LE MARCHE DE L'HYDROGENE DANS L'INDUSTRIE DU RAFFINAGE DES PRODUITS PETROLIERS EN FRANCE

THE HYDROGEN MARKET IN REFINING AND PETROCHEMICALS IN FRANCE

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SYNTHÈSE :

Le marché de l'hydrogène dans l'industrie du raffinage des produits pétroliers en France comporte plusieurs volets.

Au cours du processus du raffinage, de l'hydrogène est produit par réformage catalytique des produits légers et craquage catalytique des produits plus lourds issus de la distillation sous vide. Cet hydrogène est principalement consommé dans la désulfuration des fuels et la préparation des lubrifiants par craquage des produits lourds.

En France, treize raffineries appartenant à six compagnies produisent 73 millions de tonnes de produits pétroliers chaque année et dégagent un surplus d'environ 100.000 tonnes d'hydrogène principalement utilisé par la pétrochimie et l'industrie des engrais.

L'avenir du raffinage dépend de la qualité du pétrole brut, des caractéristiques des produits finis et du développement des marchés utilisateurs. Le processus du raffinage va devenir plus complexe d'ici 2005 entrainant une augmentation des quantités d'hydrogène nécessaire. Les raffineries pourraient alors connaître un déficit annuel entre 140.000 et 230.000 tonnes d'hydrogène.

Les sources potentielles d'hydrogène pour le raffinage recouvrent l'hydrogène sous-produit de l'industrie du chlore, produit par électrolyse de saumures, où l'hydrogène est actuellement utilisé comme combustible en chaudière ou brulé en torchère et l'hydrogène du marché des gaz industriels, issu du réformage d'un alcool ou d'un hydrocarbure.

Le choix dépend principalement de la stratégie des compagnies pétrolières.

EXECUTIVE SUMMARY :

The french hydrogen market on industrial sites can be divided into three main parts.

Captive hydrogen is produced by thermofor catalytic reforming, catalytic cracking and hydrotreating of vacuum distillates, and is consumed in hydrotreating of petrol, hydrodesulfurization of gasoil and domestic fuel oil, hydrocracking and hydrofining of lubricants.

By-product hydrogen is burnt in boilers and flare stacks. Merchant hydrogen is sold to users on the open market.

Currently, thirteen refineries belonging to six companies produce 73 million tonnes of petroleum products each year in France and release annually a surplus of some 100,000 tonnes of hydrogen.

The future of refining industry in France depends on the quality of the crude oil, the specific characteristics of the end products, and the developments in user markets. The refining process is likely to become more complex by 2005 with an increase in hydrogen requirements. Refineries could then undergo an annual deficit between 140,000 and 230,000 tonnes of hydrogen.

The choice of the appropriate process to cover this shortfall depends mostly on oil companies strategy.

THE HYDROGEN MARKET IN REFINING AND PETROCHEMICALS IN FRANCE

PRESENT STATUS AND TRENDS FOR 2005

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INTRODUCTION :

The EDF, French electrical utility, Research and Development Division (DER) works in close collaboration with industry to design innovative and cost-effective electrical manufacturing processes. The DER particularly focuses on processes that produce hydrogen, either as a chemical byproduct (for example, the electrical pyrolysis of methane), or as a valuable chemical trough the electrolysis of water.

In order to determine the investment to be made in this sector of mid-term research, EDF considered necessary to carry out a survey of the hydrogen market in France in the oil sector, concentrating on the target year of 2005.

The methodology for this study included two separate time scales:

- In-depth research on the industrial sites concerned to obtain a picture of overall hydrogen consumption at the present time, and therefore an overview of industrial requirements. The development of requirements was also examined through future projects and present trends. All research work was carried out by the CEREN (Centre d'Etudes et de Recherches Economiques sur l'Energie-Paris);

- Three possible scenarios were designed, setting the values of factors influencing the future of refining and petrochemical companies relative to their future hydrogen requirements.

