconstruction of the metallic surface due to the effect of operating conditions and of adsorbates [108,109] seems to date from the end of the 1960s [110,111].
- The concept of the strong metal–support interaction or SMSI [111–113], in which spreading and wetting phenomena play an important part [112], has been known since the 1970s. This interaction occurs frequently in catalysis, but its action is not always beneficial.
- The concept of shape selectivity was identified in catalysis through zeolites in 1960 [114] and has proved very fruitful since the 1970s.
- The confinement of the reagents in the zeolite pores was evidenced by Fraissard [115] and confirmed by Derouane [116]: this confinement in the vicinity of the walls, and consequently of the active sites of these solids, significantly increases the concentration of the molecules in the pores and promotes bimolecular reactions.
- The “edge decoration model” of the CoMoS phase (decoration by the Co of the edges of the  $MoS_2$  slabs) was evidenced by Topsoe and co-workers in the early 1980s by the Mossbauer technique [117,118]. The theoretical forecasts that can be made were successfully compared with experimental results shortly afterward [119].

Concepts that have made it possible to refine catalyst preparation techniques may also be mentioned.

- The concept of “interfacial coordination chemistry” (ICC) [94] considers the different possible roles that may be played by the surface during contact with a solution of a metal precursor: solid solvent, ionic exchanger (or supramolecular counterion) [120], supramolecular ligand [121], reactant through solubilization [122,123].
- Surface organometallic chemistry (SOMC) is used for the heterogeneization of homogeneous [124,125] and enzymatic [125,126] catalysis or for the monitored preparation of supported bimetallic catalysts [95,127].

If these concepts have come to light, it is largely due to the enormous amount of knowledge that has been acquired for decades in the field of catalysis with respect to reactions, their mechanisms and the catalytic surface. Mention may be made, by way of example, of the knowledge of carbocationic intermediates accumulated for nearly a century and to which Olah made a major contribution [128], or knowledge of the mechanisms of reactions involving metal catalysts [129–131] or metal sulfides [132,133]. Knowledge of carbocations, for example, which is currently proving re-



markably helpful in rationalizing reactions involving acid catalysts, has made significant progress due to characterization techniques such as NMR, particularly  $^{13}\text{C}$  NMR, UV and IR spectroscopy, Raman diffusion, mass spectrography, and ion cyclotron resonance spectroscopy. Furthermore, isotopic methods have often played a decisive role in elucidating reaction mechanisms. With respect to catalysts, numerous characterization methods have played and continue to play a very important part in catalysis and the principal ones are listed in Ref. [11].

### 3. Long-term industrial catalysis (2020 and beyond) in refining and petrochemicals

#### 3.1. The foreseeable context of development: the main directions of economic development in the field of energy

The orientation of world economic development has already been set by the major technological and industrial challenges in the fields of the environment and energy.

##### 3.1.1. The environment

Optimum protection of the environment means clean human activity without any pollutant discharge, whether gaseous, liquid, or solid. Where the air is concerned, this implies the following:

- The elimination or nonproduction of noxious emissions by transport vehicles. As shown in Fig. 3 [2], it is estimated that by 2010 the amount of the various noxious products emitted into the air should be three to eight times lower than in 1995 and 2.5 to 4 times lower than in 2000.
- Minimizing the production of greenhouse gases. The European Union is committed to reducing greenhouse gas emissions by 8% in relation to 1990 levels over the period 2008–2012.

The treatment and systematic depollution of industrial waste water, and the protection of the oceans and ground water against pollution, will gradually become standard

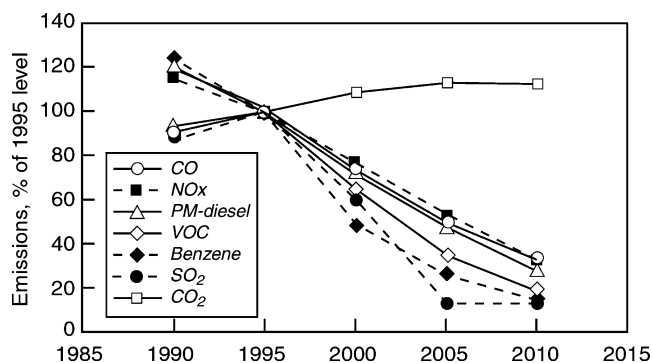


Fig. 3. Gaseous emissions from 1990 to 2010.

practice and in some cases could involve catalysis. Similar rules will apply to potentially noxious solid waste, and to spent catalysts in particular.

