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# Catalysis, the turntable for a clean future

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**Abstract**

Upgrading the bottom of the barrel for clean fuel production, developing new engines with optimized catalytic posttreatments, implementing clean catalytic combustion technologies, improving the overall $CO_2$ balance via catalytic processes and, lastly, developing new water purification techniques represent major upheavals in catalysis linked to refining and environmental protection. This paper, thus, will focus on the determining contribution of catalysis to the most recent achievements in these domains. A technico-economic approach will follow, underlining their main incentives and drawbacks within the framework of future environmental constraints.

*Keywords:* Future of catalysis

## 1. Introduction: Environmental protection by catalysis

As stated very recently by Mills and coworkers [1], the main objectives in environmental protection by catalysis are the following:

- Preventing pollution by developing energy-saving processes free of pollutant formation.
- Decreasing pollution by achieving higher selectivity in fuel and chemical manufacture, and by developing new and improved catalytic processes for the removal of pollutants.
- Developing competitive processes for the production of hydrogen, chemicals and energy sources, providing reduced $CO_2$ production.
- Defining research objectives in heterogeneous catalysis enabling the production of major products with greater energy and feedstock efficiency, and with improved environmental issues.

Indeed, all of these objectives are ambitious, since, they imply major upheavals in every domain in which industrial heterogeneous catalysis is acting today or will be involved tomorrow.

## 2. Clean fuel production

### 2.1. Evolution of refining [2-7]

As seen in Fig. 1, worldwide oil production has grown from 2.8 in 1973 to 3.1 billion tons in 1990. It is expected to reach 3.5 billion tons in the year 2000.

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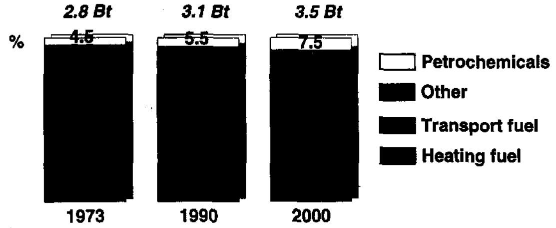
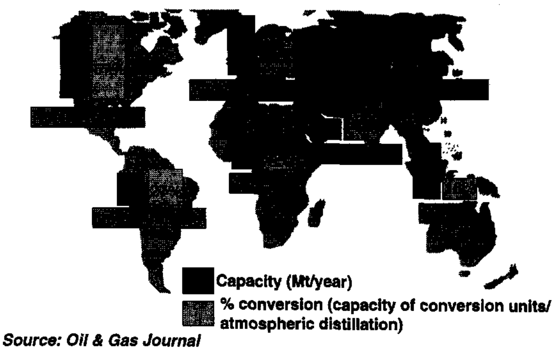


*Source: IFP*

Fig. 1. World oil markets.



*Source: Oil & Gas Journal*

Fig. 2. World refining capacity (end of '93).

In 1973, heating fuels were the main use of crude oil (1.5 billion tons) with only 1 billion tons for transport fuels. In 1990, heating fuels were only 1.3 billion tons right behind transport fuels (1.44 billion tons). Transport fuels will develop further in the future, with 1.8 billion tons consumed in 2000 versus only 1.05 billion tons for heating fuels.

Consequently, the oil market will become more and more specific (transport, petrochemicals) and difficult to be replaced with any other kind of energy.

This change in oil applications is having a deep influence on the demand by type of refined feedstocks (light cuts — medium distillates — heavy products).

The growth of the demand for light products — mostly gasoline and naphtha — respectively reflects the development of the automotive industry and the growth of petrochemical manufacturing.

The similar growth in middle distillate demand is mainly based on sharp rises in air and highway transport as well as on increased uses of diesel for commercial vehicles and cars. This entails increased consumption of products that are the most demanding as far as quality is concerned.

In such a context, the sharp decrease in heavy product uses implies processing more and more residual oil cuts. This will constitute one of the major challenges in the future.

In the last fifteen years, shutdowns of refining capacities in North America and Europe have been substituted for by new refineries in South America, the Middle East and mainly in the Far East. As seen in Fig. 2, the conversion capacities in percent of crude-oil atmospheric distillation capacity are tremendously different. The average African refinery is certainly close to the most simple refining scheme, while the US one is far beyond the medium conversion refinery. European refineries stand in the medium conversion range.

Most international petroleum markets, because of the structure of their demand, are situated within the possibilities of conventional conversion refineries (20%–40% of heavy products) and that of the structure of their supply.