This study is therefore in two parts. The first part deals with hydrogen requirements at the present time and forecasts for the year 2005. The second part deals with real or possible hydrogen exchanges between refineries and the petrochemical or chlorine production industry, and considers the strategies of industrial gas suppliers.

French hydrogen production sites are shown on Figure 1.

I REFINING :

1. Present situation

1.1. Refining companies

13 refining plants are in operation in France, which processed 75 million tonnes of material in 1989, including 69 million tonnes of crude oil. The companies involved are:

- **CRD Total France** with three refineries in Flanders, Gonfreville and la Mède;
- **Elf France** with plants in Donges, Feyzin and Grandpuits;
- **Shell Oil** based at Petit Couronne and Berre;
- **Esso S.A.F.** with refineries at Port Jérôme and Fos;
- **Mobil Oil Française** based at Notre Dame de Gravenchon;
- **British Petroleum** at Lavéra.

In addition to these twelve sites, the **Reichstett** refinery (near Strasbourg) is a cooperative of all of the above companies, with the exception of Esso.

French refineries production stands about 73 million tonnes of various products each year, mostly petrol for vehicles and supergrade petrol (18 Mt/year), diesel oil (13 Mt/year), domestic heating oil (14 Mt/year), heavy fuel oil (11 Mt/year), aircraft fuel (5 Mt/year) and bitumens (3 Mt/year).

1.2. Hydrogen in excess at present time

Crude oil is a complex mixture of various species. Refining ensures separation by atmospheric and vacuum distillation, and bleaching, converting heavy ends into light ends.
Hydrogen is used in the bleaching process (diagram 1). The two hydrogen production stages are catalytic reforming and catalytic cracking. Hydrogen consumption stages are hydrotreatment (preventing catalyst contamination and improving derivative quality), hydrodesulphurization of diesel oil and domestic fuels, hydrocracking of vacuum distillates and hydrocracking and hydrofining of oils.

Total hydrogen uses for 1989 included almost 100 kt consumed in boilers or flare stacks (diagram 2).

Hydrogen (in kt/year)	SR 1	SR 1 variant	SR 2 (central scenario)	SR 2 variant	SR 3	SR 3 variant
Production	248	248	337	337	240	240
Uses	392	435	495	528	425	467
Deficit	144	187	158 1	191	185	227

Table 1: Hydrogen forecasts in refining for 2005

A hydrogen deficit, comprised between 140 and 230 kt/year, could then be expected around the year 2005.

II HYDROGEN EXCHANGES

1. Actual sources of hydrogen for the oil refining industry

1.1. Petrochemicals
Of the 2.5 Mt of ethylene produced in1989 by the eight French steam crackers, 1.5 Mt were produced at the five sites where refining and petrochemicals plants are in close association
Hydrogen production is linked to ethylene production, and amounts150 kt/year for the 8 french sites and up to 100 kt/year for the above five sites.
For these plants 43 kt hydrogen is used in refining. The rest is used in petrol processing, chemical hydrogenation, hydrodealkylation of toluol, or is mixed in the fuel-gas pool.

1.2. Small contribution from styrene production
In organic chemistry, hydrogen is produced through the industrial preparation of styrene, carbon black, solvents (acetone), and acetylene. Only styrene production provides hydrogen on refinery integrated sites, supplying only 1 kt in 1989.

1.3. Availability of hydrogen in the year 2005
Activities in the range of the petrochemicals industry are forecast to develop in various ways between now and 2005. Self-consumption of hydrogen should increase to meet the requirements of hydrotreatment of various products.
Styrene production should also increase, as well as hydrogen availability in this process.
Overall, the hydrogen as a by-product of petrochemical industry should remain at the present level.

2. Possible hydrogen sources for refining

2. 1. Chlorine
In 1989, ten plants produced 1.43 Mt of chlorine through chlor-alkali process, of which 58% came from a mercury cathode process and 42% from a diaphragm or membrane process. 40,000 tonnes of hydrogen were produced as a byproduct. Hydrogen is used as burner fuel (58%), as process raw material (41%) and 1% being flared.