A significant reduction of  $\text{CO}_2$  emissions in the atmosphere means restricting the combustion of fossil fuels and the capture and sequestration of the  $\text{CO}_2$  produced by large industrial installations [4,134,135]. The chemical sequestration of  $\text{CO}_2$  is one of the ways in which catalysis could play a part in the future.

##### 3.1.2. Energy conservation

The problem of the scarcity of cheap, easily accessible oil reserves is a frequently mentioned topic. Depending on the degree of optimism of specialists and on the assumption that consumption will continue to grow (2% per year), ultimate world hydrocarbon reserves could come to an end between 2040 and 2060 [136,137]. The threat of no more reserves and the effect of greenhouse gases are a strong incentive to save energy. To achieve this, performances have to be improved at all levels, from the refinery to the use of hydrocarbons by industry and the public, and this involves a number of catalytic processes.

##### 3.1.3. Exploitation of new energy sources

These sources will be fossil based to start with: oil, gas, and coal will still cover 92% of world energy needs in 2020 [138]. Renewable energy sources will in the long term be called on much more massively than in the past.

**3.1.3.1. Fossil resources other than oil** During the last decade, proven world gas reserves increased considerably, and on January 1, 2000, they exceeded oil reserves in Gtoe, without counting the enormous methane reserves trapped in the form of hydrates at the bottom of the oceans. Natural gas should gradually take over from oil and become the most important fossil fuel by the middle of the 21st century. In Europe, natural gas should already supply around 30% of total primary energy by 2020 [139–141]. Coal reserves are five to six times higher than oil and gas reserves combined, which is the equivalent of over two centuries of consumption [142].

**3.1.3.2. Renewable energy sources** Renewable energy sources [143] are chiefly solar, especially photovoltaic, eolian, hydraulic, geothermal, and biomass. According to the different authors, these sources account for between 4 and 15% of world consumption of primary energy. Biomass, which is still little exploited (1 to 3%) [135,142], is a promising resource with scope for catalysis. However, it could meet only a small share of future world energy needs [135]. In all events, in the 21st century all renewable sources will have to be mobilized and fully exploited.

### 3.2. Impact on the refining and petrochemical industries

#### 3.2.1. Oil as the main energy source in the first half of the 21st century

During the coming decades, oil will still be the main source of energy [144–147] and will supply a large share of the fuel required by industry and virtually all the fuel required for transport. The possible scenario for refining and petrochemicals in 2015–2020 are not very difficult to imagine, except where future motor fuels are concerned.

Developments in refining will mainly be governed by the constraints of the new European specifications that will come into force in 2005 and 2011 (or possibly in 2008) (Table 1) [2,148]. Traditional modern heat engines are already close to zero pollutant emissions with the use of automotive postcombustion catalytic converters. Automotive emissions should again be reduced by a factor of 2.5 to 3 between 2000 and 2010 [2], due partly to the reduction of the sulfur content of motor fuels.

Regarding catalytic processes, the general trend will be toward a reduction in costs by improving catalyst activity, and more especially their selectivity [149]. The reduction of heavy fuel consumption puts conversion processes in a good position. FCC will long remain the major process for converting vacuum distillates [148]. Its good potential for the economic production of light olefins from  $C_2$  to  $C_5$ , including propylene, will be better and better exploited through improved catalysts and technology. Catalytic processes that improve the quality of FCC liquid products should be further developed and/or generalized. These involve desulfurization of gasoline on one hand, hydrogenation and in particular hydrodecyclization of light FCC gas oil (LCO) on the other hand. For these applications, improvements are expected in catalytic systems, process schemes, and technology.

In spite of its high cost, hydrocracking should develop due to the excellent quality of the middle distillates, particularly light gas oil, that it produces and for which there is a growing demand in Europe. In this respect, research will be oriented especially toward the development of more active and more selective catalysts operating at lower pressure [148].

In hydrotreatment, the removal of the last traces of sulfur (4,6-dialkyldibenzothiophenes, for example) from various petroleum cuts, the most difficult ones to convert by catalysis, will probably be performed in the medium term by adsorption and in the longer term by biodesulfurization [150] when much more active bacteria strains are available. In spite of the spectacular progress achieved in the last 10 years, biocatalytic desulfurization is still not competitive because specifications on sulfur content have become much more stringent and also because great progress has been made in conventional hydrotreatment [150].