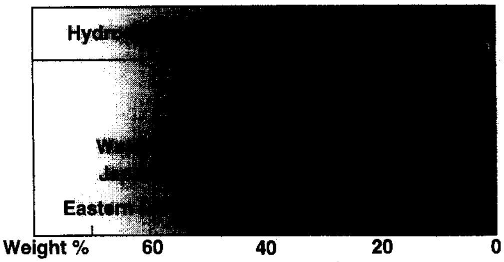
Table 1
The Growth of Refining Costs (8 Mt/y refining capacity)

| Refinery type | Investments (B$) | Refining cost ($/bbl) | Self consumption (wt.-% of crude) | $H_2$ consumption (wt.-% of crude) |
|---|---|---|---|---|
| Hydroskimming | 0.5 | 1.5 | 4–4.5 | 0.2–0.3 |
| Conventional conversion | 1–1.5 [a] | 3–4 | 6–8 | 0.5–1 |
| Deep conversion [b] | 2.5 | 7.5 | 11–13 | 1–1.5 |

[a] According to product quality

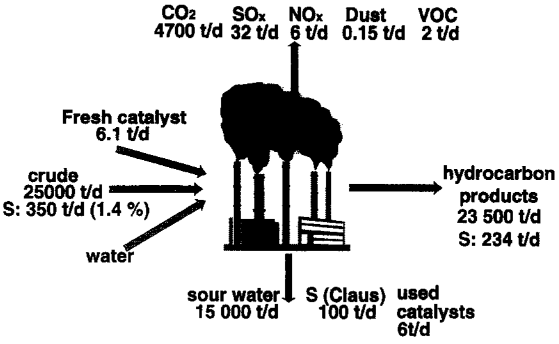
[b] Including quality upgrading units.

Source: IFP.



Source: IFP

Fig. 3. Structure of petroleum demand and adaptation of refining.



Source: IFP

Fig. 5. 1990's refinery: products and waste streams.

However, they all tend to approach the limits of this range (Fig. 3).

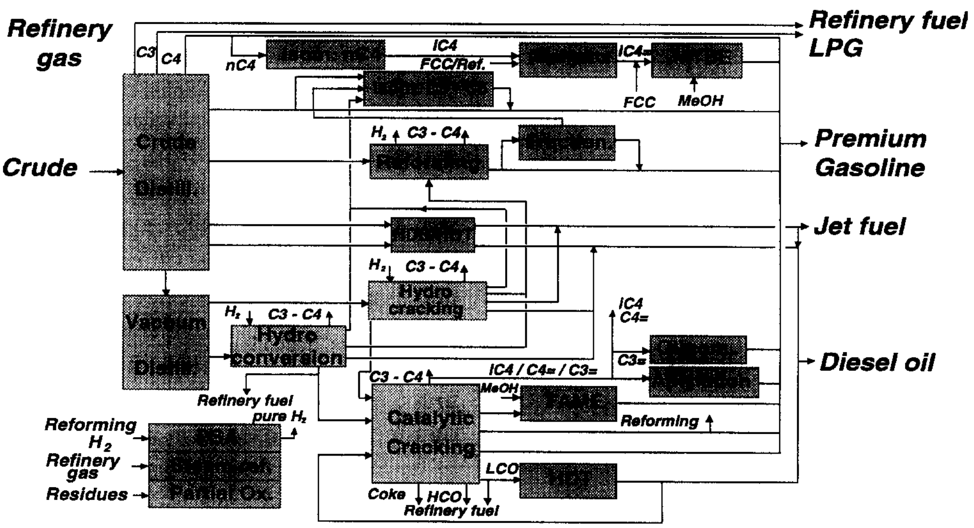
Indeed, several factors make it difficult to achieve deep conversion objectives: the size of the investments required, the increase in the resulting operating costs, as well as that of internal crude consumption and hydrogen demand.

As shown in Table 1, the refinery of the 21st century could cost five times more than a simple refinery at the start of 1970 (in discounted investments) and 2.0 to 2.5 times more than the basic refinery with conventional conversion in the middle of the 1980's.

Such a refinery (Fig. 4) is capable of producing reformulated fuels: Gasoline from $C_5$–$C_6$ isomerization, alkylation, reforming, FCC and the ethers MTBE and TAME as octane improvers. Clean jet fuel and clean diesel from hydrocracking and light olefin oligomerization. Lastly, hydroconversion of resids followed by hydropurification provides clean feedstocks for catalytic conversion units.

Furthermore, additional hydrogen production units are implemented so as to fulfil the hydrogen requirements for converting the residue as well as to improve the quality of products.

Like every industrial installation, refineries are sources of pollution as shown in Fig. 5, which concerns a refinery treating 25 000 t/d of



Source: IFP

Fig. 4. Long term refinery configuration (2010–2020).

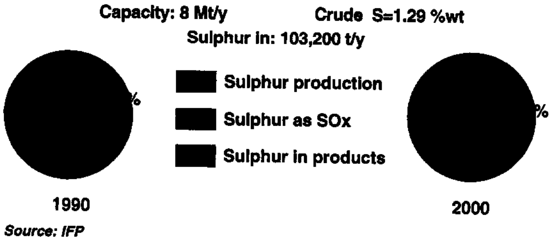
crude oil containing 1.4 wt.-% sulphur (ca. 350 t/day). Likewise they discharge several pollutants into the air ($CO_2$, $SO_x$, $NO_x$, VOCs) and into the water by drains or, accidentally, into the ground through leaks. At the same time, they prove to be sources of noise, odours, dust and waste.

Indeed refineries are at the very heart of a real problem, namely that of improving the quality of products, so as to reduce pollution at the level of consumers, which in turn results in an increase in energy consumption by refineries and creates an additional production of pollutants and $CO_2$. A good example is that of sulphur removal issues, which appears to be one of the main problems to be solved by refiners before the end of the century.