2. Perspectives for 2005

2.1. Main factors

The factors influencing the future of refining industry in France are related to government regulations and developments in the oil market.

Regulations set the limit for sulphur content in oil products (for example, for diesel oil the target for 1995 is 0.15%, and for 2005 is 0.05% or 0.1%). There are also legal regulations setting the levels of the various petrol product additives or components : lead, aromatics, oxygenated compounds, etc.

The status of the market sets the sulphur content of the crude oil supplied, the demand for petroleum products (type and amount), and in particular, the demand share of lead-free supergrade petrol.

2.2. Hydrogen deficit in 2005

Changing regulations and altering trends in market forces complicate the refining diagram with processes to make the best use of heavy ends: deep conversion, visbreaking and partial oxidation. The large share of the market taken up by lead-free supergrade petrol means that further research will be needed into octane rating (isomerization, alkylation, oxygenated additives), while keeping to the legal limits (benzene extraction from the catalytic reformate).

In correlation, the hydrogen situation will have changed considerably since 1989.

For the refining industry, the three main scenarios retained are listed below:

SR1: Important demand reduction, especially for fuels and 2 production sites closed:
- possible access to low sulphur crudes for small refineries, considering the discovery of new low sulphur reserves;
- severe restrictions on the sulphur content of diesel oil and domestic fuel;
- comparatively large share for petrol compared to diesel oils;

SR2: Demand at the same level :
- all sites retain the same crude oil supply structures, taking into account the high price difference between low sulphur and high sulphur quality;
- levels of refinery operation are high enough to ensure continued competitiveness and to keep down petrol and diesel oil imports;

SR3 : Two additional limiting factors are added to SR2 :
- the three most outdated plants are closed down,
- there is a severe crackdown on petrol aromatics content.

A variant of these three situations was included in these schemes with an increase of demand in high quality lubrication oil (obtained by bitumen hydrocracking). Hydrogen production and consumption in refineries for the year 2005 are then shown in table 1.

Perspectives:
Three possible ways for development are shown in table 2. In all cases, hydrogen generation in membrane electrolysers outruns the mercury process.

Reference	SC1	SC2	SC3
Hypothesis level	High	Medium	Low
Chlorine production level	1,43 Mt/yr Long-term stable demand	1,43 Mt/yr to 0,36 Mt/yr Mercury units closed	0,71 Mt/yr Mercury units closed and not replaced
Hydrogen avalaibility	40 kt/yr	30 kt/yr	20 kt/yr

Table 2: Hydrogen from chlorine production in 2005

Uses and distribution of available hydrogen will depend mainly on industrial gas suppliers distribution strategies.

2.2 Gas companies
In Europe, marketed hydrogen represents only 0,7% of total hydrogen production, 85% of which is in gas form.
At present time, hydrogen is not delivered to refineries by gas companies on the reason these plants are considered autonomous with an internal supplying logic.
Two cases are identified for the future:

SG1 : No active strategy for hydrogen in France, even from chlorine manufacturing processes. The oil refining industry is considered as autonomous, excess hydrogen is burnt in 1990 and an self-sufficient hydrogen production system is set-up for 2005

SG2 : In the short term, hydrogen is bought from the refining industry and the chlorine industry for traditionnal markets (electronics, space and metals). In the long term, development of independant hydrogen production units by gas companies for refineries and possible extension of hydrogen local networks; long term contracts with chlorine industry.

CONCLUSION

The oil refining industry hydrogen requirements for 2005 and the hydrogen exchanges within the chemical industry are listed in diagram 3.
These three scenario are set up from the differents assumptions for each sector.

Overall, required hydrogen levels will exceed available hydrogen levels despite the contribution of the chemicals sector, and irrespective of gas supplier strategy. This

deficit could reach 75 to 200 kt/year, according to the above scenarios.

Hydrogen deficit in 2005	SR1	SR2	SR3
SG1	107	127	197
SG2	76	90	175

Table 3 : Balance of hydrogen requirements for oil refining industry

This deficit should be made up by hydrogen production, either through the gas companies (possibility considered by SG2) or by self-production in refining industry.

