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D03714

United Nations Industrial Development Organization

Distribution
LIMITED

ID/WG.123/25
4 July 1972

Original: ENGLISH

Expert Group Meeting on Transfer of Know-how
in Production and Use of Catalysts

Bucharest, Romania, 26 - 30 June 1972

TRENDS IN THE DEVELOPMENT OF CATALYTIC PETROLEUM REFINING PROCESSES[1]

by

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CONTENTS

1. [illegible] OF CATALYTIC PROCESSES DEVELOPMENT

The trends in the development of catalytic processes used in oil processing are a direct response to some of the major challenges facing the contemporary world: providing adequate resources to meet the steeply increasing world-wide energy demand and providing feedstocks for the great organo-chemical industry which is increasingly turning into a "petrochemical" one.

As regards the prospects of world energy demand and of ways to meet it, a massive growth in energy requirements is predicted amounting to more than 50% over the 1970 level and more than 50% of these requirements are to be met by oil. In order to meet such demands, the crude processing capacity in 1980 shall have to soar to 170% of the 1970 figures (1). Assuming the crude processing capacity to have been 2.6 billion tons/year on January 1st 1970, it may be assumed that it will be in excess of 4.2 billion tons/year in the late seventies (2).

Considering the present distribution pattern of oil products and the trends manifested in various countries, it may be assumed that also, in the future, the developments in crude processing will be differentiated according to social-economic conditions and to the resources available in particular countries. This differentiated development is tellingly illustrated by the oil products distribution pattern in the U.S.A. and in Western Europe. The comparison shown in Fig. 1 is significant in that the two opposed tendencies prevailing in the management of crude processing are presented : in the U.S.A., the crude processing is oriented towards maximising of gasoline production, while in Western Europe it is directed towards obtaining of heavier fuels (1). This is naturally reflected on the share the catalytic techniques take in crude processing: in Table I, a comparison is given between the capacities of the main processes as reported to the crude processing capacities in Western Europe and the U.S.A.

TABLE I

Process capacities in refineries as reported to total crude processing capacity

	Western Europe	U.S.A.
Crude capacity	100	100
Catalytic cracking and hydrocracking	8	51
Catalytic reforming	13	22
Alkylation	1	7
Thermal cracking	4	13

The present development trends have been computed from the capacities of the units expected to be built in various countries after January 1970. As the construction of these units may be expected to take about three years, this computation in fact offers a most up-to-date picture of the trends in the building of refineries around the world. The capacities of various processes, also reported to crude capacities, are given in Table II (1). Note that the table leaves out thermal cracking processes as no data on their capacities have been available; most of the projects refer to coking units.

TABLE II

Present day developments in crude processing in different parts of the world

	North America	Latin America	Western Europe	Middle East & Africa	Japan	Asia and Australia
Crude capacity	100	100	100	100	100	100
Cracking :						
- Catalytic	17.4	28.7	8.4	17.7	13.3	0.0
- Hydro	33.1	1.6	3.8	15.1	9.5	0.0
- Total	50.5	30.3	12.2	27.8	22.8	0.0
Cat. Reforming	44.5	10.9	1.6	22.2	12.2	10.5
Alkylation	6.4	0.0	0.8	1.2	0.0	0.5

Comparing the data in tables I and II., we may see that the trends previously presented for Western Europe and the United States have not changed greatly. It can be noted that in North America but also in the developing countries in Africa and Middle East, there is a sharp increase in the application of the hydrocracking processes. This is an expression of the desire to obtain higher yields from petroleum resources, thus making it possible to get middle distillates such as jet fuel, Diesel fuel or high-quality lube-oils. It should also be noted that the interest for catalytic cracking and reforming processes is maintained in all areas.

Another major challenge facing the oil processing industry is that of supplying feedstocks to the chemical industry, that is to say, of making "petrochemistry". Although such feedstocks make up at present a rather low percentage of the crude, well below 10%, it is expected that such demands shall more than double in 1980 as compared to present-day figures (1). And, to meet these requirements, the catalytic processes, such as gasoline reforming, hydrotreating of pyrolysis products, hydrodealkylation, etc., are relied on to play a major part. The flow scheme of some refineries will therefore be adapted to suit these objectives also, resulting in the so-called "chemical refineries", just as some other refineries will undoubtedly continue to be oriented towards the production of lubricants.

Among the present preoccupations leaving their mark on the development of catalytic processes, mention should be made of the automation and optimization of management of such processes, and of the attempts made to avoid pollution of the environment, all these aspects affecting to a considerable extent, the economics and choice of operating and constructive solutions for the new units.

While aiming at higher-quality oil products, the possibility has been considered of utilizing some more general terms to denote the quality of oil products, besides the ones in current commercial use. Such a broader term, also related to the refining treatments of various fractions can characterize oil products in a more complex manner and can offer an orientathan conventional process flow sheets. Thus, it has been found that all product characteristics are determined largely by the molecular weight and hydrogen content, the former being correlated with distillation, and the latter with physico-chemical properties (5). Such a characterization becomes all the more interesting as it can be related to the most widely used processing technologies available, viz., catalytic processes. From an economical and chemical point of view, one is often faced with the problem of selecting and combining the most advantageous techniques from the two major groups available to the refiners today: "hydrogenative" processes, e.g. hydrocracking, or "non hydrogenative" processes, e.g., catalytic cracking.

Since petroleum fractions are dependent on the hydrogen content over a given distillation range, it has been found to be of interest to express as a condition the minimum hydrogen content in order to meet certain quality requirements. This content decreases as the distillation range of the respective fraction increases, from approximately [illegible] for the liquified gases, down to less than [illegible] for fuel oil. In the following, some examples shall be given to illustrate the possibilities opened up by this approach.

The severe octane number conditions, imposed by many countries on motor gasoline, are known; thus, "premium" gasolines obtained today by various techniques, especially by catalytic ones, have a content of about 14% H. In order to both ensure a good performance in the motor and to meet antipollution requirements, this content should be no less than 13.2%.

Combustion or engine performance of jet and Diesel fuels can also be expressed by the hydrogen content of the respective fractions. Thus, relations have been found between this content and the Diesel index of fuel oils. For instance, for a satisfactory Diesel fuel with an D.I. = 50, the hydrogen content will be around 13%.

[illegible] of their [illegible], is governed by a number of factors, among which economic considerations prevail. Considering as a typical criterion the maximum hydrogen content of products and the fact that hydrogen addition to the fractions resulted in refining, implies rather high costs, characteristic for pressure hydrogenative processes, it is easy to understand the interest shown for those flow schemes and processes which maintain a maximum hydrogen content in the products as compared to the input hydrogen fed in with the crude. This "hydrogen efficiency" of processes has been continually improved, resulting in higher selectivity and a lower percentage of coke and non-saturated gases. A typical example in this respect is furnished by the late development of cracking over zeolite catalysts.

The increasing number of cars in use poses besides economic and quality requirements for products, the problem of keeping down air pollution in the great urban centres. Of course, the severity of pollution problems is different with each country, depending on the number of cars in use, on their density on traffic routes and various climatic factors. Regardless of those variations, pollution problems are faced everywhere, the tendency of increasing the number of gasoline vehicles assuming a general character; as a consequence, despite the fact that research projects and even elaboration of anti-pollution laws are under way only in those countries with the highest density of road traffic, affirmation of some such tendencies is of interest to all countries. Those tendencies actually delineate to a great extent the future developments in oil refining, and implicitly, the development of catalytic processes and of catalysts.

It should be of a practical interest to discuss the problem of lessening pollution in the case of spark-ignition engines in relation to the characteristics of gasolines and the trends of improvement of such characteristics.

Since lowering of gasoline volatility entails the cold start and [illegible] problem, this cannot be pushed very far. As compared to the usual Reid vapour pressure limit of 520 mm Hg col., 10 psi RVP respectively, no lowering below approx. 465 mm Hg. col, 9 psi RVP respectively, is expected. Also, it is not assumed that any modifications of distillation characteristics would be made (4).

The loss of aromatic hydrocarbons is carefully controlled because of their toxicity and of their role as carcinogeneous and smog producers. Aromatics are besides responsible for an increase in gasoline sensitivity and increased deposits in engines. For all these reasons, although no legislatory steps are expected, it is desirable to obtain gasolines with as low a percentage of aromatics as possible. It is noteworthy however, that the avoidance of air polution with aromatics is being achieved largely by motor combustion, completed by catalytic conversion of engine exhausts.

Gasoline sulphur is being drastically brought down today through catalytic refining processes, and the sulphur content is expected to be brought even lower through the more intensive use of catalytic hydrotreating processes, even where sulphur-rich crudes are consumed.

Olefines are quoted as producing photo-chemical smog, a problem characteristic for California, but which may become of concern for other hot climate countries as well. This, along with their depreciating effect on the Research Octane Number makes it likely that some limitations on their concentrations in gasolines would be introduced, e.g. max. 15%.

As regards metallic additives in gasolines, especially lead ones, ample disputes have been heard; it has been concluded today that in future, the metallic additions would be greatly diminished or even eliminated altogether.

For a first stage, no increase of gasoline octane number is expected; it is noticeable, even in the U.S.A., the tendency to manufacture lower octane number engines. Thus, on the average, the research octane requirements of the automobiles manufactured in the U.S.A. in 1971 have been of 91 RON. Some predictions even go so far as to assume a decrease of RON down to 95 for premium gasoline and 85 for regular gasoline in the U.S.A., after the mid-seventies. However, taking into account the fact that the present ON levels shall have to be attained without additives, the average antiknocking value of gasolines shall have to be improved through increased severity of refining processes, that is to say, by coming up with different flow-diagrams where catalytic processes will continue to play a predominant part.

By reason of a marked decrease in fuel consumption and even of lowering the crude requirements for covering the gasoline demands, some specialists, however, envisage a future increase of the octane number of lead-free gasoline. Thus, it is predicted that in the U.S.A., the level of 95 RON will be attained in a first stage and then a 97 RON level (4,5,6).

Based on the above considerations, in table III. is given a synopsis of quality predictions for the gasoline which will be utilized most in the U.S.A. in future.

TABLE III.

Future predictions on motor gasoline (U.S.A)

Gasoline grades	2 minimum
R.O.N. (average)	95 - 97
M.O.N. (average)	min. 87
Metallic additives contained	nil
Vapour pressure (RVP)	min. 420 mm. Hg.col. (9 psi)
End boil point*	less than at present
Sulphur content	less than at present
Olefines content	bromine index max.30
Aromatics content	no greater than required by engine characteristics

[illegible] obtaining higher octane number gasolines by various refining schemes have been considered, applying the available or improved processes in different arrangements, and the conditions for the production of specific gasolines have been estimated in terms of economics (4,5,6). In these alternative diagrams are present in all cases C_3-C_4 alkylation, gasoline hydrofining and reforming, catalyst cracking of some heavy distillates and for residue processing a thermal process (visbreaking, delayed coking). In the deeper processing alternatives there are added butane and C_5-C_6 cut isomerization, hydrocracking of various distillates, hydrogenation of cracking recycle or dehydrogenation of C_3-C_4 cut to increase olefines potentiality for alkylation, all these processes implying various separation techniques.