Another challenge for the refining industry is the production of motor fuels, particularly gasoline, with some of its blending components under pressure due to restrictive environmental specifications: reformat with a high alkyl-

benzene content, FCC gasoline with a high olefin content, MTBE because of its threat of ground water pollution [151]. These blending components could be less used in the future, which would then encourage the use of other components involving the following processes [148]: isomerization of light paraffins (including  $C_7$  paraffins), alkylation of isobutane by butenes and by pentenes, selective oligomerization of light olefins.

Growth in demand for diesel fuel could encourage recourse in the medium term to dimethylether (DME) [148,152], whose direct synthesis from syngas or methanol does not pose any particular problems, and also, in the longer term, the appearance of Fischer–Tropsch synthesis units [148].

With regard to petrochemicals, growth in annual world demand for polyolefins is estimated at 5.5% on average until 2010 at least [153] and this ensures sustained growth in ethylene and especially in propylene over the same period [6]. The European market for aromatics, which was  $13.5 \times 10^6$  t in 1998, including 50% for benzene, is still enjoying sustained growth but is likely to suffer considerably from the 35% ceiling on aromatics content in gasoline to come into effect in 2005. This will result in a 10 Mt surplus in relation to demand [154]. This context, together with the need to reduce production costs, constitutes a strong incentive to improve olefin and aromatics transformation processes in which acid, metal, and sulfide catalysis can play a major part. The foreseeable surplus aromatics will be hydrogenated in the short term. In the medium term they could be hydrodecyclized or used to produce hydrogen by gasification [155].

Another problem which has to be tackled now is that of the  $CO_2$  emitted by modern heat engines. Two ways of reducing them are being studied [156]:

- Taking advantage of the greater efficiency of the diesel engine and hence increasing the diesel fuel/gasoline ratio to reduce consumption; this trend is absolutely irreversible in Europe.
- Developing smaller-cylinder-capacity engines that use less fuel; the target of 3 liters of fuel per 100 kms should be reached in a few years.

In view of the targeted phasing out of solid pollutant waste, the retreatment or recycling of spent catalysts, particularly those containing heavy metals, will probably be compulsory in most countries after 2010. In addition, the scarcity of some noble metals could be an incentive to reduce their content by using them more efficiently or replacing them with other more common nontoxic elements in metal catalysts (some hydrogenation or dehydrogenation operations, depollution catalysis) whose applications will be further developed.

#### 3.2.2. The gradual appearance of alternative energy sources

In the still longer term, alternative energy sources, namely coal and more especially natural gas and biomass, and

new energy carriers, particularly hydrogen, should gradually develop. Their use will necessarily involve adaptations and/or technological breakthroughs, allowing a significant reduction in costs.

**3.2.2.1. Natural gas** In Europe natural gas is already used, to produce electricity and, to a lesser extent, directly as a motor fuel (in compressed state) [144,157,158]. The latter utilization should gradually develop in spite of a number of disadvantages related to its distribution and storage in vehicles.

In the longer term it will be increasingly used to produce liquid motor fuels and intermediates for the chemical industry. Figure 4 [157,159] shows current and future possibilities of producing alternative fuels from natural gas.

There are two different ways of converting natural gas.

- The indirect method involves the transformation of natural gas into syngas followed by Fischer–Tropsch (FT) synthesis or methanol synthesis. The preparation of syngas is a technique that has been used for a long time. The number of ways of preparing syngas that are currently useable are limited to steam reforming or partial oxidation [160,161], and to autothermal steam reforming that combines these two techniques [160,162]. Steam reforming is a key technology for the future. Although it is a mature technology it still has scope for progress, particularly where the Ni-based catalyst is concerned, the main problem here being coke formation [163], especially by the whiskers mechanism [162]. FT synthesis, which produces hydrocarbons, and high-quality middle distillates in particular, has been known since the 1920s but can still progress where the catalyst and the process are concerned. Methanol, and/or dimethylether, produced from syngas can be the start of catalytic syntheses of a number of chemical basestocks,

particularly base products such as light olefins, ethylene, and propylene, by an MTO-type process for example.