As seen in Fig. 6 for an average 8 Mt/y crude refinery in 1990, more than two-thirds of the sulphur from crude is exported as part of the end products, 8% is converted to $SO_2$ and only 26% issues as elementary sulphur. With a deep conversion refinery in the year 2000, only 26% of sulphur will be reexported in products, 5% will go to the nearby atmosphere as $SO_2$ and about 70% will be converted into elemental sulphur, which will make the refiners the main sulphur producers of tomorrow.

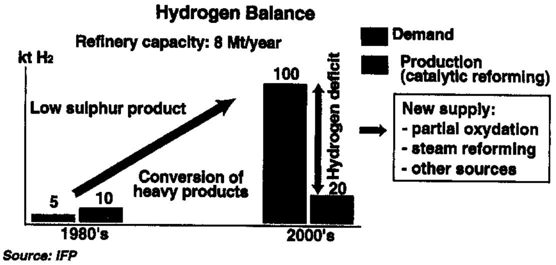
### 2.2. *Upgrading the bottom of the barrel [2–6]*

Upgrading the bottom of the barrel via refining is one of the main challenges of heterogeneous catalysis in the future. The objective is to produce less and almost no heavy fuel oil, whereas much higher quality products would be issued.



Source: IFP

Fig. 6. Evolution of sulphur breakdown in a refinery.



Source: IFP

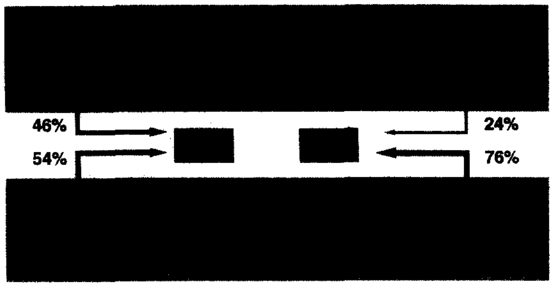
Fig. 7. Improving quality and more conversion: hydrogen balance.

Deep conversion challenges can be summarized as follows:

- Hydrorefining (HDS, HDN, metals removal) and converting the residue with higher selectivity, less coke and milder process conditions. More active and stable catalysts are expected.
- Converting refined products: New FCC catalysts, converting the bottoms more deeply with less coke production and, in view of heavy-cut hydrocracking, new catalysts with improved selectivities to middle distillates would represent major issues. In addition, improved sulphur traps to control $SO_x$ emissions as well as dedicated $DeNO_x$ technologies would be welcome.

However, deep conversion requires the availability of a larger hydrogen supply for hydroprocessing. As shown in Fig. 7, the hydrogen balance of the 1980s was good, since, hydrogen production from reforming units was beyond the hydrogen demand for hydroprocessing. In years after 2000, hydrogen demand will grow sharply because of new deep conversion units and new constraints on product quality. Hence, a new hydrogen supply will become mandatory and specific hydrogen production units will be developed (see also Fig. 4), based on the thermal oxidation route (partial oxidation of asphalts, residues) and/or catalytic routes (steam reforming and catalytic partial oxidation of refinery gases).

Lastly, the total sulphur recovery will be improved with more active Claus catalysts, tail



ource: French Academy of Sciences, 1993

Fig. 8. $SO_2$, $NO_x$: sources of emissions.

gas treatment catalysts and dedicated technologies, giving rise to a total sulphur recovery of 99.8%–99.9%.

### 2.3. Product quality [1,2,5,6]

New environmental requirements are demanding improvement in the quality of products, since, air quality coupled with all tropospheric pollution problems involves careful control of the chemical composition of fuels, unburned hydrocarbons and other pollutants.

Fig. 8 points out that 54% of $SO_x$ emissions and 76% of $NO_x$ emissions issue from anthropogenetic sources. Indeed, the combustion of heavy fuel oils is responsible both for most of $SO_x$ emissions of petroleum origin and for a high rate of $NO_x$ emissions. With reference to these two facts, standards on limitation of such emissions are becoming more and more severe. Besides existing and future $SO_x$ and $NO_x$ removal technologies, a more challenging issue deals with the production of cleaner heavy fuel oils at acceptable prices.

In addition, other priority challenges in product quality deal with the improvement of motor fuels, which indeed will be a major upheaval for heterogeneous catalysis.

#### 2.3.1. Gasoline

Even though user-friendly gasoline comes from highly branched paraffins and perhaps some ethers, aromatics and olefins will remain at a reduced share in the gasoline pool.

Highly branched paraffins are issuing partly from $C_5$–$C_6$ isomerization: low temperature active environmentally friendly catalysts, operating at 120°C or even less, would be welcome.