The different flow diagram variations have been labelled for instance, as offering, in principle, a solution to the problem of producing gasolines of the required quality by one of two ways : (1)

1. "Aromatics" route
2. "Aliphatics" route

These two refer mainly to the processes employed for the conversion of paraffinic hydrocarbons (7*). The "aromatic" route is based on the reforming process, which, besides naphthene dehydrogenation, achieves a major O.N. gain by aromatization of C_7^+ paraffins. The improvements on catalysts and reforming processes in recent years have made it possible to operate under conditions of higher severity (lower pressure, lower H_2 recycle ratio) for the production of higher octane number gasolines, at a higher liquid and hydrogen yield, due also to improved catalyst stability.

In order to make the "aliphatic" route [illegible], the yield and octane number potential of an average naphthenic gasoline is shown in Table IV; this gasoline underwent a processing along the route called "aliphatic" (4). In the first column is given the analyses of the gasoline which, being processed by dehydrogenation and dehydroisomerization, gives the yields and octane numbers in column two and three respectively. If, by some process, the paraffins could be converted into their respective alkylates, an 93.5 ON product would be obtained, with the same yield, and, finally, an 103.6 ON gasoline at a 94% yield. Should such a conversion be possible, it would certainly be most advantageous.

TABLE IV.

Yield and Octane number potential of a medium naphthenes content gasoline (4)

	Feedstock	Yield	Octane No.
Paraffins, % vol.	50	50	93.5
Naphthenes, % vol.	40	34	115
Aromatics, % vol.	10	10	115
Total :	100	94	103.6

In order to boost gasoline production along this line, besides production of cat-cracker gasoline, the production of C_3-C_4 olefines for alkylation would have to be augmented. This could be achieved either by more severe catalytic cracking, and subjecting to cracking also some hydrogenated recycles, being thus able to obtain a cracking conversion as high as 96%, or by combining catalytic cracking and reforming with pyrolysis of some gasolines, or even of some light hydrocarbons (e.g. isobutane). Among others is also quoted a hydrocracking process by which paraffinic hydrocarbons in the gasoline boiling range are broken in the middle virtually without methane or ethane and with little propene production (4). The feedstock for such a process can also be a heavy gasoline fraction or a raffinate derived from reformed gasoline. In figure 2 are given the flow schemes in an usual catalytic processing in figure 3 is shown a process flow for light fractions which yield high octane number aromatic gasoline and a paraffinic fraction which constitutes the feedstock for the catalytic or thermo-catalytic processes mentioned above.

These widely different ways to meet requirements make it necessary, in order to select a particular approach, to make complex economic evaluations in many variants which should take into account, besides the technical and economic characteristics of the processes, also the types of feedstock available, the unit capacities and the additives allowed. Such a calculation has been made on a computer, assuming four additivation levels, i.e., 3.0 - 0.5 - 0.25 - 0 expressed as TEL/gal., and four crude capacities, i.e., 4,800, 9,600, 18,200 and 36,400 cu.m./day (7). These calculations have shown that the production pattern of the refineries would change drastically once the additivation level is lowered, but is virtually unaffected by changes in throughput. Besides the basic processes mentioned previously, i.e., distillation, hydrofining, reforming, catalytic cracking, alkylation and delayed coking, it appears imperative that, as additivation is being lowered, new reforming processes should be brought into play along with the introduction of additional catalytic processes such as C_5-C_6 isomerization, hydrocracking as an additional source of isoparaffins for alkylation, C_3-C_4 dehydrogenation, as well as new hydrofining and alkylation capacities. These calculations would show on the other hand that, by maintaining a low additivation level, i.e. 0.25 cc TEL/gal, sizeable cuts in installed costs would be made possible. In Figs. 4 and 5 are shown the refining schemes mentioned, where, in dotted-line frames, are shown the processes called for lowering of gasoline additivation levels. However, regardless the limit to which the additivation levels can be lowered, the ever increasing significance of catalytic processes becomes evident.

The increasing emphasis laid on the building of refineries oriented towards production of feedstocks for the chemical industry, has been pointed out previously. This emphasis is explained by the higher market value thus obtained for crude, as well as by the fact that only thus can some countries cope with shortages of some products, such as benzene.

In Fig. 6 is given the flow scheme of such a refinery based on chemical processing, in which catalytic reforming and pyrolysis are key processes (8). Besides gasolines, kerosene and fuel oils, individual aromatic and olefinic hydrocarbons are obtained as products of high value. Or course, such a flow scheme can be completed with other catalytic and separation processes which make for a deeper processing depending on market demand or other conjunctures. Among these we should mention pentane isomerization and m-xylene isomerization.

As an example of the actual trends, Fig. 7 shows the rate at wich processes are being added to USA refineries (1).

II. CATALYTIC CRACKING

Among the catalytic processes employed in crude refining, Catalytic Cracking looks back on a history of 30 years of steady progress. Since May, 1942, when first applied in crude processing, the fluid-bed catalytic cracking process has known a most dynamic development and has remained to this day the main way to convert heavy distillates into gasoline and petrochemical feedstocks. It can be seen from Fig. 8 how the significance of this process had increased between 1940-1970.

In 1954 the growth rate was 18 % in USA and 41% outside the United States. Between 1955 and 1963 the cat-cracking capacity had increased by 8 % in the USA and by 6 % outside the United States, amounting to 42 % and 8 % of the total crude throughput respectively (9).

Besides the other cat-cracking processes - fixed and mobile bed - the fluid bed process has gained prominence from the beginning; in 1955 it accounted for 72 % and 1965 for 82 % of the entire cat-craking capacity in the USA and for 79 % outside the United States.

Following 25 years of service, in 1967, FCC was being written off by some as a tired holdover. The growth rate has settled at about 50 % of the total crude capacity in USA. The leading position in the growth race was taken by

./.

hydrocracking, the quickest conversion process then. Since that time, [illegible] of catalytic cracking has been brought about by the introduction of zeolite catalysts. These new catalysts, by the higher conversions and better selectivity they attain, have lead to the conservation of more than 30 million m3 crude in U.S.A. only

The savings brought about by such catalysts have been estimated at 250-350 million dollars/year (10).

More recent statistic data show that between January 1st, 1969 and January 1st 1971 the cat-cracking capacity had increased by about 1.25%/year in the U.S.A., i.e. from 923,000 m3/SD to 959,000 m3/SD (12). It has been conceded, however, that this growth does injustice to the true state of affairs, since FCC growth was 3%, but the capacity decrease in other catalytic cracking processes has brought down the total growth rate (13).

These capacities account for 50% and 47.[illegible]% of the crude processing capacity respectively, and indicate a slight re-distribution of crude among various processes.

The world-wide distribution of cat-cracking capacities is evident from the data given below (1st January 1969) (11) :

Area	Cat-cracking capacities m3/SD	Percentage of crk. through- [illegible] %
Africa	4,000	3.4
Middle East	13,300	3.3
Asia & Pacific Area	57,600	7.2
Western Europe	109,000	5.5
South America	95,000	12.-
North America	1,010,000	68.3

Owing to the decidedly leading position of Fluid Catalytic Cracking on account of the major advantages it offers, our further considerations shall deal only with this type of process.

The application of the fluidization technique of finely divided solids renders this process more complex than the fixed-bed catalytic process.

As we have already shown, after the 1942-1954 period in which the process was brought to maturity, the main incentive for development during the next 10 years was the covering of increasing demands on the oil product market. The yields were oriented within possible limits towards maximizing gasoline production (the case of the U.S.A.) or petrochemical feedstocks and middle distillates production, respectively, as it was the case of the markets in Europe and elsewhere.

The main trends within this period were:

- catalyst development
- construction of larger units with capacities up to 1,500 m^3/SD.
- increases of operating cycle lengths
- constructive refinement on existing units aiming at elimination of bottlenecks
- refinement in unit design
- operating improvements

The share of synthetic silica-alumina catalysts has grown over that of the natural ones, and the 25% or 28% Al_2O_3 catalyst has claimed increasing attention as the most stable and active. At the same time, the technique of micro-spherical catalysts manufacture has generalized, which, in turn, by improved circulation, have simplified unit operation and have decreased catalyst losses and equipment erosion.

Setting up of larger units has brought installed costs per capacity unit down to about 1/4 of the 1954 level (9).

Mechanical sophistication, on-stream repairs and improvements of operating conditions have increased cycle lengths from 1-2 years to 2-3 years on the average, bringing down operating costs.

[illegible] in the air distribution system of the regenerator and replacing reciprocating type [illegible] with turbine compressors, have [illegible] to eliminate the main bottlenecks in the FCC units, i.e., coke combustion capacity and gas handling equipment performance.

In design novelties we could mention the location of the regenerator below the reactor level, which has lead to better regeneration by an increase in oxygen partial pressure and better energy recovery by the possibility offered to burn carbon monoxide into dioxide in CO-Boilers. The design of low-pressure turbines has allowed expansion of flue gas in turbines, and the energy thus recovered provided the driving power for the regeneration air blower (9).

In unit operation some basic approaches have changed, leading again to an increase in overall process efficiency. In order to increase the maximum yield of gasoline [illegible] crude, the recycle ratio was brought up from 20% to [illegible] in the 1955-1964 period. In order to avoid over-cracking of fresh feed, the catalyst contact time of feed has been shortened by lowering catalyst level in the reactor and [illegible] riser cracking.

The optimization of the interactions between the many operating variables of the fluid bed catalytic cracking has now become a field of application for electronic computers. In 1965, the U.S.A. refiners were employing 15 [illegible] for optimization of some FCC units (13), and product value increased consequently by 5%.

Improvements have been recorded in FCC feed preparation by lessening vacuum-tower entrainments, [illegible], solvent extraction or coking of residual feedstocks in order to lower the metal [illegible] of feedstocks before cracking.

The catalytic hydrogenation of feedstocks [illegible] improves [illegible] ability, by [illegible] the [illegible], [illegible], Conradson carbon and aromatics contained, aiding to [illegible] of coke production and [illegible] of gasoline [illegible] higher [illegible] susceptibility.

Catalytic cracking, due to its capacity of processing heavy feedstocks, has contributed to a substantial decrease of residual fuel in U.S.A. between 1955 and 1967 from 15% to 5% in good agreement with market changings (9).

Present position and future trends

The present position of catalytic cracking as a major process of heavy feedstock conversion should be viewed in conjunction with the introduction of hydrocracking, which, due to its great flexibility, has been welcomed as the most suitable tool for the conversion of the heavy ends of the barrel into a variety of products with remarkable marketing potentialities. Hydrocracking is at present much more expensive than catalytic cracking, which, in its turn, due to the boost given by the introduction of zeolitic catalysts, will continue to hold a major share in the production of gasoline.

Since most of the technological improvements brought to the catalytic cracking lately are centered around zeolite catalysts, the latter deserve a closer scrutiny.

Out of the great variety of crystal aluminosilicates, known also as molecular sieves, the ones noted X and Y have gained paramount importance in the field of industrial catalysis. Certain cationic forms of these "ion-exchangers" and especially those containing trivalent rare earth ions, are remarkably stable even at high temperatures and in the presence of steam. The cracking activity of such cationic forms is higher than that of amorphous silica-alumina by several orders of magnitude and would permit the use of much smaller reactors. This development is, however, limited by two basic restrictions related to the process itself. In a thermally balanced cyclic process such as the reaction-regeneration process, cracking reaction rate cannot exceed coke burning rate; on the other hand, the catalyst takes on also the important role of a heat transfer medium between regenerator and reactor.