Figure 1

REFINING, PETROCHEMICAL AND CHLORINE SITES

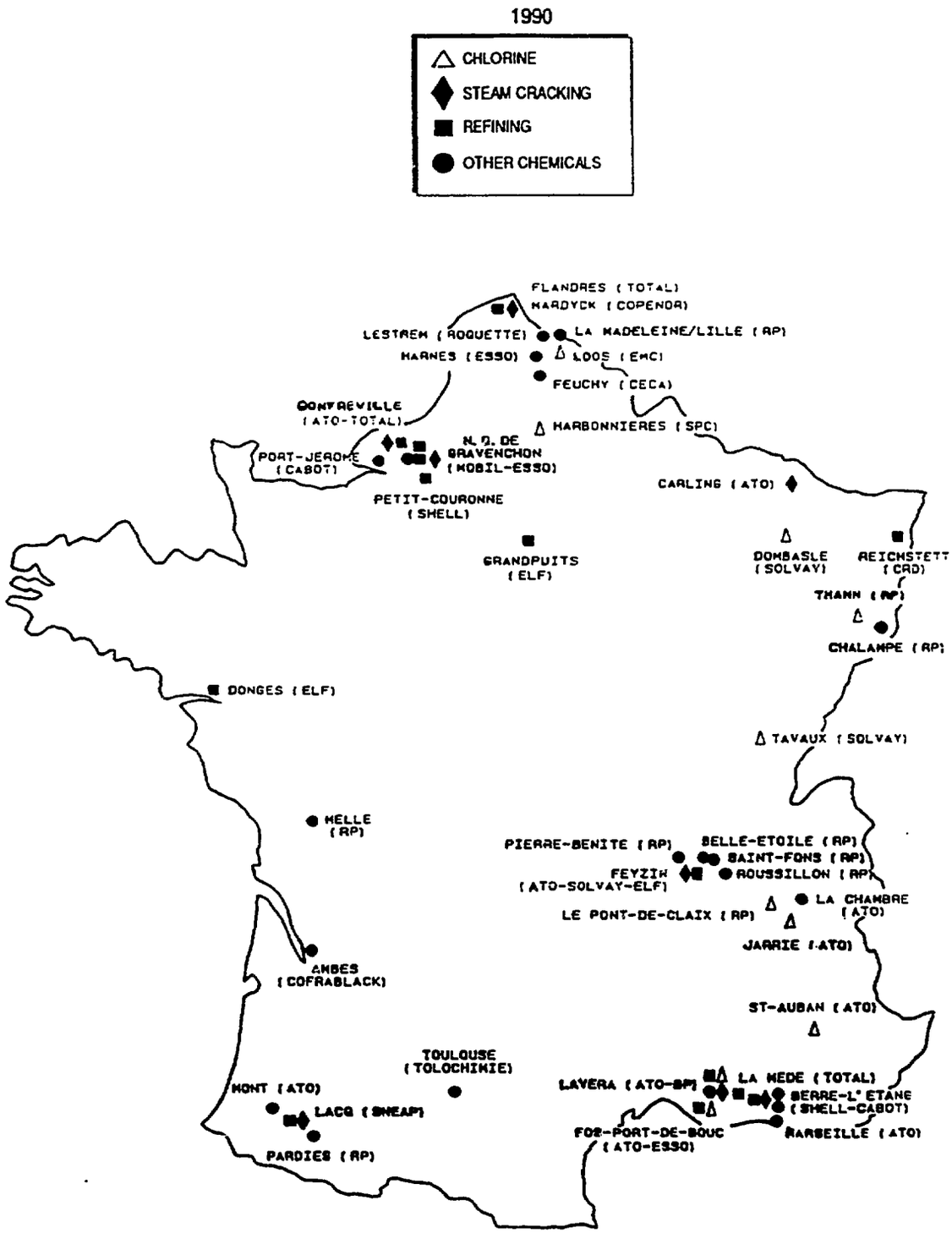

Diagram 1