$C_7$–$C_8$ paraffin isomerization catalysts are

Table 2
Qualities of finished products — future key constraints

| | Possible evolution 2000–2020 | | |
|---|---|---|---|
| | Europe | North US area | California [b] |
| *Premium gasoline* | | | |
| RON (clear) | 95–98 | | |
| MON (clear) | 85–88 | | |
| Benzene (vol.-%) | 1–2 | 0.95 | ≤ 1 |
| Aromatics (vol.-%) | 20–30 | 24 | ≤ 25 |
| Olefins (vol.-%) | 5–10 | 9.2 | ≤ 6 |
| Sulphur (ppm) | 50–100 | 185 | ≤ 40 |
| Oxygen (wt.-%) | 2.1 < ox < L [a] | 2.1 | 1.8 to 2.1 |
| *Diesel oil* | | | |
| Sulphur (wt.-%) | 0.02–0.05 | | |
| Cetane number | 50–55 | | |
| Aromatics (vol.-%) | 10–20 | | |
| *Heavy fuel oil* | | | |
| Sulphur (wt.-%) | 0.5–1 | | |
| Nitrogen (wt.-%) | 0.3–0.5 | | |

[a] Probable limit to be fixed (problem of driving comfort).
[b] Applicable from march 1996.

presently on a lab-scale. More selective, hence, more stable catalysts would represent major issues.

Catalytic reforming, thanks to the low pressure CCR technology, allows higher selectivity to hydrogen thanks to limited side reactions. However, low benzene contents in reformate become mandatory (Table 2). This will imply reducing the catalyst dealkylation activity with better control of all the benzene precursors in the feedstock.

Focusing on FCC gasoline and its further upgrading, two major research topics can be underlined.

The first one deals with improved FCC catalysts giving rise to improved octane ratings; the second one concerns post treatments of FCC gasoline, whose objectives are good sulphur removal and partial hydrogenation of olefins without octane losses.

Last but not least, 64.4 million tons/year of alkylates require the consumption of more than 2 million tons of sulphuric acid and about 27 000 tons of hydrofluoric acid. The major upheaval of the 2000s would be the substitution of these dangerous materials through the challenging development of an environmentally friendly superacid solid. This challenge is considerable since the tonnage of acids consumed in aliphatic alkylation (ca. 2.1 Mt; US $ 200 million/year) exceeds that of the oil-refining and gas-catalyst market (600 000 tons; US $ 2 billion/y).

### 2.3.2. Diesel fuel

Environmentally friendly diesel fuel consists of S and N free slightly-branched paraffins in the $C_{12}$–$C_{20}$ range.

The best available diesel fuel issues from the middle distillate cut from hydrocracking. Hence, as said before, improved hydrocracking catalysts yielding improved selectivities for middle distillates are required.

As for diesel-oil cuts from FCC and thermal processes, the main challenges deal with the high aromatic sulphur and nitrogen contents of such cuts and their very low cetane indexes. It is, therefore, necessary to develop much more active hydrorefining catalysts, as well as new catalysts dedicated to aromatics hydrogenation at more reasonable temperature and pressure.

Besides, active and selective catalysts for polyaromatics hydrogenation and further selective ring opening giving rise to monoalkyl aromatics would be welcome.

In the future, other ideal diesel oils should develop, since, Fischer–Tropsch synthesis of middle distillates still represents one of the best issues for the chemical upgrading of natural gas.

### 2.3.3. Biofuels

In addition to technical and catalytic issues enabling oil products to meet environmental constraints, alternative routes deal with renewable sources of energy.

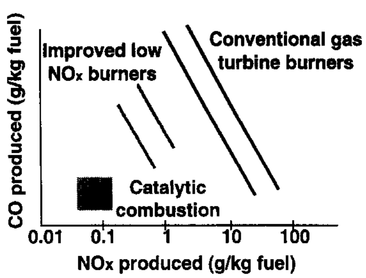
Since the first oil crisis, efforts to diversify energy sources have been made in favour of biomass upgrading to motor biofuels. Their development, which was slowed down by the drop in oil prices, was sharply stimulated by the EEC agricultural policy within a context of an increased awareness of environmental issues. Hence, markets for ETBE and rapeseed esters are expanding.

Independently, there is a potential contribution of biofuels to the prevention of climatic changes (greenhouse effect), which is today well established. As seen in Table 3, net $CO_2$ production from the combustion of biofuels is considerably less than that from conventional ones. The $CO_2$ consumed to generate the initial

Table 3
$CO_2$ emissions from alternative fuels

| Feedstock | $CO_2$ |
|---|---|
| Oil | 1 [a] |
| Natural gas | 0.7–0.8 |
| Ethanol from beets | 0.30–0.65 |
| Diester from rapeseed oil | 0.16 [b]–0.84 [c] |

[a] 3.4 tons of $CO_2$ per ton of fuel.
[b] 100% of diester.
[c] 30% of diester.
Source: OECD/IFP/Ecobilan.



*Source: IFP*

Fig. 9. Abatement of $NO_x$ production by means of catalytic combustion.

biomass compensates for most $CO_2$ emissions from biofuel combustion.

Consequently, there are some incentives to improve existing catalysts and processes. In addition, new catalysts are needed to upgrade vegetable oils, biofuels and by-products to fine chemicals [7].

## 3. Catalytic combustion

### 3.1. Energy production [1,8–12]

Catalytic combustion technology is well integrated into the design of future gas turbines (3–100 MW) operating with ultralow emissions and without the complexities of the selective catalytic reduction of $NO_x$ process.