The problem of heat transfer has been overcome by dispersing 5-25% zeolite in a silica-alumina gel which assumes the role of a heat reservoir. The zeolite particles, which are catalytically active, must be accessible to feed molecules, thus calling for a porous form of the matrix.

The zeolite matrix system features important synergisms as tables V and VI show (10).

TABLE V.

Matrix effect on zeolite stability

Catalyst :	Zeolite 1)		10% zeolite in silica-alumina 2)		Silica-alumina 2)	
	a	b	a	b	a	b
Conversion % wt.	67.8	6.3	67.5	58.2	34.4	35.2
Gasoline, % wt.	58.3	5.8	56.7	49.7	28.8	30.6

1) Conditions : 480°C LHSV = 16; time, 10 minutes.
2) Conditions : 480°C LHSV = 4; time, 10 minutes.
a. Air-calcinated for 10 hours at 550°C, then calcinated for 24 hours in 100% steam at 1 atm.
b. Treatment (a) followed by 48 hours at 850°C in 5% steam-air.

TABLE VI.

Effect of matrix on zeolite activity

	Pure zeolite		Zeolite dispersed in silica-alumina			
			I		II.	
			a	b	a	b
Conversion % vol.	43.4	64.3	45.7	63.1	46.9	65.9
Reactor zeolite, g	7.5	17.0	3.1	7.3	2.9	6.7
Conversion modification, % / Increase of zeolite q-ty, g	$\frac{21.0}{9.5}$ = 2.21		$\frac{17.4}{4.2}$ = 4.14		$\frac{19.0}{3.8}$ = 5.0	

The catalysts had been diluted with quartz at 200 c.c.
I. Ion-exchanged with $(NH_4)_2 SO_4$
II. Ion-exchanged with $(NH_4)_2 SO_4$ + RE Cl_3 (rare earth chloride)
a. 4% zeolite; b. 10% zeolite

The stability against high temperature and steam is thus much increased by dispersing zeolite in amorphous silica-alumina (Table V) and a maximum gain of conversion per gramme of zeolite in the reactor is obtained in this case also (table VI.).

Zeolite catalysts exhibit a remarkable high hydrogen transfer activity which is reflected in the product distribution pattern and in the very high hydrogen efficiency of cracking (Table VII) (10).

TABLE VII.
Catalytic cracking at 480°C of a West-Texas crude distillate

Catalyst	Amorphous		Zeolitic
	15% Al_2O_3	25% Al_2O_3	
Recycle ratio	1.0	1.6	1.0
Conversion, % wt.	58.5	65.0	55.4
Gasoline, % vol.	35.8	44.9	59.0
Coke, % wt.	5.2	5.2	2.6
Hydrogen efficiency at 60% conversion	86	89	94

The zeolitic catalysts are undoubtedly pointing to a new direccion and the fact that now more than 90% of the catalyst inventories of all the FCC units in the U.S.A. is made up of this type of catalysts, constitutes a proof of their operational and economic efficiency, at least for the North American area.

Maximizing of gasoline production and simultaneous increase of [illegible] octane content does not enjoy universal acceptance. **Refiners** in various areas of the world have grown more sensitive even where slight changes in incremental values are concerned, and in some areas important product demand shifts are taking place. The conclusion reached by a great catalyst manufacturing company is that a single type of catalyst is no longer sufficient (14). The catalyst producers have developed or are making researches on new types of catalyst, the so-called "oriented yield catalysts" in order to meet the demands differing with season and geografic location.

Davison Chemical Division of WR & Grace Co. have reported (14) the following catalysts tailored to such needs .

- catalysts for the production of C_3-C_4 olefines
- olefine producing catalysts retaining good gasoline and coke selectivity
- superactive stable catalysts for maximum production of C_5+
- catalysts for increasing of light cycle oil yield.

Of course, these considerations have not exhausted the topic. Continuous improvement of physical and mechanical characteristics is also a subject of continued investigation.

The catalysts of the near future should offer prospective users :

- higher equilibrium activity and selectivity by increasing the zeolite content as well as by ensuring a better accessibility of the catalyst dispersed in the amorphous matrix and minimizing the latter's cracking effect,
- higher mechanical strength and the reduction of fines (minus 20 microns) in order to meet environmental pollution regulations;
- [illegible] to contaminants (heavy metals, alkalies, chlorides and nitrogen).

Some facts about the process

Before going on to discuss the changes in operation and construction of FCC units, it would be useful to remind the main zeolitic catalysts properties which have brought about such developments :

- they crack naphthenes and paraffins quickly and very selectively;
- they crack aromatic nuclei slowly and with low selectivity;
- their cracking rate is relatively little affected by the feedstock boiling range;
- their efficiency is adversely affected by deposits limiting access to zeolite.

These properties lead to the following considerations in the conditions under which the process could be applied :

- a contact time from 1 to 4 seconds is sufficient for achieving complete conversion of non-aromatics in the feed;
- the optimum conversion is largely dependent on the contents of polynuclear aromatics;
- cracking conditions should be selected such as to avoid gasoline re-cracking;
- the regeneration should ensure lowest coke level on the catalyst entering the reaction zone and the reactional system should ensure the most favorable relationship between coke and conversion; those conditions leading to over-heating of catalyst particles and consequently sintering which blocks access pores to zeolite, should be avoided.

Replacing amorphous catalysts in existing units with zeolitic catalysts has often failed to bring about the expected results as the process conditions did not allow the potentialities of the new catalysts to be used to the last advantage.

Figures 9 and 10 give a suggestive picture of the conditions required for zeolitic catalysts. Thus, it becomes apparent from Fig. 9 that, for a contact time longer than 3 minutes and residual coke on the catalyst in excess of 0.2%, zeolite performances are no longer evident. Figure 10 suggests the counterindication of aromatic feeds of a characterizing factor below 11.3.

TABLE VIII. (15)

Incremental yields for riser minus bed cracking x)

Operating conditions	Increments
Temperature, °C	+ 40
Throughput ratio, vol/vol.	-0.35
Conversion, % vol.	+5.0
Yields, % vol.	
C_5 - 200°C gasoline	+7.[illegible]
$C_4 + C_4$	+1.4
iC_4	-0.7
nC_4	-0.5
C_4	+2.6
$C_3 + C_3$	-0.9
C_3	-0.9
C_3	0.0
Cat. gas oil	-5.0
Total	+3.1
Coke % wt.	-1.3
C_2 and lighter, % wt.	-0.4
Octane ratings	
Motor clear	0 to -0.5
+3 cc TEL	0 to -1
Research, clear	+ 2 to 3
+3 cc TEL	+ 1 to 2

x) Orthoflow "B" unit, zeolite catalysts, 75 microactivity. Charge stock inspections: sp. gravity 0.920, volume average boiling point 425°C, aniline point 77°C.

The introduction of zeolite catalysts thus poses two design problems:

1. Adaptation of existing units
2. Design of new units.

The adaptation of existing units consists mainly in going over from bed cracking to riser cracking. Table VIII gives the yield changes as a result of going over to riser cracking. Table data show unmistakeably that riser cracking modifies favourable product distribution pattern. At a reaction temperature higher than 40°C, a 7.6% gasoline yield increment is obtained, pointing to one of the major advantages of riser cracking - the possibility of using higher reaction temperatures without re-cracking of gasoline.

The regenerator, and especially its internals, shall have to allow high operating temperatures. Regenerator velocities shall have to be generally increased in order to improve diffusion conditions. Since coke combustion rate is directly proportional to partial oxygen pressure, higher regenerator pressure is sought whenever possible.

Coke yield, reduced greatly through the use of zeolite catalysts and by riser cracking calls for higher heat inputs. That means better feed preheating by re-evaluation of heat exchangers and furnaces. Unfortunately, not all the old units could be converted into modern high performance ones.

Progress in design

Most of the considerations made around the adaptation of existing units apply also for the design of new units, but, naturally, more efficiently.

In Table IX are given some of the design criterion.

TABLE IX.

DESIGN CRITERIA FOR NEW FCC UNITS

1. Reaction system
   - all riser cracking
   - high temperatures for octanes and olefines
   - minimal recycle
   - feedstock preheating
   - flexibility of product distribution pattern

2. [illegible]
   - coke on regenerated catalyst 0.005 - 015%
   - minimum inventory, associated with make-up and regeneration rate
   - high temperatures, high partial oxygen pressure
   - air distribution and catalyst circulation patterns

3. Stripping section
   - minimum inventory, minimum steam
   - stripping in disperse phase

4. General considerations
   - functionality and simplicity

Keeping in mind zeolitic catalyst and riser cracking properties, the high temperature, riser-limited once-through cracking of naphthenes and paraffins is predicted, without cracking of polynuclear aromatics or gasoline re-cracking. The two reaction types are practically inseparable.

Gasoline recracking may be diminished by less severe conditions in the riser and recycling of the material not converted at the first pass.

This operational approach does not preclude, unfortunately, the cracking of recycle polyaromatics and as a result coke deposits on catalyst are increased and catalyst accessibility is poorer, thus the yield of naphthenes and paraffin cracking is lowered.

Unlike this operational approach, high-temperature once-through cracking results only in a slight re-cracking of gasoline, but with better control of naphthenes and paraffins cracking besides aromatics cracking. Since gasoline re-cracking results in formation of C_3 and C_4 olefines, these could either be recovered as gasoline by alkylation, or by use as a petrochemical feedstock.

In the case where a maximum yield of middle distillate is sought, relatively mild conditions are required for the first pass and a recycle in a proportion ensuring heavy cycle oil disappearance.

TABLE X.

Yield from heavy paraffinic gas oil from Lybian crudes (16)

Component	Yields % wt.		
	Maximum gasoline	Maximum middle distillate	Max. vol. $C_3 - C_4$
Gas (C_2 and lighter)	3.0	1.3	4.9
Propane	2.5	0.6	3.2
Propylene	4.1	2.3	7.0
Isobutane	5.1	2.8	8.9
n-Butane	0.9	0.5	2.1
Butylenes	7.5	9.4	10.4
Debutanised naphtha	59.7	38.3	44.3
Light cycle gas oil	7.2	39.5	7.2
Heavy cycle gas oil	3.5	3.5	3.5
Coke	2.5	2.5	8.5
Total :	100.0	100.0	100.0

If the main requirement is the attaining of maximum proportion of isobutane to olefines, FCC units could be designed with additional bed cracking. Naturally, under such conditions, the loss of some gasoline through re-cracking is unavoidable.

In table X is shown the distribution pattern of the products obtained in cracking a heavy cycle gas oil from a Lybian crude, when maximum of gasoline, maximum of middle distillate, C_3-C_4 cut respectively, are sought after (16).

The FCC process is therefore very flexible. However, this flexibility can only be attained at some sacrifice of the co-product yields and, evidently, with higher unit costs.

Pollution problems

In the highly concentrated industrial areas, the air pollution problems affect the FCC units by :

- restrictions on particulate matter in the flue gas;
- [illegible] on product sulphur content, including [illegible];
- the trend to reduce lead contained in gasolines.