The indirect way is the only technique that is currently useable and is therefore important for the future. It effectively transfers the energy of the gas to the liquid products formed but its operation and the investment required are costly. The production of syngas by itself amounts to over 60% of the capital cost [160,162,164].

- The direct way of converting natural gas into motor fuels and liquid fuels will not be feasible without scientific and technological breakthroughs and is a major challenge for catalysis in the 21st century [159,164]. Several possibilities can be considered [159]:

- The partial oxidation of methane into methanol and formaldehyde.
- Oxidative coupling of methane, a process that is far from the industrialization stage, with much progress needing to be made before it can be considered viable.
- Direct conversion of methane into aromatics at high temperature ( $\sim 700^\circ\text{C}$ ).

**3.2.2.2. Coal** Coal presents two serious problems: first, it contains large amounts of sulfur, nitrogen, and metal contaminants and therefore has to be purified, and second, it is rich in carbon and its combustion produces enormous amounts of  $\text{CO}_2$ .

It can be transformed into useable products in two ways: liquefaction or gasification. Liquefaction is more economical for producing relatively aromatic liquid motor fuels. Gasification is the only way of producing gaseous hydrocarbons for the petrochemical industry or liquid hydrocarbons for clean liquid motor fuels with a low aromatics content. Gasification is performed by partial oxidation [161] at high temperature ( $1300\text{--}1400^\circ\text{C}$ ). It is costly but it provides efficient control of pollutant emissions. The syngas obtained after the partial conversion of CO through the water–gas shift

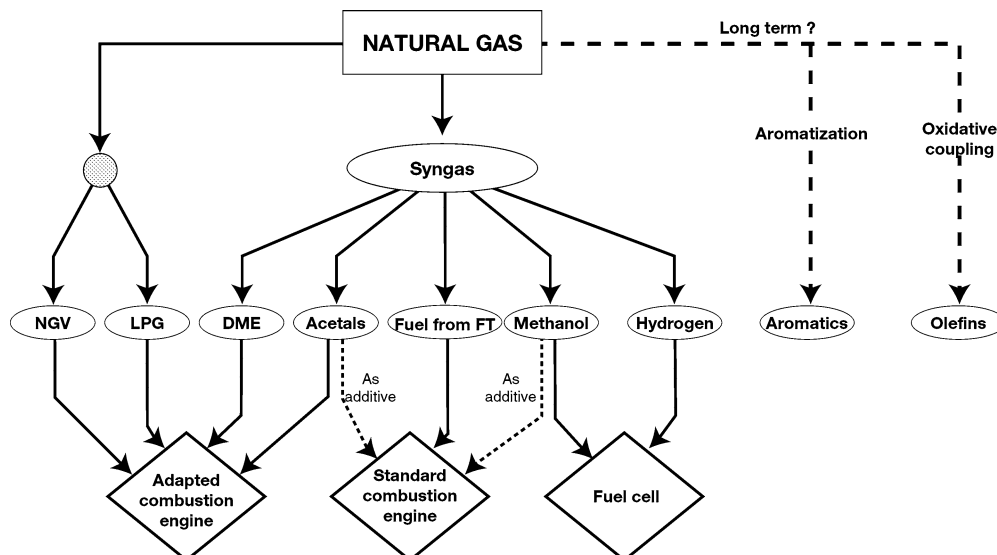


Fig. 4. Alternative fuels that may be produced from natural gas.

reaction and desulfurization can be used to produce two categories of product: either motor fuels similar to those produced from petroleum by the Fischer–Tropsch method or methanol.

**3.2.2.3. Biomass** Biomass is the unique irreplaceable source of food for human beings. It is also a perishable, fragile resource and its current pace of renewal is incompatible with intensive use as a source of energy on a global scale [135]. It will therefore be necessary to identify some plant species with a high energy yield and a very rapid rate of growth if biomass is to become a genuinely renewable energy source. The CO<sub>2</sub> emissions related to harvesting and to the required fertilizers are far from negligible and have to be taken into account.

There are three principal ways of transforming biomass into an energy source [135].

- Non catalytic pyrolysis in the absence of oxygen transforms lignocellulosic biomass into coal, gas, or pyrolytic oil containing oxygenated compounds [163].
- Chemical transformation in the presence of catalysts leads to the production of basestocks for biofuels or biolubricants or to gasification.
- Fermentation due to enzymes leads to its anaerobic decomposition into methane or produces alcohols.