Fig. 9 [10] details CO and $NO_x$ emissions from conventional gas-turbine burners, improved low $NO_x$ burners and catalytic combustion burners. Indeed, burning natural gas or fuels to completion at lower temperatures than conventional burners so as to control the $NO_x$ formation from atmospheric nitrogen represents the main incentive to scale up catalytic combustion to industrial achievements.

This innovative technology is already in an advanced demonstration stage [9] with proven low emissions: $NO_x$ 0.5–2 vpm; CO 0.8–2 vpm; HC 1.7–2 vpm, a combustion efficiency of 99.5% or more and a pilot-scale durability of 7000 h. The main applications cover gas turbines (power plants, boilers), furnace and process heaters, and liquid-fueled turbines in the future. The main limitations concern cost and technology as well as the stability of catalysts (supports, active elements) and medium temperature activity (breakthrough point).

Table 4 summarizes the main challenges and issues for improving today catalysts.

### 3.2. VOC removal [12,13]

For the time being, one of the major environmental priorities of the industrialized countries is the reduction of VOC. According to the EPA (Environmental Protection Agency), 'so called Volatil Organic Compound represents an organic compound, that after being emitted in the atmosphere is able to remain there a sufficient time to participate in photochemical transformation'.

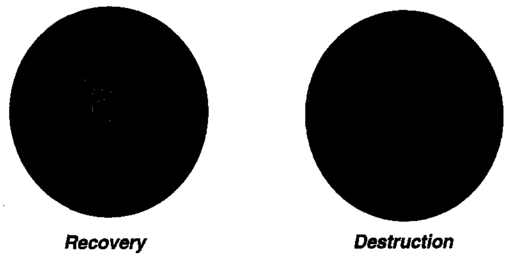
Only non-methanic HCs are concerned even though $C_1$ hydrocarbons and chlorohydrocarbons are frequent pollutants, along with formaldehyde. Some VOCs can be avoided by eliminating the use of organic solvents. In the field of car painting, for example, aqueous medium paintings result in a VOC reduction of more than 70%.

However when it is unfeasible to implement basic elimination, the only alternative is to treat the effluents before discharging them into the atmosphere. Two main routes can be considered: recovery or combustion (Fig. 10). Recovery mostly uses physical techniques, whereas destruction implies thermal or catalytic total

Table 4
Catalytic combustion

| Challenges | Issues |
|---|---|
| Thermal stabilization of supports | Doping (as for TWC) Hexaaluminates |
| Ignition temperature | Stabilized precious metal nanoparticles |
| Stability of performances | Promoted metal oxide catalysts |
| Control of $NO_x$ from fuel bound nitrogen | Dedicated formulae, A/F stoichiometry, NG fueled turbines |

Source: IFP.



Source: IFP

Fig. 10. VOC removal processes.

oxidation. As seen in Fig. 11, thermal oxidation technologies are dedicated to the higher flowrate or the higher VOC contents, whereas catalytic oxidation prevails for moderate flow and VOC contents.

Concerning the process technology, different routes have to be considered. At first, the VOC content induces the choice between so-called unsteady-state oxidation or regenerative oxidation, dedicated to low VOC contents and standard oxidation technology dedicated to higher VOC contents. In the former approach, the heat of reaction is absorbed in a series of parallel ceramic beds, which can be alternatively cycled on and off stream. During the off stream cycle the bed preheats the feedstock. The latter approach is based on feed-effluent heat exchange technology and has a lower yield in heat recovery: 70% instead of 90%–95%.

Indeed, the low temperature, made possible by the catalytic oxidation approach, makes it possible to avoid the formation of secondary pollutants such as $NO_x$ and dioxin from halogenated VOCs [14]. Hence, the catalytic oxidation approach will prevail for a clean future.

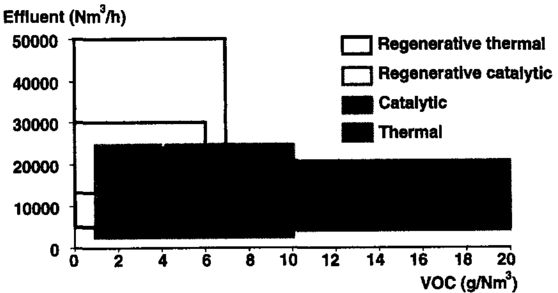
Lastly, it is always difficult to get some market information in this field. If we can approach the global amount of VOC emissions (2 to 3 million tons per year in a country like France), these pollutants are issued from various industrial sectors and broadly depend on operating conditions, which are very dissimilar (nature of the components, flows, concentrations, etc.).

## 4. Exhaust gas treatment [1,15]

### 4.1. Automotive emission control

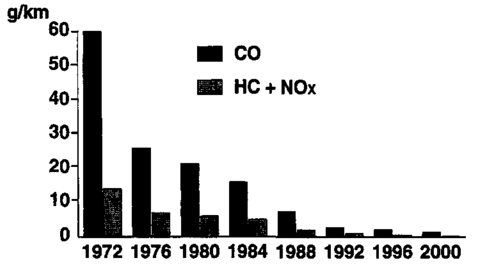
'Automotive pollution controls necessarily the interrelated fuel composition, engine combustion performance and catalytic posttreatment efficiency'.