A recent study worked up for the Air Pollution Control Administration by the Midwest Research Institute, Kansas City Mo. (17) has shown that the FCC units in the U.S.A. release into the atmosphere about 45,000 tons/year of particulate matter. Although this is a small percentage of the total of [illegible] million tons/year released by all stationary sources in the U.S.A., the precautions which shall have to be taken in order to meet pollution standards, are going to subject refiners to important non-productive expenditures. These anti-pollution measures shall consist both in an increase in efficiency of solids retaining equipment and in working out catalysts with better mechanical strength and lower contents of fines (0-[illegible] microns), as well as in designing of the new units such as to bring to a minimum the production of dust by attrition.

The restriction on sulphur content in the cat-cracker products shall lead to a more extensive use of hydrogenation (18). Depending on the specific application, hydrogenation may be mild for the primary purpose of removing sulphur, or [illegible] for intensive hydrogenation of aromatics; hydrogenation could also be applied to the feedstock or to [illegible] products, cycle [illegible] respectively.

In the production of low or no-lead gasoline, the fluid bed catalytic cracking (FCC) with zeolite catalyst and riser cracking shall take a prominent place (15,19), especially due to the production of feedstock for alkylation, whose relevance for tomorrow's gasolines is on the way.

[illegible]

An investigation into the cost of FCC units [illegible] difficult enough.

Most of the units operate primarily on gasoline production. The degree of feedstock conversion into gasoline not only depends on the type of the unit and on the operating conditions, but also is decisive on the rate at which non-converted material is recycled through the reactor. These two factors may be combined in a wide range of values for the installed and operating costs.

Most of the units operate at present at conversions ranging from 70% to 80%, with recycle ratios within 25-30%. There are units, however, which operate on a single pass at conversions usually ranking from 50% to 60%, whilst there are units which attain conversion values close to 90%.

Because of these broad limits, the installed and operating costs must be viewed carefully and many of the values reported by process proprietors should be assessed reservedly. For instance, several types of cat-cracking processes have been reported by the licensors as having installed costs of $1250-1570/m3/SD. It would be more realistic to assume $2500-3200 per m3/SD as representative values for most of the new facilities (20). A small unit of say, 1600 m3/SD meant for high conversion rates could, under severe conditions, incur costs as high as $5,000/m3/SD.

Operating costs do not vary so widely, generally ranging from $1.9 to 2.5/m3. Like in the case of most processing facilities, the economics of a FCC unit increases rapidly with slight conversion and yield improvements for the case of good overall efficiency. For this reason the prior hydrogenation of feedstock might look attractive since it not only improves the quality of the finished product, but has also a beneficial effect on conversion and yields, usually by keeping coke down.

Although feedstock hydrogenation costs might be about $1.25/m3 and more probable somewhere between $1.9 and 2.5/m3, such a combination might benefit overall economics. It is attractive for those units which are bottlenecked at coke combustion.

The refinements in catalytic cracking technology and the possibility of combining it with feedstock hydrogenation assessed as "poor man's hydrocracker" have probably limited somewhat the extension of hydrocracking for gasoline production, the two processes being extended on, depending on local economic conditions.

III. CATALYTIC REFORMING OF GASOLINES

The catalytic reforming process has known in the last years an impetuous development, which surpasses in novelty, scientific foundation or consequences, all that had been achieved in the previous 20 years of exploitation of this process. These progresses have been classified in four groups (20): improvements and optimizations of the process, subsequent processing of the reformed product, new applications of the process, and new or improved catalysts.

Improvements and optimizations of the process

Catalytic reforming achieves the increase of the octane rating of the gasolines especially by converting into aromatics and isoparaffins the hydrocarbons contained in the feedstock. The purpose of the improvements in the last years, was the manufacture of products highly concentrated in aromatics which also constitute a source of feedstocks for the separation of the individual aromatics - respectively with increased octane number - about 100 clear. The use in this direction of more severe operating conditions, like the increase of the temperature or the decrease of the pressure, is limited by the increase of the hydrocracking reactions, leading to the decrease of the liquid yield and in coke lay-down on the catalyst. Using the conventional reforming catalysts, of platinum/alumina, processes operating in high severity conditions have been applied since several years, but with cyclic regeneration of the catalyst. Thus, in the Ultraforming or Powerforming processes, one of the reactors is under regeneration, while the others are operated in normal conditions. The running of such plants, however, implies higher operating costs and requires higher investments in equipment and catalyst charge.

In the last years the studies of the optimization of regenerative reforming processes led to a series of publications treating mathematical models of the reactions, computerized analysis of the process parameters, reaction mechanism and kinetics in the highly complex field of the catalytic reforming process. The conclusion of such studies led to the process alternative called Magnaforming (21, 22, 23).

The Magnaforming process (see Fig. 11), tested initially with the RD-150 catalyst, aims to maintain in the different reactors, the most suitable operating conditions, to be able to increase the severity and the selectivity of the process. In the first two reactors, of a total of four, where the most rapid reactions of naphthene dehydrogenation take place, a lower inlet temperature is maintained, to eliminate hydrocracking reactions; the lower temperature allows the decrease of the hydrogen recycle ratio which favors the conversion of naphthenes into aromatics. The temperature is increased gradually toward the reactors III and IV, to obtain thermodynamically more advantageous conditions for the conversion of paraffins into aromatics. To protect the catalyst, in these reactors the hydrogen recycle ratio is increased by adding to the stream leaving reactor II, a new stream of hydrogen discharged by the hydrogen recycle compressor. Thus the hydrogen flow rate is doubled. It was show that the differentiated flow of hydrogen, as well as the use of a new inlet temperature profile in the reactors increase, and at the same time a correct distribution of the catalyst in the four reactors leads to a gain in the gasoline yield of about 3% at a high octane number level.

The tendency to intensively exploit the possibilities offered by the reforming catalyst is significantly illustrated by a recently introduced commercial process. Thus, the UCP. Co. announced a new type of reforming plant with continuous catalyst regeneration, which allows more severe operating conditions, thermodynamically more advantageous, avoiding high cokes, specific to plants with cyclic regeneration. The flow sheet of this plant is given in Fig. 1 ([illegible]). The principle of this plant is the continuous withdrawal of a part of the catalyst from the last reactor, regeneration of the catalyst in the exterior, in a separate equipment and returning of the regenerated catalyst in the first reactor. To allow the circulation of the catalyst from one reactor to the other, they are superposed in a column; the effluent from each reactor passes through a furnace and then enters in the lower reactor.

Such plants possess a series of advantages which have been exploited fully also by using new catalysts. Thus, the catalyst only partially deactivated by coking is regenerated in ideal conditions due to the continuous regeneration system and specifically, after which it enters again in the reactor; in this way the entire system of reactors benefits continuously of the advantages of fresh catalysts: maximum activity and selectivity. It was also shown that the catalyst charge is reduced in the regenerator, thus not increasing markedly the volume of the catalyst in the entire plant.

Subsequent processing of the reformate

The subsequent processing of the reformate has been considered in order to avoid too severe conditions in the reforming process. In principle, an aromatic concentrate can be obtained by extraction with very high octane number, but the yield is too low. On the other hand, the recycling of the raffinate, such as suggested by some older processes, seems to have the inconvenience of accumulation in the feedstock of the most refractory components, thus reducing the efficiency of the process.

Another more modern way consists of the separation of the n-paraffins and i-paraffins by molecular sieves, processes which are also expensive, which, however, are justified economically when the high purity n-paraffins constitute feedstock for the chemical industry.

An interesting solution has been brought forward by the process called selectoforming (29) in which the reformate product is processed globally in such conditions as to hydrocrack selectively the n-paraffins. An increase of the global octane rating is thus obtained with higher yields than those which could have been obtained by a more severe processing only by reforming. Table VI. shows a comparison of these yields when processing a gasoline to obtain ON = 102 (ethylated), the reforming process, prior to hydrocracking, being operated at two distinct degrees of severity (2). It should be noted especially the increase of the yield of the depentanized product.

TABLE VI.

EFFECT OF SELECTOFORMING ON YIELD

	Reforming	Reforming and selectoforming	Yield	Reforming	Reforming and selectoforming	Yield
Reformer octane number C_5+, Res.+3 ml	102.0	97.9	–	102.0	99.2	–
Selectoformer octane number C_5+, Res.+3 ml	–	102.0	–	–	102.0	–
C_5+Vol-%	44.0	50.0	+6.0	43.8	51.3	+7.5
C_4+Vol-%	61.5	61.5	0	60.9	62.3	+1.4

Another way of subsequent processing, a very simple one, is applicable in the case of severe reforming conditions; separation by fractionation of the light parts of the reformate, which consists especially of paraffins and treating only this cut, for example by isomerisation, selectively, to obtain a valuable blending component, or by pyrolysis to obtain additional feedstocks for alkylation.

For illustration, Table VII. shows the increase of the octane number of a reformed gasoline, when the light cut, amounting to 25% of the reformate, was subjected to isomerisation. The octane number of this cut increased from [illegible] to [illegible]. After blending with the heavy reformate cut [illegible] gasoline with ON = 102 was obtained with respect to the initial value of 99.7 with a yield closely equal to 100 (23).

TABLE XII.
FRACTIONATION-ISOMERISATION
[illegible] OF REFORMATE

Total reformate octane number (research clear)	99.7
Overhead 25 vol.% Octane number (research clear)	77.8
Bottoms 75 vol.% octane number (research clear)	105.1
Isomerization of overhead 25% yield, vol.% based on feed to isomerization	98.8
Octane number (research clear)	92.8
Final blend yield, vol. %	99.7
Octane number (research clear)	102.0

New applications of the catalytic reforming process

In a direction similar to the previous one, is oriented the reforming process, alternative characterised by the use of a very acid catalyst and which, consequently, produces a severe hydrocracking of the gasoline with the manufacture of liquid petroleum gases (23). This third group, which includes new applications of the reforming process, got no wide use.

Improved reforming catalysts

The most interesting and maybe the most revolutionary improvements in recent years, have been achieved, we feel, in the field of catalysts by introducing on a large commercial scale the bi- or polymetallic catalysts.

Ample studies, carried out along the years, on metals with catalytic activity have shown the leading position of the platinum. Thus, various investigators have proved that platinum exerts the most intensive catalytic activity in the reactions of dehydrogenation of the naphthenes, respectively, the hydrogenation of aromatics, the rate of these reactions being considerably higher in the contact with platinum than in contact with any other metal, including other platinic metals or non-platinic metals of the VIII-th group of the periodic system.

Researches on individual hydrocarbons have shown the ability of platinum to produce aromatics, clearly different from that of other elements of the VIII-th group, where this tendency is very weak or even absent, the chief reaction being hydrocracking (26). All these studies, as well as those carried out with gasolines, led to the concepts upon which the classical catalysts were developed, avoiding the impurification with metals, during the preparation of the catalyst, as well as during its commercial use.