REFINING : DIAGRAM

1989

Loads in millions of tonnes

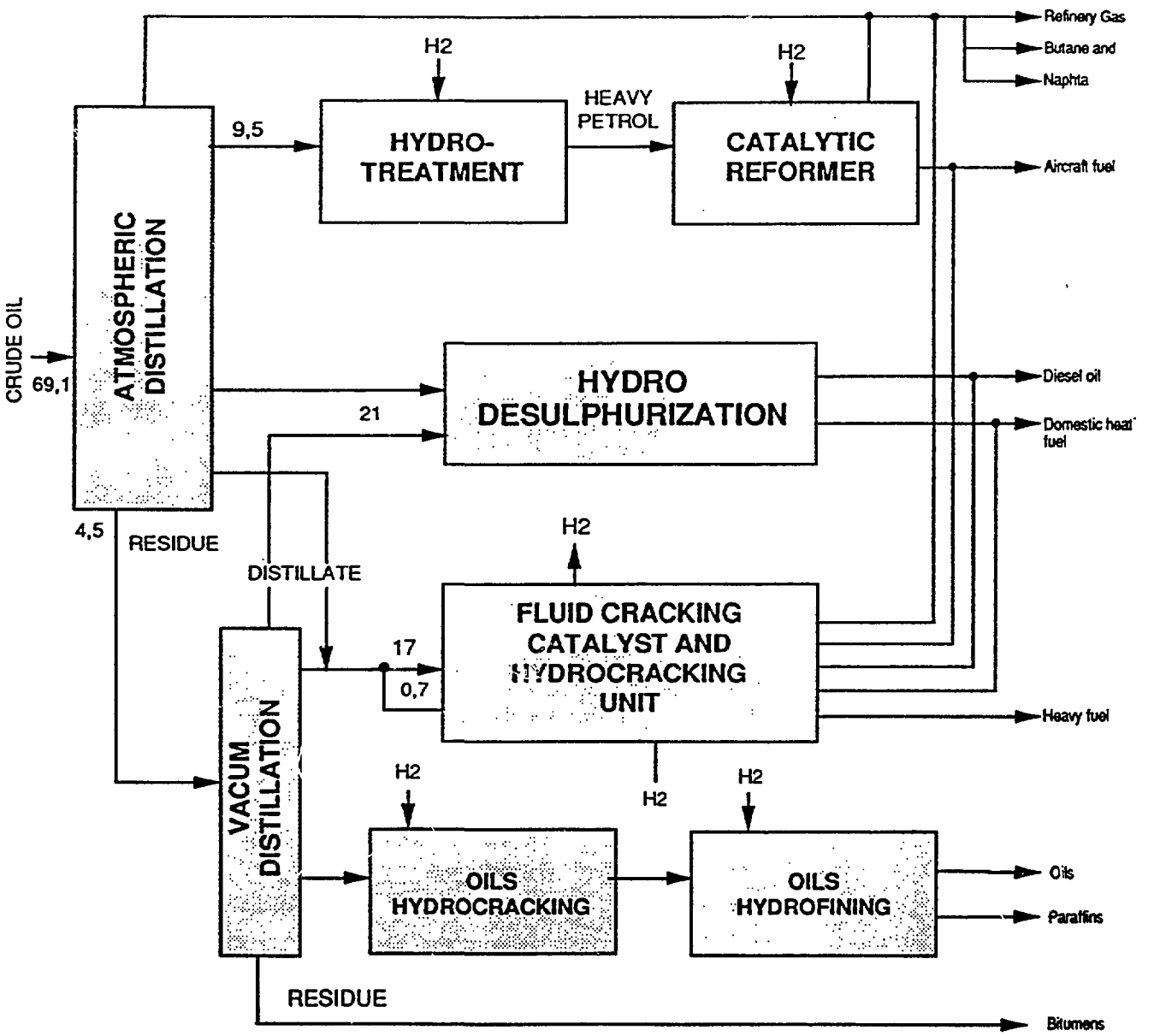

Diagram 2