In Western Europe, vehicle emissions have been subject to regulation since 1972. At the end of the century, partly because of a 35% decrease in engine consumption and partly because of the implementation of exhaust-gas catalytic converters based on three-way catalysis (TWC), noxious gases emitted by passenger cars will be considerably lower than those issued from the equivalent cars in 1972 (Fig. 12). Hence, between 1972 and 2000 a great reduction will be achieved, whereas further improvements (towards ULEV) will be more difficult and expensive.



Source: IFP

Fig. 11. Fields of application of VOC combustion systems.



Vehicule emissions significantly reduced in 30 years.

Source: Concawe

Fig. 12. European emission standard for passenger cars.

Table 5
Automotive emissions control TWC — main challenges

| | |
|---|---|
| Availability of precious metals | > 90% of world rhodium production consumed in TWC |
| Low temperature ignition (light off) | More than 50% NHMC and CO pass unreacted during the cold start |
| High temperature stability | Close coupled catalysts |
| Secondary pollutants | $H_2S$, HCHO, $N_2O$ and $CH_4$ contributing to greenhouse effect, ozone formation, odours |

Source: IFP.

Table 6
World precious metals supply and demand (1993)

| | Supplies (metric tons) | Demand (metric tons) | Autocatalysts | |
|---|---|---|---|---|
| | | | Demand [a] (metric ton) | Share (%) |
| Platinum | 124.2 | 114.5 | 40.1 | 35.0 |
| Palladium | 117.2 | 120.8 | 18.4 | 15.2 |
| Rhodium | 10.6 | 10.2 | 9.2 | 90.7 |

[a] Net demand = (gross demand-recovery).
Recovery: 8% of Rh, 14% of Pd, 17% of Pt.
Source: Johnson Mathey, 1994.

### *4.1.1. Three-way catalysts*

The main challenges in three-way catalysis have been summarized in Table 5.

- The first one concerns the availability of precious metals.

The needs required to equip future worldwide private car fleets risk being far above the supply possibilities, especially for rhodium. Table 6 gives more details on the supply and demand for platinum, palladium and rhodium [16].

Actually rhodium free catalytic systems, and even non-noble metal based ones, will represent major upheavals in the future.

- A second challenge deals with the ignition temperature of existing converters.

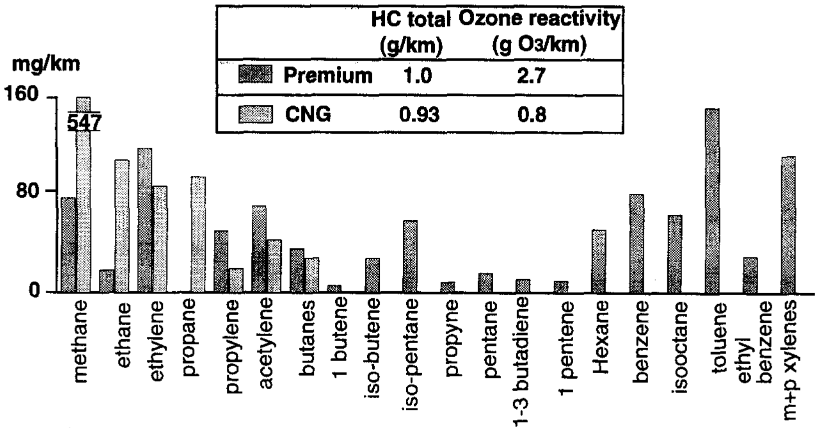
Despite recent improvements in scientific knowledge on the basic phenomenon (alkynes and $SO_x$ inhibition of sites) [17], improvements of both the catalytic formulas and the converter technology at acceptable cost are still needed.

- Another challenge relates to high-temperature stability, particularly for closed coupled catalyst formula. More progress in thermal stabilization of metal particles and oxides is expected.

- Likewise, secondary pollutants such as $H_2S$, $N_2O$, HCN and $NH_3$ contribute to tropospheric pollution and odours. Mastering their formation, and/or their destruction, implies specific approaches for each one.

### *4.1.2. Fuel reformulation*

Fuel reformulation has become a priority research topic, since, the concentration of some pollutants is often correlated with fuel composition.



**Premium gasoline and natural gas fueled engines give out similar HC emissions (1g/km) but the ozone reactivity is 3 times less with CNG.**
***Source: IFP***

Fig. 13. HC emissions: premium vs. CNG–EEC urban cycle.

Indeed, it is clear that further improvements cannot be made with only a hypothetical further reduction of the three main pollutants, CO, HC and $NO_x$, since, ozone and smog formation in the lower atmosphere linked to unburned or evaporated HC is more and more worrying. This is why fuel reformulation constitutes one of the effective approaches to the improvement of air quality.

A good example of the potentialities of fuel reformulation and even fuel substitution is that of compressed natural gas (CNG) versus premium gasoline.

Fig. 13 compares the detailed emissions by the same engine with these very different fuels.

Though they give out similar HC emissions, the ozone reactivity is three time less with CNG. In addition, butadiene, benzene and other aromatic emissions are not detectable with the latter fuel. Hence, there are strong incentives to develop CNG fueled engines.