The commercial use of reforming catalysts containing besides platinum one or several other metals, the respective catalysts being called bi- or polymetallic, did not find consideration but in severe processes, at low pressures, introduced in the last years. Although the majority of the patents or articles claim advantages in the yield of reformed gasoline, the principal claim of the platinum-rhenium catalyst, the most frequently used of the new bimetallic catalysts, is its higher stability in comparison with conventional reforming catalysts (27, 28, 29, 30). These advantages led to a rapid spreading of this type of catalyst so that, today, all big reforming catalyst manufacturers in the world are offering catalysts or reforming processes with Pt-Re or other bimetallic catalysts. Thus :

- Chevron Research Co.,(U.S.A), offers Rheniforming process and catalyst (31).
- U.O.P. (USA), the catalysts R16 and R20 (24).
- Houdry (USA) the HR-71 catalyst (32).
- Engelhard Ind. (USA), catalysts with Pt-Re, E-500 şi E-600 (21)
- Esso Research and Engineering Co. (USA), multimetallic catalysts for Powerforming (33).
- Inst. Français de Petrole (France), bimetallic catalysts Naphthene 255 (34).
- Leuna (GDR) the catalyst 8816.

Since all the above-mentioned manufacturers claim in principle, the same kind of advantages, in the following, as an example, the qualities of one of the Pt-Re catalysts will be described :

Good temperature stability, lower fouling rate than the best platinum catalyst.

Very low yield decline with temperature. This allows working at higher temperatures.

This characteristic can be expressed in another way by the different ratio in which the temperature influences the rate of dehydrocyclization and hydrocracking reactions, which is summarized in Table XIII.

Good regeneration stability, the regenerated catalysts regaining their initial activity.

TABLE XIII.

EFFECT OF TEMPERATURE ON REACTION RATES IN REFORMING

$$\frac{d\,(\text{Rate of dehydrocyclization})}{dT} = A$$

$$\frac{d\,(\text{Rate of hydrocracking})}{dT} = B$$

Conventional reforming catalyst	$B > A$
Platinum-Rhenium catalysts	$A > B$

Another claimed quality, resistivity against poisons, or capacity of regeneration after accidental poisoning, is not confirmed. On the contrary, certain sources indicate that the activity of the Pt-Re catalyst is conditioned by the severe purification of the feedstock (29). The conclusions of the 1970 Question and Answer Session of the National Petr.Ref. Association (35) were similar. Thus, it has been shown that the increase of the sulfur content in the feedstock over 2-3 pp produces serious declines of the operating cycle, respectively an important increase of the reactor temperature. Therefore, a maximum limit of 1 ppm sulfur is recommended for feeding reforming plants with bimetallic catalysts.

Summing up the advantageous behavior of the bimetallic catalysts, it is asserted that the operation of plants with such catalysts has the following consequences (29) :

Operation at higher octane levels
Operation at higher feed rate
Operation at lower pressure
Operation at lower H_2/hydrocarbon ratios
Longer runs
Improved yields
Savings in platinum investments

For illustration, Tables XIV and XV show comparatively certain performances obtained with classical catalysts and with Pt-Re catalyst (30). Figures 13 and 14 show the change of temperature and of reforming gasoline yield, when manufacturing a gasoline with ON = 100 (F_1-clear) (27).

TABLE XIV.
PERFORMANCE OF A MID-CONTINENT RHENIFORMER

	Previous operation	Rheniforming Initial run	 Post regeneration^x
Feed rate, bbl/oper.day	16,000	17,000	18,000
Octane, F-1 + 3 cc	100	100-101	102
Recycle ration, molar H2/HC	3.6	2.6-3.2	2.4
Run length, months	2.4	7.5	(Note 1)
Catalyst average temperature+	900	890	900
Yield, LV % C_5^+	84	85	84
Yield decline,.. LV %	4.6	1	(Note 1)

---

x) Second run has been in operation for more than 3 months with essentially no yield decline
+) Start of run
..

[illegible]

[illegible] Ca[illegible]

	Typical operation before Rheniforming		Current[x] operation	
	Regular	Premium	Regular	Premium
Feed rate, bbl/oper.day	11,800	8,900	15,000	12,800
Octane, F-1 clear	86	96	93	99-100
Pressure, last reactor out, psig	500		425	
Run length between regenerations, months	3-5		3-5	
Yield decline, LV % C_5^+	5		1	

---

x) Operating data after three regenerations (about 113 b/lb).

Note : Refinery estimates yield improvement through lower pressure, adjusted to 95 F-1 clear average octane as :

C_5^+ 1.5 LV %

H_2 100 scf/bbl

Of course, all the above mentioned advantages are described perhaps too optimistically. They cannot be obtained simultaneously and the existing plants cannot be easily converted for operation in the most advantageous conditions for bimetallic catalysts. It is mentioned operation at about 10 kgf/cm2, with the inherent advantages of working at very low pressures, but in new plants, with continuous system of catalyst regeneration. Working with such specific plants, one can predict even the possibility of operation at 7 kgf/cm2 pressure in the case of very paraffinic feedstocks (36). Also, one cannot neglect the higher costs of the catalysts, their sensitivity towards sulfur and water (37).

It is, of course, of interest the interpretation of the way in which act the bimetallic Pt-Re catalyst or the catalysts promoted with [illegible]

[illegible] clear [illegible] in this [illegible] to [illegible] with the [illegible] but a different [illegible] of the [illegible] effect [illegible] following process. Conversions have been made however, and suggestions have been formulated to explain the higher stability of the catalysts. Thus, one of the causes could be the higher melting point of rhenium, 3440°C as compared with 1755° in the case of platinum, which is correlated with the higher resistivity against sintering of the Pt-Re alloy from the catalyst. The specific existence of the "alloy" effect has been proved by the fact that the promoting action of rhenium is conditioned by a given proportion with respect to platinum (Fig. 15) (20).

Working in highly severe conditions, a larger amount of coke is unavoidable deposited on the catalyst. If, in the case of conventional platinum catalysts, a coke deposit of 5-10% imposes regeneration, the bimetallic catalysts admit much larger deposits, amounting to 20%. This observation can lead to the assumption that the existence of the "alloy" has a dispersing effect on the coke deposits (38).

The developments and the results obtained with the Pt-Re catalysts have stimulated investigations directed toward other "alloy" type catalysts, based on platinum. Thus, tending to reduce the catalyst costs and the severity of feedstock purification, new types of catalysts have been announced containing additional metals with promoting effects, sometimes in combination with the addition of a sulfur compound. The subject is treated in patents, mentioning the use of platinic metals like palladium and iridium, group IIIA elements like scandium, group IVA elements like zirconium or group IVB elements like germanium, stannum or lead, or of group [illegible]. [illegible] a catalytic system [illegible] by the [illegible] of [illegible] - [illegible] 20 - which [illegible] [illegible]

[illegible] the processes which [illegible] metallic catalysts of [illegible] regenerative type, working at low pressure [illegible], have shown good performances also [illegible] (..).

[illegible]

The reforming process of gasolines is applied today at different levels in every country in the world. Consulting the statistics, one realizes that reforming plants are present everywhere where oil is processed, regardless of the oil processing capacity and regardless of the economical development of the country.

The increasing demand of high octane fuel, of aromatic hydrocarbons and of hydrogen for hydrotreating processes, and th progresses made in recent years in the field of catalysts and processes, intensified the spreading of the process. Thus, the present reforming capacity of the world (except socialist countries), is of about 14% of the crude oil distillation capacity which is to be compared to 13% five years ago ([illegible]). The informations about new constructions show for the following years, an even increased tendency of introducing gasoline reforming processes. Among the countries with highly developed petroleum processing industry, U.S.A. reached, in 1972, a reforming capacity of about 175 million m³/year, representing about 22% with respect to the crude distillation capacity.

In connection with the qualitative evolution of the process one can remark that a general tendency is manifested toward the introduction of bimetallic or polymetallic catalysts and of plants of low pressure working at 10-20 atm.

Of course, for the full use of the abilities of the new catalysts, the new type of plant with cyclic or continuous regeneration [illegible] economic [illegible], obtaining a production of higher value [illegible] investments and manufacturing costs, variable [illegible] of the plant capacity, and the characteristics of the processed gasoline.

One can obtain the results of the effects of the [illegible] which will be produced by the substitution of [illegible] catalysts [illegible] polymetallic catalysts in existing [illegible] and the possibilities of replacement of the catalyst without modifying the plant. In case of changes with no equipment changes, limited increases can be obtained for the capacity or for the octane number, by reducing the pressure and the recycle ratio, as well as by temperature increase. In view of a better exploitation of the new catalysts, besides the changes of the operating conditions mentioned above, it [illegible] economically more attractive to increase the capacity of the furnaces and the insertion of an additional reactor (20). Of course, the possibilities of adaptation are multiple and the decision will be dictated by local conditions.

IV. [illegible] HIGH [illegible] COMPONENTS [illegible] OTHER

To meet the present trends of increasing the octane rating of clear gasoline, it is required to transform light gasoline cuts, consisting especially of C5 and C6 hydrocarbons, to obtain the largest possible amounts of isoparaffins. There are, in principle, three ways of increasing the isoparaffin concentration : alkylation, isomerization and isomer separation.

Alkylation, as a process for manufacturing light gasoline cuts with clear octane number close to [illegible], is applied today on a large scale in the western hemisphere, especially in USA. This process has been used for alkylation in western Europe and in developing countries. [illegible] expensive process, other processes have [illegible] especially [illegible] which [illegible] of their [illegible]. [illegible], however, that the [illegible] [illegible] [illegible] alkylation in other countries [illegible].

...

Of the two commercial alkylation processes, the capacity of sulfuric acid alkylation plants is about double of that of HF acid alkylation plants, and recent-year developments did not change this ratio. The efforts which have been devoted to the improvement of the alkylation process, refer to mechanical aspects of corrosion, acid recovery, product purification, etc. This is, however, beyond the purpose of this work, which refers to processes using solid catalysts and to catalysts themselves.

The isomerization processes, especially of n-pentane and hexanes, although representing a small capacity with respect to the total processing capacity, recently became of interest for the increase of the antiknock properties of the light gasoline cuts. It should be reminded that light gasoline cuts, containing especially C5 and C6 and representing 10-15% of the total gasoline, have usually an octane number between 65-70, hence markedly lower than actual requirements. The reforming processes, even the modern ones working at low pressures, are not fed with these cuts since no satisfactory isomerization is obtained, only a mild aromatization of the C6 hydrocarbons. Even the light top of the reformate might constitute the feedstock for isomerization.

The isomerization of light paraffinic cuts produces an increase of about 13-15 octane units, the increase depending obviously on the nature of the feedstock and on the applied isomerization process. If working with recycling, a practically total conversion to isoparaffins is obtained and the octane number of the cut reaches 85, which leaded, raises to 95. Table XVI gives the Motor and Research Octane numbers of the main C_4, C_5, C_6 and C_7 paraffins (41).

To understand the limitation and present trends in developing the isomerization process, it is useful to remind the thermodynamical aspects of the reaction of isomerization of C_5 and C_6 paraffins. Fig. 16 and 17 show the change of the equilibrium composition of the C5 and C6 cuts as function of temperature; it results clearly the advantage of isomerizing at the lowest possible temperatures, the proportion of isoparaffins increasing with the decrease of the temperature. In the case of n-hexane the slope of the curve is less abrupt.

TABLE XVI.

OCTANE NUMBERS OF PARAFFIN HYDROCARBONS

	Motor method	Research method
n-butane	90	94
isobutane	99	100+
n-pentane	62	62
iso-pentane	90	92
n-hexane	26	25
2-methylpentane	73	73
2.2-dimethylbutane	93	92
n-heptane	0	0

It is interesting to remark the steep increase upon temperature decrease, of the concentration of 2-2-dimethylbutane, an interesting component due to its high octane number.