REFINING : HYDROGEN BALANCE 1989

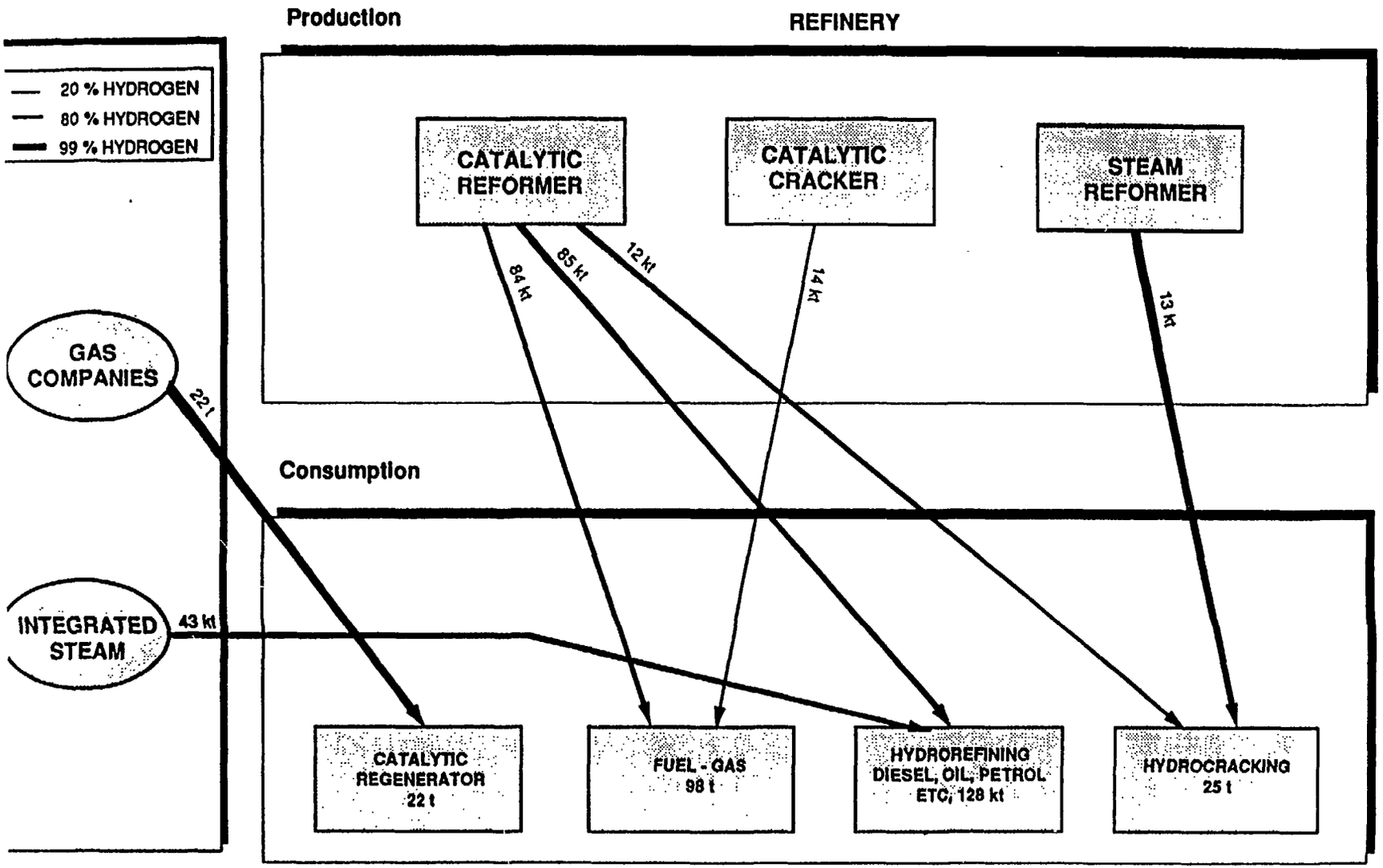

Diagram 3

HYDROGEN AVAILABILITY AND REQUIREMENTS