### 4.1.3. *Lean burn engines; $NO_x$ removal*

New direct-injection diesel engines, as well as lean burn gasoline engines (2 and 4 strokes), will make for significant energy savings, about 30%, with reference to conventional gasoline fueled engines with TWC depollution technology [18]. In addition, such new engines will give rise to significantly lower $CO_2$ emissions.

Since diesel fueled engines are today's proven issues for partly solving the emission problems and lowering $CO_2$ emissions, it is worthwhile to assess the possible improvements related to diesel engines. Two categories can be distinguished: fuel quality itself and the $NO_x$ removal issues.

The main diesel fuel requirements involve higher cetane numbers (Table 2) with the lowest sulphur contents in order to limit particulates emissions and allow efficient catalytic posttreatments.

Indeed, $NO_x$ decomposition (to $N_2 + O_2$) or reduction to nitrogen via catalysis represents the main challenge to sustain further developments of all lean-burn engines including the diesel fueled ones.

Table 7
$NO_x$ decomposition or reduction

| Challenges | Issues |
|---|---|
| Decomposition: low rate; oxygen and often $SO_x$ inhibited. | Innovative formulae still expected. |
| Reduction: over 80% $N_2$ yield at GHSV = 100000 $h^{-1}$ and 200–600°C. | Improve both activity and selectivity of existing catalysts, innovative formulae,selection of dedicated,reducing agents |
| $NO_x$ elimination under oxidizing medium is worldwide considered as a high priority research topic | |

Source: IFP.

The main difficulties concern the activity, still insufficient, the selectivity to nitrogen since most catalysts form $N_2O$ rather than $N_2$, and the stability of performances (hydrothermal aging).

Table 7 summarizes the main challenges and issues of this difficult research topic.

### 4.1.4. *Overall view of catalytic posttreatments*

As an overall view, exhaust gas posttreatment via catalysis has to overcome major challenges:

- finding innovative catalysts;
- getting major breakthroughs in the optimization of existing ones.

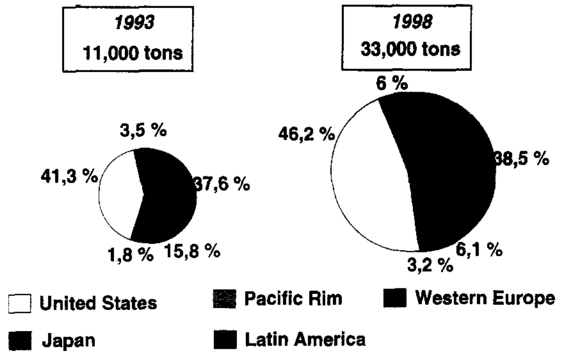
Issues will indeed arise from:

- significant improvements in basic knowledge on catalytic sites, kinetics and the reaction mechanism;
- catalyst testing and characterization procedures in an reconstituted exhaust gas medium;
- a parallel optimization of catalyst and process with an innovative technological approach.

## 4.2. *Fixed plant emission [1]*

Control of $NO_x$ emissions from power plants is being carried out commercially by selective catalytic reduction with ammonia. This proven technology, widespread in Japan and Western Europe, has experienced a large growth (> 20% per year) in the US.

As seen in Fig. 14, world consumption of



Source: IFP

Fig. 14. Selective catalytic reduction market.

SCR catalysts has tripled in five years.

Despite the impressive stabilities of existing catalysts (up to 10 years in gas turbine SCR) there are some needs today for catalyst improvements:

- inhibition of $SO_x$ oxidation to $SO_3$ (ammonium sulphate formation);
- improving the selectivity to nitrogen and resistance to poisoning (mostly towards arsenic as for the coal-fueled power plants);
- improving the resistance to abrasion (coal-fueled power plants).

Long term issues deal with the selective decomposition of $NO_x$ to $N_2 + O_2$, (as for $DeNO_x$ of lean burn engines) and the competing challenge with catalytic combustion technologies for natural gas fueled plants.

## 5. Water treatment [19]

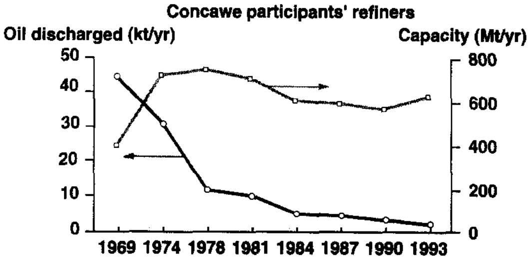
There are a number of water treatment processes that can be used independently or in combination to remove contaminants from waste water prior to discharge from industrial units. As proposed by CONCAWE for European refinery effluents, they may be divided into three main categories: gravity separation (API separators, plate interceptors, tank separation, etc.), advanced treatment (floculation, air flotation, sedimentation, filtration, etc.) and biological treatment (biofilters, activated sludge, aerated ponds, etc.). For example, in 1993, concerning a total number of 95 European refineries, 6 percent were using the first type of treatment, 8 percent the second and 85 percent the last possibility.

As was seen in Fig. 5, a 25 000 t/day refinery of the 1990s produces 15 000 t/day of sour water, which is treated according to one of these technologies and recycled. A make up of about 5% of outside water is necessary to compensate for losses.