Isomerization occurs through an ionic mechanism, by formation of carbocation intermediates, which undergo structure changes. The active catalysts in this reaction can be classified into two groups:

- catalysts based on $AlCl_3$ or other similar Friedel Crafts catalysts;
- bifunctional catalysts containing besides the acid function, also a hydrogenation-dehydrogenation function.

The first commercial processes of isomerization, working with Friedel Crafts type catalysts, gave a series of difficulties like high reactant requirements, losses through formation of residual products, strong corrosion, pipe fouling, difficulties in isomerized product purification. Subsequent develop-

[illegible], which take place at the temperature of the gasoline reforming process, can be processed using bi-functional catalysts at high temperatures. Although operated with increased safety and without corrosion, these processes are disadvantaged by the thermodynamical equilibrium, specifical for the working temperature. Due to the relatively low conversion into isoparaffins, the costs of the plant and the manufacturing costs are relatively high, as a consequence of the need to recycle n-pentane and sometimes, n-hexane.

In view of reducing the working temperature, important progresses have been achieved toward the increase of the catalyst acidity by incorporating strongly acid promoters into the catalyst or by the very modification of the carrier. The most interesting results toward modifying the carrier were obtained by introducing molecular sieves type Y or mordenite.

Following this route, the working temperature was decreased successfully to about 300°. Combining the advantageous characteristics of the bifunctional catalysts with the strong acidity of the Friedel Crafts catalysts, the latest types of catalysts have been achieved, which today are used in "low temperature" processes (42). The developments which led to this solution are outlined in Fig. 16, in correlation with the main characteristics of the respective processes – temperature (43).

The isomerization processes called "at low temperatures", which work below 200°C, are using a fixed bed of noble metal catalyst deposited on an acid alumina carrier to which a strongly acid promoter of Friedel Crafts type is added.

The latest processes are continuously introducing such promoter, for example, an organic chlorinated compound together with the hydrogen-hydrocarbon feed. The organic compound is decomposed in contact with the catalyst forming HCl, generating in situ a catalyst with such high acidity that the process can be carried out at advantageously low temperatures. To be mentioned that this catalytic system, although using HCl, practically is not corrosive, due to the lack of humidity (44, 45).

These last low temperature isomerization processes have the advantage of deep conversions coupled to high product yield, stability and catalyst regenerability, which by a reactivation process, can be used for indefinite periods, safety, and low manufacturing costs.

As a consequence of these advantages it is expected that future capacity increases will proceed along the line of low temperature processes.

[illegible] problems, [illegible] con-nection of [illegible] with the major conversion processes, [illegible] of catalytic hydrogen treating processes have been developed, whose common characteristic is the improvement of the quality of certain hydrocarbon cuts.

The removal of heteroatoms like sulfur, nitrogen, oxygen, saturation of double bonds from different olefinic structures, the removal of the heavy metals and of the asphaltenes, are the main purposes of these processes, whose flow sheets, operating conditions and catalysts, have been developed in close relation with the practical requirements which are to be achieved.

Recent literature has treated in detail the wide field of industrial applications, and especially the proceedings of the VII-th World Petroleum Congress, held at Mexico-City in 1967, have devoted a large amount of work to the analysis of the status and of the progresses of hydrogen treating processes. Therefore, in the following only tendencies which seemed to us most significant for the actual and future development of this field, will be discussed.

Returning to the proceedings of the VII-th Congress (1-5), the discussed themes showed the tendency, which in the following years has strengthened, to widen the applications of hydrogen treating. Thus, besides the progresses in distillate desulfurization, novelties have been discussed in residue desulfurization, catalytic cracking feed hydrotreating, lube hydrotreating, and pyrolysis naphtha hydrofining, whose increasing amount claims a rational use of their aromatics content and of their octanes.

The hydrogen treating capacities are increasing in USA with a yearly rate of over 7 %, representing today over 35 % of the crude oil processing capacity. This makes the hydrogen treating [illegible] the second place, following the catalytic cracking.

The distribution of the hydrogen treating capacities in the world, results from the following data, which describe the situation at 1 January 1969 (11).

Region	Capacity m3/sd.	% of the processed crude
Africa	18.300	15
Middle East	40.000	11
Asia-Pacific	159.300	20
Western Europe	365.000	18
Latin America	50.000	6,4
North America	900.000	34

Table XVII shows the distribution of different kinds of processes and their dynamics in the last two years, in the USA.

Table XVII

Hydrogen treating of various petroleum cuts (12)

Feed	Capacity, m3/s.d.				
	1.01.70	Δ% year	1.01.71	Δ% year	1.01.72
1. Reforming feed	343.000	+ 12	392.000	+ 8	423.000
2. Middle distillates	163.000	- 7	156.200	+ 6,5	166.000
3. Catalytic cracking feed & cycle oil	42.000	+ 0,5	42.500	0	42.500
4. Naphta saturation	39.200	- 1	38.800	+ 15	44.000
5. Lube oils	21.500	- 7,5	23.300	+ 0,5	23.500
6. Heavy gas oil hydrofining	14.000	- 18	12.100	+ 18	19.600
7. Residue desulfurization, etc.	26.200	+ 15,0	25.900	0	25.500
Total :	644.700	+ 8	690.400	+ 7,9	744.100

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The yearly increase of the capacity of hydrogen treating processes surpasses, in most of the geographical areas of the globe, the rate of increase of the catalytic reforming, which still remained the most convenient hydrogen manufacturer. More frequently are used other sources of hydrogen, especially due to development of hydrocracking, which requires large amounts and also due to the application of the hydrotreating in refineries without catalytic reforming, like those for lubricating oils.

In connection with the feedstocks for reforming, the main purpose of the hydrofining remained the removal of the sulfur and especially of nitrogen from the feed, as well as of the metals like arsenic and lead. The tendency to blend the reforming feedstocks with increasing amounts of naphtas from thermal decomposition (coking and visbreaking, has supplemented the duties of the hydrofining with the saturation of the olefins and diolefins.

The development of the reforming catalysts, which lead to the commercial use of promoted platinum catalysts, raised also new problems in the hydrofining of naphtas.

Improvements have been achieved both in the process technology and catalysts.

Thus, the thermally cracked naphtas can be successfully hydrofined in two stages, avoiding the fouling of the reactor with gums resulting from diolefins.

In such processes it is preferable to operate the first stage in very mild conditions to saturate selectively the diolefins. Space rates (LHSV) of 10 - 15 and temperatures of 150 - 200°C are used. The second stage is operated in the conditions required to achieve the desired degree of desulfurization (51).

Complete elimination of the contact with air, by feeding discharge of the coker naphta direct to the hydrofining reactor, seems also to be a solution to avoid the fouling of the reactor [illegible] (52).

In hydrogen treating of coker naphta, the [illegible] [illegible], depending on the operating [illegible] [illegible] [illegible].

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hydrogen treating under mild conditions, as e.g. [illegible] between 250 – 370°C and pressures of 30 – [illegible] [illegible] of the [illegible] of oil and the stability of the oil, [illegible] represents the hydrofinishing process. This substitutes successfully the finishing operation with clay, both of oils and of waxes, in classical flow-sheets which include solvent extraction.

More severe treating not only eliminates completely the hetero-atoms from the oil, but due to higher hydrogenating reactions on suitable catalysts and operating conditions, the hydrocarbon skeleton is modified, leading to a marked raise of the viscosity index. This last process is sometimes called hydrotreating (49), sometimes is considered an alternative of mild hydrocracking (9). That for, we will discuss this process later.

The advantages of hydrogen treating in the lube oils manufacture, determined the increase of the processing capacities of the plants from 5500 m3/sd in 1961 to 23.[illegible] m3/sd in 1972 (12, 53), representing about 70 % of the total capacity of finished lubricants (53).

The success of the hydrogen treating of the oils is due to the increased yield of the finished oil, with [illegible] to the corresponding extraction processes, for an equal viscosity index (40, 54), the inherent losses due to acid treatment are avoided, and the byproducts of the process (naphtha and gas oil) have [illegible] commercial value (49).

The replacement of the acid and clay treating by hydrogen treating gains actually in importance also due to the fact that the elimination of wastes avoids the pollution of the environment.

A few comparative data between [illegible] lubricating oils and conventional clay finishing [illegible] Table XXII. It is seen that the major [illegible] finishing consist in lower [illegible] [illegible] of the [illegible] decrease of the [illegible].

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Table XVIII

Hydrofinishing Gulf Coast high V.I. stocks (49).

	250 Neutral			Bright stock		
	Feed	Clay Treated	Hydro-finished	Feed	Clay Treated	Hydro-finished
Temperature, °C			315			315
Pressure, atm			32			32
H_2 consumed, m3/m3			9			7
Yield, % vol.	-		99,4			99,6
Product inspection						
Viscosity index	90	92	92	89	90	90
Sulfur,% wgt.	0,13		0,05	0,22		0,16
Colour stability						
NPA color, initial		2-	1-		6-	4-
Aged at 100°C						
24 hr.		2-			6-	4+
48 hr.		2 1/2-			7-	4 1/2-
72 hr.		3-			8	4 1/2

The simultaneous elimination of oxygen, reduces the acidity of the oil. Nitrogen is removed to a smaller extent in the conditions of hydrofinishing. In condition in which over 90 % of the sulfur is removed, the denitrification is only 55 - 70 %, depending on the viscosity of the stock (55).

The degree of removal of the heteroatoms S and N, markedly influences the oxidation stability of the oils, as confirmed during the development of the hydrofinishing process for romanian paraffin base oils. In such cases it is important to keep a minimal concentration of sulfur compounds in the oil, because these compounds act as oxidation inhibitors (55).

From engine testing, resulted a good additive - response of the hydrofinished oils, toward detergent - dispersant and antiwear additives. Toward dispersant additives, the behavior of the hydrotreating process in the [illegible] only [illegible] oils.

Good results have been obtained [illegible] of electroinsulating oils, by hydrofining, [illegible] (56). By hydrogen treating at 390° and 60 atm, and subsequent light finishing with clay, the resulting oils were superior to those refined with 18 % H_2SO_4.

The increasing market demand for fuels with low sulfur content, stimulated the increase of residue desulfurization capacity from 16.200 m3/sd to over 25.000 m3/sd in the last two years. The regulations against pollution have promoted to a large extent this developement, which became possible due to the improvements of the process and of the catalysts. Although the long practice in distillate desulfurization, was applicable to a large extent to the desulfurization of the residues, there are however two major distinctions among the two processes :

1. the presence in the residual feedstock of asphaltenes and of other polyaromatics with high molecular weight;
2. the content residues of organo-metallic compounds (with Ni and V) which form deposits on the catalysts, giving troubles during regeneration.

To solve these problems, catalysts formulation were, and still are investigated, about which only few data were disclosed in the patent literature. From published data, at the last two World Petroleum Congresses, it results that in most cases the catalysts contain the usual active elements of the VI-th and VIII-th group of the periodic system (Mo, W, Co, Ni), deposited on alumina or alumina-silica carriers, with a large variety of pore-size distribution (57).

Theoretical arguments concerning the contacting of petroleum ... with catalysts, show that [illegible] is ... improved by the decrease of the size of the catalyst particles (58). [illegible] the [illegible] [illegible] [illegible] [illegible] (59).