Figure 5 shows the main categories of products whose synthesis can be considered using biomass [165–168] and involves catalysis.

Biomass already has some applications as a substitute for petroleum products. Examples, are ETBE from ethanol and vegetable oil methyl esters, which are monoesters produced by catalytic transesterification, in liquid or heterogeneous phase, of vegetable oil triglycerides by methanol [167] and which are added in small quantities to some diesel fuel [169]. Biofuel and biolubricant applications will probably undergo further development in the future.

**3.2.2.4. Biotechnologies** [150,169,170] Generally speaking, biotechnologies, particularly biocatalysis, are destined to play a very important part in the future in supplying the planet with energy carriers and other substitutes for petroleum products and for environmental protection. With a view to sustainable development, biogasification is an alternative for the production of syngas or hydrogen. The applications which primarily concern the environment involve the biological treatment of gaseous emissions (biofilters) and solid waste, and bioremediation of polluted water (sea water in particular) and soils. These applications will develop with the help of the increasingly sophisticated genetic engineering techniques, such as recombining ADN.

**3.2.3. Hydrogen: increasingly needed for refining, then as an energy carrier**

Hydrogen production is becoming a major industrial domain [155,171–176], and this trend will prevail. Today it is used almost entirely as a chemical reagent in the oil and chemical industries [171]. Annual world production of hydrogen is in the region of  $500 \times 10^9 \text{ Nm}^3/\text{year}$ , or  $45 \times 10^6 \text{ t/year}$ , which accounts for only 1.5% of world production of primary energy [172]. The needs of the European refining industry are estimated at  $20 \times 10^9 \text{ Nm}^3/\text{year}$ , or around  $1.8 \times 10^6 \text{ t/year}$  (around 30% of total hydrogen consumption in Europe) and covered exclusively by fossil fuels, particularly natural gas [172]. If it is to become a widespread energy carrier, it is estimated that it will have to cover around 20% of world energy needs by 2050, which would mean multiplying current world production capacity by a factor of around 25 [172].

Hydrogen is a sophisticated and promising energy carrier that offers high energy yields and limits secondary reactions. It can be transported in gaseous state (by pipeline), as compressed gas, and in liquid form (by cryogenic technology). It is in the latter state that its energy content is the highest, but like natural gas, liquefaction alone consumes 35% of the energy it contains.

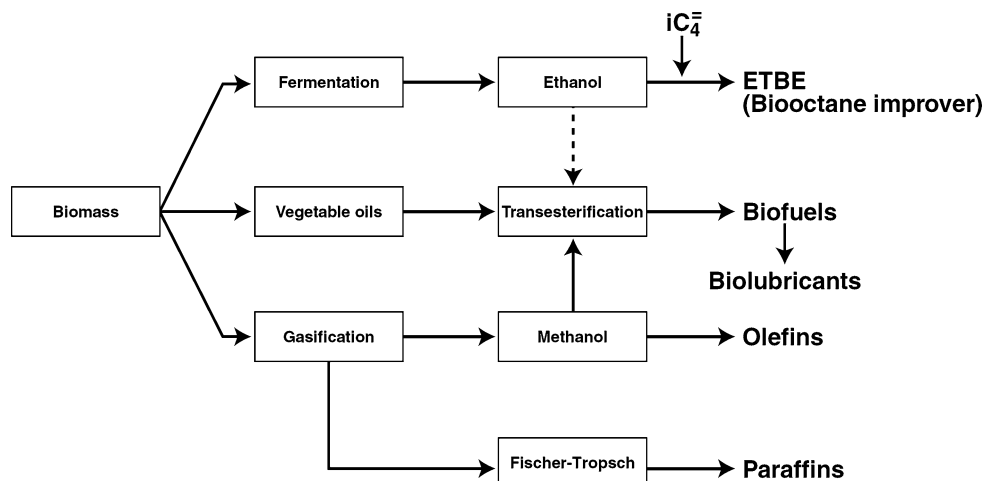


Fig. 5. Biomass conversion to products and motor fuels (FT, Fischer–Tropsch).