Water discharges (tons of water/ton of crude oil capacity) have deeply decreased (8 in 1969; 3.4 in 1981; 3.0 in 1993) due to the increase of air cooling, recirculating water cooling systems and more extensive re-use of water.

The most frequently measured quality parameter, as for refinery effluents are concerned, is the hydrocarbon content (oil in water). Fig. 15 shows that, despite a stable total capacity of refineries of CONCAWE participants (since 1974), a continuous reduction in the amount of oil discharged has been achieved giving rise to lower oil contents in lower water discharges.

It is evident that these considerations related to a specific industrial sector of activities are very restrictive. However, considering the level of hydrocarbon contaminants, as mentioned, for example, for refinery waste water, it appears that a new category of processes will be necessary to comply with more drastic specifications. In this case, catalytic treatments, already scaled up for other discharges [20], will bring the solution sought after to solve the problem, espe-



Source: Concawe

Fig. 15. Trends in oil discharged and refining capacity (1969–1993).

cially for processing effluents issuing from petrochemical plants, for types of pollutants other than hydrocarbons.

## 6. $CO_2$ fixation and uses [21]

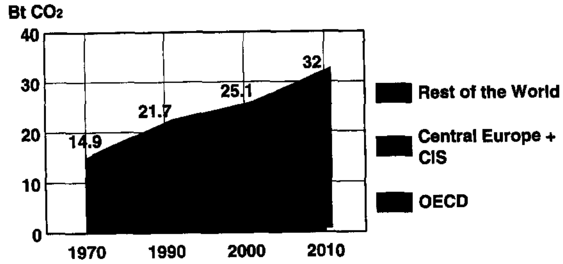
According to recent studies by the IEA (International Energy Agency), world emissions of $CO_2$ will increase by 50% in 2010 as compared to 1990. This increase will mostly come from the developing countries, as shown in Fig. 16.

Besides $CO_2$, CFC's, $N_2O$ and $CH_4$ intervene to increase the greenhouse effect.

It is difficult to estimate the total worldwide carbon dioxide consumption as reliable data for production and shipments are reported only for the position of the market sites served by liquid carbon dioxide and solid carbon dioxide produced by industrial gas companies. Large quantities of additional $CO_2$ are recovered for captive use or to be pipelined for enhanced oil recovery, with the possibility of recycling, thus, adding more confusion to estimates of the demand for carbon dioxide.

However, $CO_2$ has its main applications in oil and gas recovery, the food industry, water treatment and metallurgy. Marginal uses concern the manufacture of urea and some inorganic salts. Lastly, chemical upgrading of $CO_2$ deals with syngas production ($CH_4 + CO_2$) and methanol synthesis.

Except for enhanced oil recovery and urea manufacture, all applications of $CO_2$ result in the final discharge to the atmosphere as $CO_2$.



Source: IEA

Fig. 16. Changes in world $CO_2$ emissions.

Table 8
$CO_2$ emissions and true fixation in urea synthesis processes

| Mt | 1995 | 2000 | 2010 |
|---|---|---|---|
| $CO_2$ emissions | 24300 | 26900 | 32000 |
| $CO_2$ needs for urea | 62 | 70 | 90 |

Source: IEA/IFP.

Table 8 shows that a magnitude factor of 400 exists between $CO_2$ uses in urea and world emissions.

Hence, strong incentives exist to limit the increase of world emissions of $CO_2$. Catalysis is highly concerned with natural gas versus oil uses (higher H/C ratio), catalytic combustion and catalytic posttreatment of lean burn engines. Besides various attempts to develop futuristic technologies to lower $CO_2$ emissions, new catalytic routes are expected.

## 7. Overall view

Catalysis will remain the turntable for a clean future. Indeed, all industry is expecting new and improved catalysts to answer the demand of the future years.

The inevitable evolution of refining with the objective of upgrading the bottom of the barrel implies the development of resid hydrorefining and conversion together with new hydrogen production processes.

Cleaner and reformulated motor fuels will issue from new and improved catalysts and processes yielding clean products for reformulated gasoline, high quality diesel oil and, later, clean kerosine.

Processes for clean combustion will be developed, and future generation gas turbines with ultralow emissions, thanks to improved catalytic combustion technologies, will challenge the SCR ones. In addition VOC control will be met, via catalysis.

Reduction of pollution from fixed and mobile sources will develop. Among others, clean DeNO$_x$ technologies, non-precious-metal based catalysts (catalytic converters), improved SCR catalysts and innovative sulphur recovery processes (99.9% efficiency at least) are strongly expected.

Hazard minimization is expected to accompany environmentally friendly catalysts (capable of replacing today's liquid acids from aliphatic alkylation, for example) and the development of clean reprocessing technologies for safe catalyst disposal.

Limiting world CO$_2$ emissions is the most ambitious challenge in the field of catalysis. One can expect that indirect answers (depollution of lean burn engines, catalytic combustion, natural gas upgrading) and direct ones will issue in the future.

Indeed, the new and improved catalysts of the future will face these challenges, in as far as academic and applied research teams devote their best efforts and succeed, thanks to fruitful synergy.

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