[illegible] quality of [illegible] catalyst, [illegible] operation, [illegible] to compensate [illegible] losses [illegible] attrition (47, 52). As communicated at the Vienna Petroleum Congress, in the more recent H-Oil plants, microspherical catalysts are used, with particle distribution between 0.044 and 0.4 mm (50 - 325 mesh) (57), which seems to solve the problem of attrition, accentuated when extrudates are used.

The mentioned difficulties, concerning the desulfurization of residual stocks, have been solved commercially, also in fixed bed of catalysts.

It is worthwhile to quote, in this sense, the communication by H. Kubota and J. L. Kassner, at the World Petroleum Congress at Moscow (58). They analyse the commercial experiences on the first plant in the world for the desulfurization of a reduced crude, started in 1967 by the Idemitsu Kosan Co., Ltd., Tokyo, Japan. The plant, a UOP licence, is incorporated in a complex processing scheme, which contain an RCD Isomax plant, a hydrogen plant by steam reforming of a heavy naphta and a plant for the recovery of the sulfur and of the ammonia (see fig. no. 19).

The plant processes a Kuwait residue with the following inspections :

d_{15}	0,9626
sulfur % wt.	4,1
total nitrogen % wt.	0,22
insolubles in heptane % wt.	2,44
Conradson Carbon residue	8,13
Metals	
Ni ppm	11
[illegible]	[illegible]

[illegible]

Three undisclosed types of catalysts have been tested, which were the latest developments of the UOP Company. Due to the metal laydown on the catalyst, the tendency is to develop cheap catalysts, which after about six months are replaced ("throw-away catalyst") or regenerated, if desired (58, 60).

A second RCD Isomax plant, started at early 1969 at Kuwait (American Independent Oil Co.) processes a far more difficult residue, also at 1 % sulfur in the resulting heavy fuel. The feedstock in this case is a blend of Middle East residues with 5.6 % S, 3.000 ppm total nitrogen, 10 % insolubles in heptane, 40 ppm Ni and 85 ppm V.

The difficulties of " direct " residue desulfurization can be sometimes bypassed by " indirect " desulfurization, which means leveling the sulfur content of the residual fuel to the required limit, by dilution with desulfurized gas oil.

The residue hydrodesulfurization process is still relatively expensive, with respect to the petroleum processing industry standards. Investments and manufacturing costs, both depend markedly on the feed stock. In a comparison (59), it is shown that in the case of two residues, resembling with those quoted above, the differences between the manufacturing costs were 1.25 dollars/m3, in favor of the less sulfurous stock (S = 4.3 % and 5.2 % respectively; S = 1 % in the product) for the same final sulfur content in the product.

VI. HYDROCRACKING

The technical progress achieved in the last twenty years, concerning design, construction and operation of high pressure catalytic reactors, together with the results of investigations in the field of bifunctional catalysts, have offered to the petroleum processing industry the hydrocracking process of petroleum cuts, considered today as the most flexible and versatile of all the conversion processes in refineries. The situation of the energy market favored the application of the process and although in USA the capacity increase was the most rapid, hydrocracking is spreading relatively quickly in other parts of the world also.

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The development especially in USA is promoted by the excess of residual fuels on the market and its seasonal fluctuation, to which recent regulations against pollution of the environment should be added. A large part of this product, which is difficult to sell, can be transformed by hydrocracking in much more appreciated products like liquefied petroleum gases, jet fuel, diesel fuels and high viscosity index lubricating oils.

The conversion of heavy cuts into middle distillates with valuable properties as commercial products and into petrochemical feedstocks is a more specifically european grievance.

The quick acceptance of hydrocracking in the 60-s is proved by the number of 50 plants on stream in June 1970, with total capacity of 120.000 m3 per day, to which 60.000 m3 per day in construction or under design in 1970, should be added (61).

The total world capacity is distributed among the continents as follows :

	m3/day	% of total
North America	159.000	80,2
Europe	10.000	5.8
Asia	4.140	2,3
Africa	1.600	0,9
Latin America	4.000	2,2

Since hydrocracking is in impetuous development, the actual values are of course beyond the above figures.

The following figures illustrate this situation, but unfortunately only for the USA where hydrocracking grew in the last years with a rate of 22 %. The distribution of the capacities among feedstocks results also from the following figures (12).

Feedstock	Capacity, m3/day				
	1.01.70	Δ %	[illegible]	Δ %	1.01
distillate upgrading	94.000	7,5	[illegible]	23	[illegible]
residue upgrading	2.050	205	[illegible]	4,5	[illegible]
lubricating oil manufacture	96	300	[illegible]	[illegible]	[illegible]
other applications	–		[illegible]		–
Total :	96.145	25	[illegible]	22,4	152.2

Very high relative increases have been observed especially for the more recent application of the hydrocracking, viz. the processing of residual cuts and manufacture of lubricating oils. Hydrocracking applications for lubricating oil manufacture have been announced also in Western Europe, the Soviet Union and Australia (62 - 64).

The hydrocracking reaction mechanism differs from the previously discussed hydrogen treating processes in as much as it produces dominantly products with lower molecular weights than the feedstock. This destructive hydrogenation of heavy oils, known and applied since the '30-s is fundamentally distinct of the modern application, by the use of bifunctional catalytic systems of high activity, which enable the conversion of the feedstocks in relatively mild conditions of temperature and pressure (400 - 450°C and 100 - 200 atm.).

Without discussing the chemistry of hydrocracking w is widely discussed in the literature, it should be reminded only the predominance of branched paraffin and naphtene structures and the practically total absence - at deeper convers of S, N, O heteroatoms, in the reaction products.

Depending on the catalytic system-noble metal or oxy catalysts - the process can be achieved in one or more stages. In the case of noble metal catalysts on acid carriers, the feedstock is subjected to a severe pretreating to eliminat much as possible the nitrogen and the sulfur, by means of ox type catalysts of low acidity and subsequent actual hydrocracking.

Using oxyde catalysts on strongly acidic supports, the process cand be achieved in a single stage.

The technological applications of hydrocracking have surpassed the supply of basic knowledge in this relatively new field, with its complex problems, covering the field of heterogenous catalysis, chemical reactor engineering and metallurgy; the large number of papers in this field, proves the effort devoted by a large number of scientists to the foundation of the scientific basement of the commercial applications and their improvements.

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To illustrate the versatility of the process, a few data on the most important applications will be given in the following.

Important amounts of liquefied petroleum gases are consumed in several countries. L.P.G. can be manufactured by hydrocracking preferably gasoline cuts, preferably C 7. The co-product is a C 5 – C 6 high octane gasoline.

If the main purpose of hydrocracking is gasoline manufacture, as is the case in the USA, it is possible to process, for example, a 165 – 450°C cut, to obtain a C 5 – 85°C gasoline having a octane number F1 + 3 ml TEL of 99,5 at a yield of 35 vol % and a naphta with the same octane number of 85, at a yield of 70 vol %. The hydrogen consumed for the mentioned case was 285 Nm3/m3.

Jet fuel is another important target of hydrocracking. In 1960–1975, doubling of the requirements are predicted [illegible] (65), increasing from 79.000 m3/day to 178.000 m3/day, but the increase of jet fuel demand is a global phenomenon due to the world wide development of transports.

By hydrocracking a wide gas oil cut (275 – 500°C), in an one stage process, with extinction recycling, one can obtain 80 % vol. jet fuel, 23.5 % vol. gasoline with a volume yield of C_4+ of 115.4 % and a chemical hydrogen consumption of 360 Nm3/m3 (65). For a 260°C end point, according to ASTM specifications, the freeze point was -59°, as compared with the specified ASTM requirement of -48°C for intercontinental flights.

More recent plants also have been erected to manufacture naphtas for petrochemical uses by processing vacuum gas oils. A typical feed for this case had an end point of 550°C, 1,7 % sulfur and 122 ppm nitrogen. Consuming 350 Nm3/m3 hydrogen, yields of C_4+ of 130 % vol. were obtained, with petrochemical gasoline (85 – 180°C) containing about 60 % vol. cyclics, an ideal feedstock for the manufacture of xylenes (61).

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Another interesting application is the [illegible] cracking of less valuable heavy distillates like heavy recycle oils [illegible] FCC decanted oils, coking and thermally cracked heavy distillates . Processing these distillates by an once- through process, the operating conditions can be adjusted for three typical cases :

a. manufacture of light distillates and feedstocks for catalytic cracking;
b. catalytic cracking feedstocks;
c. low sulfur fuel oils component.

The only operating parameter which should be changed in order to modify the yields is the reactor temperature.

Recently hydrocracking has added another proof to its versatility by processing residual stocks. Although the opportunity to convert residuals is not so acute in various parts of the world, it may become a more general problem, as a consequence of energy balances and due to the generalization of the regulations for the protection of the environment. To the last argument it should be added that in many parts of the world increasingly larger amounts of sulfurous crudes are processed, giving highly sulfurous residues. The material boiling above 350°C can be converted into lighter distillates in a proportion of 75 %.

Due to the different conditions in the case of distillates, the residue hydrocracking is considered even as a distinct process. The major differences consist of the feedstock characteristics, catalysts operating conditions, heat of reaction and hydrogen demand.

The essential difference in the feedstocks, consists in the previously mentioned large amount of mineral substances which determines the application of new concepts in developing catalysts.

It is obvious that due to the different characteristics of the residue feeds the operating cycles [illegible] fixed bed of catalysts are usually [illegible] than in the case of distillates hydrocracking, especially due to the [illegible] on the catalyst [illegible] into the bed of mineral [illegible].

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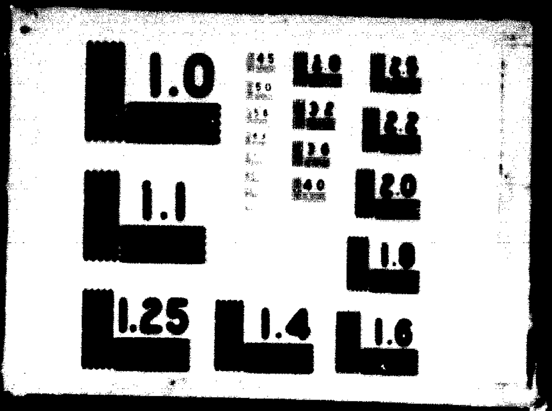

these are blocking the access to the catalyst surface and rather increase of the pressure drop through the bed leading to plant shut-down (65). In such situations the procedure of oxidative regeneration is impracticable. The possibility to compensate the catalyst activity loss, during the cycle, by temperature increase, has a limitation in residue hydrocracking where decomposition is obtained as function of the temperature and to a lesser degree by catalyst activity. Especially in the case of reactors designed for maximum conversions, temperature increase above the normal operating temperature, may lead to reactor coking (66). The heaviest parts become more and more hydrogen deficient, as the conversion increases, remaining nonconverted probably also because these cyclic polycondensed compounds practically cannot diffuse into the catalyst pores. Due to the higher temperatures, the hydrogenation reactions are less favored than in distillate hydrocracking, which, together with the so far limited conversions, leads to smaller hydrogen consumption for residue hydrocracking. It should be emphasized that in both cases hydrogen consumption varies between wide limits in strong dependence on the nature of the feed stock. In accordance with the above considerations, the exothermicity of residue hydrocracking is usually smaller than in the case of distillate hydrocracking, the average values being below 500 kcal/m3 hydrogen consumed.