It is currently produced by gasification of coal, of petroleum residues, and, to a much lesser extent, of biomass [175], or by steam reforming of methane or electrolysis of water [161,171,172]. When hydrogen production involves syngas it is optimized by converting a maximum CO through the water–gas shift reaction. The various technologies differ by their complexity, their yield, and the purity and the cost of the hydrogen obtained. In the long term it is not unrealistic to imagine the development of more ecological technologies, such as selective catalytic disproportionation of hydrocarbon sources into hydrogen and carbon residue or useable liquid products [155], hydrogen production from water by enzymatic catalysis assisted by light, such as that slowly performed by Fe or Ni hydrogenases [176], and electrolytic dissociation of water from nuclear or solar (photo-voltaic) electricity.

During the present decade hydrogen could start to slowly replace some of the traditional oil-derived motor fuels for vehicle propulsion. There are two main ways of producing mechanical energy from hydrogen: either through direct use in internal combustion engines or through a fuel cell [173,177]. Both methods encounter a number of serious problems related to the need for mass distribution logistics and hydrogen storage [173,174].

The fuel cell (FC) can be used to produce the electricity required for propulsion from hydrogen and appears to be the most promising technology, particularly for urban use. It is clean and quiet and provides gross electricity yields of 50% (80% in the case of cogeneration) [171,173], but its direct use of hydrogen stored onboard cannot be considered on a large scale for the moment. Between now and 2010–2020, FC vehicles should generally be equipped with an autonomous hydrogen production unit fueled by gas, hydrocarbons, or ethanol, or even methanol. The real development of hydrogen as a fuel is not expected to take place until 2020. Another long-term option is the direct use of methanol as an FC fuel. Whatever solution is adopted, major advances or technological breakthroughs will have to be made if commercial products are to be made generally available. The size and cost of the FC will have to be reduced, its lifetime increased, and its performance and reliability improved. A major technological breakthrough, for example, would be to replace at least partially the noble metals of the electrodes by more economical and abundant metal components.

### 3.3. Impact on applied catalysis and fundamental catalysis

The above considerations show that a number of challenges in which catalysis is of prime importance await the refining and petrochemical industries at the dawn of the 21st century. To meet these challenges, progressive improvements and in some cases technological breakthroughs are required. The major areas of catalysis in which progress and

solutions are especially necessary are the following:

- New micro- and mesoporous catalytic materials, catalytic membranes, or membrane reactors; new materials for hydrogen storage.
- The replacement of noble metals and/or rare metals in all the “diffused” activities (automotive postcombustion, for example; fuel cells for vehicles).
- The development of biocatalysis for processing petroleum cuts in the medium term; depollution and the transformation of biomass in the longer term.
- Optimization of the use of catalysts through new industrial implementation techniques (decentralized or onboard and miniaturized small-scale energy production units, for example).
- Improved knowledge of reaction mechanisms, and of catalysts and their mode of action through the use of current advanced characterization techniques and the development of new techniques.

Innovation in mature fields such as refining and petrochemicals calls for increasingly sophisticated techniques. Since 1980, there have been enormous advances in information technology and physics and as a result the following tools are available to specialists in catalysis: access to electronic documentary sources, storage, sorting of experimental data for correlation, molecular modeling, increasingly high-performance analytical techniques, and high-throughput or combinatorial catalysis. These facilities and those yet to come will be a necessary and precious aid in meeting the many challenges that lie ahead.

## 4. Conclusion

During the present decade and probably also in the next, the refining and petrochemical industries will have to pursue the changes that have been under way for the last 30 years in order to adapt to the demands and constraints imposed by the necessary protection of the environment, by the effort to combat greenhouse gases (particularly CO<sub>2</sub>), and by international competition. Although these industries are considered to be mature, the changes will call for progress at all levels, especially with regard to catalysis. Catalytic selectivity in particular will be a major concern.

In the longer term, well after 2020, with the gradual replacement of oil by other energy sources, a profound change and maybe a major upheaval will be necessary and it will gradually take place in these two industries and in the world of end users that drives them. From this point of view, catalysis will have a major role to play in overcoming the many technical difficulties that lie ahead, some of which will require scientific and technological breakthroughs. Catalysis is not an emerging discipline but is not yet a mature discipline. It is vital for future progress and will continue to play an active part in technical and economic development by providing original and innovative solutions.

## Acknowledgments

I extend my gratitude to D. Commereuc, P. Courty, J. Lynch, and G. Martino of IFP for their help in providing technical information.

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