The commercial plants erected so far, are using both, fixed bed and up-flow reactors with ebullated bed catalysts. The later seems to offer the opportunity to solve some of the important problems of residue hydrocracking process, i.e. the increase of the pressure drop and activity loss, making it possible to maintain the activity at a constant level by continuously adding make up catalyst during operation.

The hydrocracking process reached today sufficient maturity to appreciate the opportunity of its incorporation in refinery development projects and especially in the flow sheets of [illegible]-scale refineries. Published studies offer general conclusions but each stresses the need to consider carefully the feed sources, the required products and local economic conditions (67 - [illegible]).

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In connection with the relation between hydrocracking and catalytic reforming and also jet fuel manufacture, the solution is not unique. Hydrocracking can be operated for example either to obtain a high yield of naphta which requires severe reforming, or to obtain lower naphta yield, with higher aromatics content which requires no, or only mild reforming.

It is possible however to obtain directly high octane naphtas (70 - 71). In the production of jet fuel it is possible to meet the product quality requirements directly from hydrocracking; in other cases it was considered useful to saturate the jet fuel cut in a separate plant, on an active hydrogenation catalyst and to reform the gasoline cut (72).

Comparing the relative advantages and disadvantages of hydrocracking and catalytic cracking on zeolitic catalysts, the conclusion seems to indicate that of combining both processes is economically favorable. This combination leads to the most advantageous balance of the use of butanes and ensures a great processing flexibility (61).

A main problem of hydrocracking are the catalysts. The versatility of the process claims catalysts with optimum composition and texture for each particular application. The literature is however very poor concerning informations about the catalysts. In a communication at the last World Petroleum Congress a review of the literature, including patents, was given, the conclusions being the following (57):

- the catalysts for the manufacture of [illegible] and gasoline are bifunctional with relatively high acidity, having as hydrogenation component NiMo or NiW sulfides on alumina-silica carrier.

More recent catalysts are using as carrier Y-type molecular sieves combined with hydrogenating components which sometimes are noble metals, such as Platinum or Palladium.

If hydrocracking is directed towards [illegible] distillates the cracking component (silica) of the support is limited. The use of [illegible] supports acidulated [illegible] is [illegible].

For the hydrocracking of residues weakly acid the catalysts are preferred, consisting of Ni and Mo [illegible] on alumina or amorphous silicaalumina carriers. Additionally important factors in this case are seeming to be the large external surface (small sized particles) a wide pore size distribution and a large pore volume. These properties permit the accumulation of large amounts of asphaltenes and metals.

The contribution of catalysts improvements to the hydrocracking process economics is undoubtedly important and as an example it can be mentioned that the reactor volume for a 1970 Isomax plant was only about one third of the volume required by the same type of plant in 1965 (57). The continuous efforts devoted towards the improvement of the catalysts will constitute of course, also in the future one of the important factors for the improvement of the process economics, hence the attractiveness of hydrocracking.

Last years development in the manufacturing technology of lubricating oils with high viscosity index have proved that catalytic hydrogenation is an interesting route in this field too. Therefore some brief concluding remarks on these processes will be given. Although the manufacture of engine oils by hydrogenation is known since the '30-th, the process did not develop than, due to the high costs of synthetic hydrogen and to the competition of more economical solvent extraction processes. The present demands of high quality lubricating oils, the decrease of raw material sources for high quality oils, progresses in technology and the availability of cheaper hydrogen, let to the reconsideration and to the successful commercial application of this technology.

Hydrocracking at low conversions of [illegible] distillates, leads after dewaxing to lube bases [illegible] with high viscosity indexes, to a great extent independently on feed quality.

The process may substitute solvent [illegible] and conventional finishing operations, offering yield [illegible] and [illegible] ability advantage.

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The process flow sheet is typical for hydrogen treating processes in general, consisting as an one stage fixed bed catalytic system, as shown in Fig. 20. After flowing through the reactor and separation of the recycle gases, the liquid product is fractionated under atmospheric pressure and the oils are separated in a vacuum column.

The operating conditions depend to a great extent on the quality of the feed and on the desired viscosity index level. The hydrogen partial pressure is reccomended to be high (150 - 200 atm) to maintain a favorable equilibrium for the hydrogenation of aromatics at the relatively high reaction temperatures (410 - 430°C) and to obtain good color stability of the oil.

In mor severe process conditions usually higher viscosity indexes are obtained but also a decrease of the product viscosity, simultaneously with the yield decrease.

Although the highest viscosity indexes are obtained from feeds with the highest viscosity index, in conditions of corresponding severity, viscosity indexes of 125 (ASTM D 567) can be obtained starting from a feed with viscosity index of 25 (52). The distribution of the viscosity indexes as function of viscosity is a very important feature. This depends strongly on the nature of the feedstock, especially at low process severity but the differences diminish gradually with increased severity, especially for inferior feedstocks, due to the structural changes which anihilate the influence of the initial composition. In Figs. 21 & 22 one can observe the effect of severity on the distribution of the viscosity indexes.

The lubes obtained by hydrocracking have raised some new problems which had to be solved to make them marketable. Thus the color stability of the hydrocracked lubes is unsatisfactory especially in daylight or uv radiations. It was observed that the instability is due to minute amounts of partially hydrogenated polycyclic aromatics (52). Not only the patent literature contains indications about the different ways of removing the instability by solvent extraction (73), or catalytic dehydrogenation (74) but also many refinery flow [illegible] stabilization at ultraviolet by extraction with solvent for instance in the new Puerto Rico refinery of [illegible]

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The oxidation stability of hydrocracked lubes can be smaller than that of solvent extracted ones but the inhibitor response of the first is markedly good, giving thus lubes with high oxidation stability.

In connection with engine tests the hydrocracked lubes were found equivalent in many aspects to conventional lubes, without special aditivation formulas. In some cases it was observed however that in the diesel engine tests where high temperatures predominate, more abundant deposits are formed on the pistons both for single-grade and multi-grade oils. By new specific additivation formulas, these inconveniences can be also overcome.

Since in multigrade lubes which contain hydrocracked components, the content of polymer type viscosity index improver is smaller, these oils have a better mechanical resistivity against shear (76). The lower volatility of the hydrocracked lubes reduces consumption in comparison with conventional multigrade lubes (52).

In a recent article (77) parallels are analysed between solvent extraction and hydrocracking. Almost all the advantages are for the hydrocracking. If however there are few commercial applications so far, the reasons can be :

- lack of increasing demands
- existence of adequate facilities
- availability of viscosity index improvers.

In RSR the situation favors the application of hydrocracking for the manufacture of oils with high viscosity indexes. Own investigations led to the development of a technology which will be applied commercially in the next future.

Brief considerents about hydrotreating processes of a wide variety of feedstocks for an equally wide variety of purposes, cannot but outline the wide field of these modern commercial applications in the processing of petroleum. If today some of the more recent applications are still under discussion, then the cause is the relatively high cost of investments and of manufacture, especially for deep hydrocracking of residual stocks. The economics of these are rather obscure, especially due to their relative novelty and to the very different operating conditions.

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From operating costs of 30 - 60 c/m3 for mild hydrogenation of oils or gasolines, 1,25 - 1,9 Dollars/m3 is reached in middle distillate desulfurization and 3 - 4,5 dollars/m3 in the case of residues. In the case of some residue hydrocracking the operating costs of about 12 dollars/m3 can surpass even the cost of the feedstock. It seems that for a while hydrocracking will be more expensive than other process alternatives, but with the technical developent and the erection of larger plants one can expect the decrease of the operating costs from 4 - 7 dollars/m3, today to 2,5 - 5 dollars/m3 (19).

From the scarce informations concerning the costs of investments for hydrocracking plants, one can estimate a value of 5.000 - 7.500 dollars/m3,sd or even higher.

In many cases direct comparison of investment or operating costs is irelevant. More interesting situations arise where processes or combinations of processes are superposed with regard to the results which can be obtained. In such situations the costs must be balanced with the technical advantages of the various possible alternatives.

In the cracking of the heavy cuts and of residues, hydrocracking meets the competition of thermal cracking and coking processes. A more recent development announces here a new important combination - that of coking and hydrocracking. By the relatively cheap coking of the most refractory feedstocks a large amount of the sulfur and other impurities are concentrated in the coke. The coker gas oil, too sulfurous for catalytic cracking, becomes a suitable feed for hydrocracking operating at moderate costs.

In view of the present tendencies of the market, with demands for jet fuels, petrochemical naphtas and all sorts of engine fuels, as well as the need to reduce, until disappearance, the heavy and residual stocks, it is sure that the combined or coking schemes and the wide[illegible] of individual cracking processes will constitute the route also for the future.

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VI. [illegible]

[illegible] in the present and future development of refinery, the catalytic processes are the main tools for the production of high quality fuels and feedstocks for petrochemistry. More over almost all the available catalytic processes are necessary to be applied for getting products meeting the market requirements.

In the last time even in the lube oils production the catalytic processes penetrate more and more, gradually replacing the conventional technology of manufacture high quality lubricants.

In the extension of existing and in the errection of new refineries the flowsheets include almost in every case catalytic reforming and hydrotreating. Depending on the specific profile determined by the crude sources, the market demands and other regional considerations, the refining schemes are completed with other catalytic processes such as catalytic cracking, isomerisation alkylation, various hydrocracking alternatives, hydrotreating of various cuts, etc.

It should be noted that the most important progresses, which determined the present and future development of the basic catalytic processes, are due especially to the development of new types of catalysts. This justifies the importance which is given today to the research and development of catalysts for petroleum processing.

Although the above shown trends are more evident in the industrial developed countries, there is a very clear trend toward such route of oil processing in the developing countries too. Of course the development of the oil industry based on catalytic processes requires not only availability of suitable resources of crudes and financial and technical potentialities, but also a high qualified staff as well as finding of efficient ways for cooperation in transmitting large amount of know-how, related to these processes.

Acknowledgement

I would like to express thanks to Mr. Tr.Filotti and Mr. [illegible], for the assistance given in carrying out this work.

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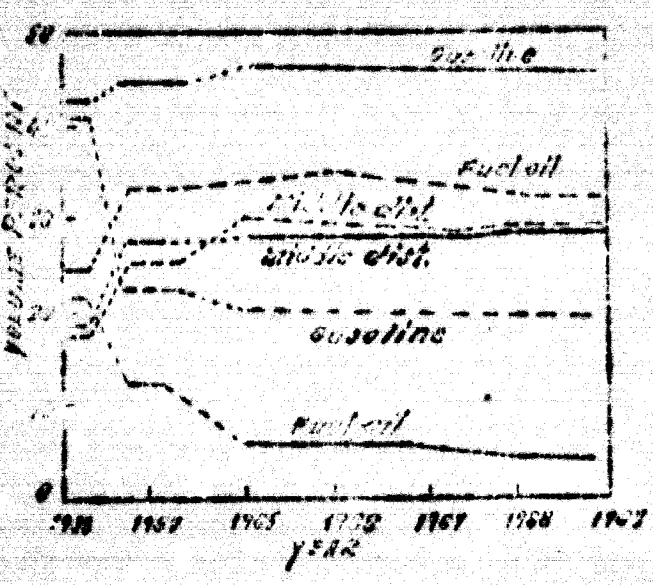
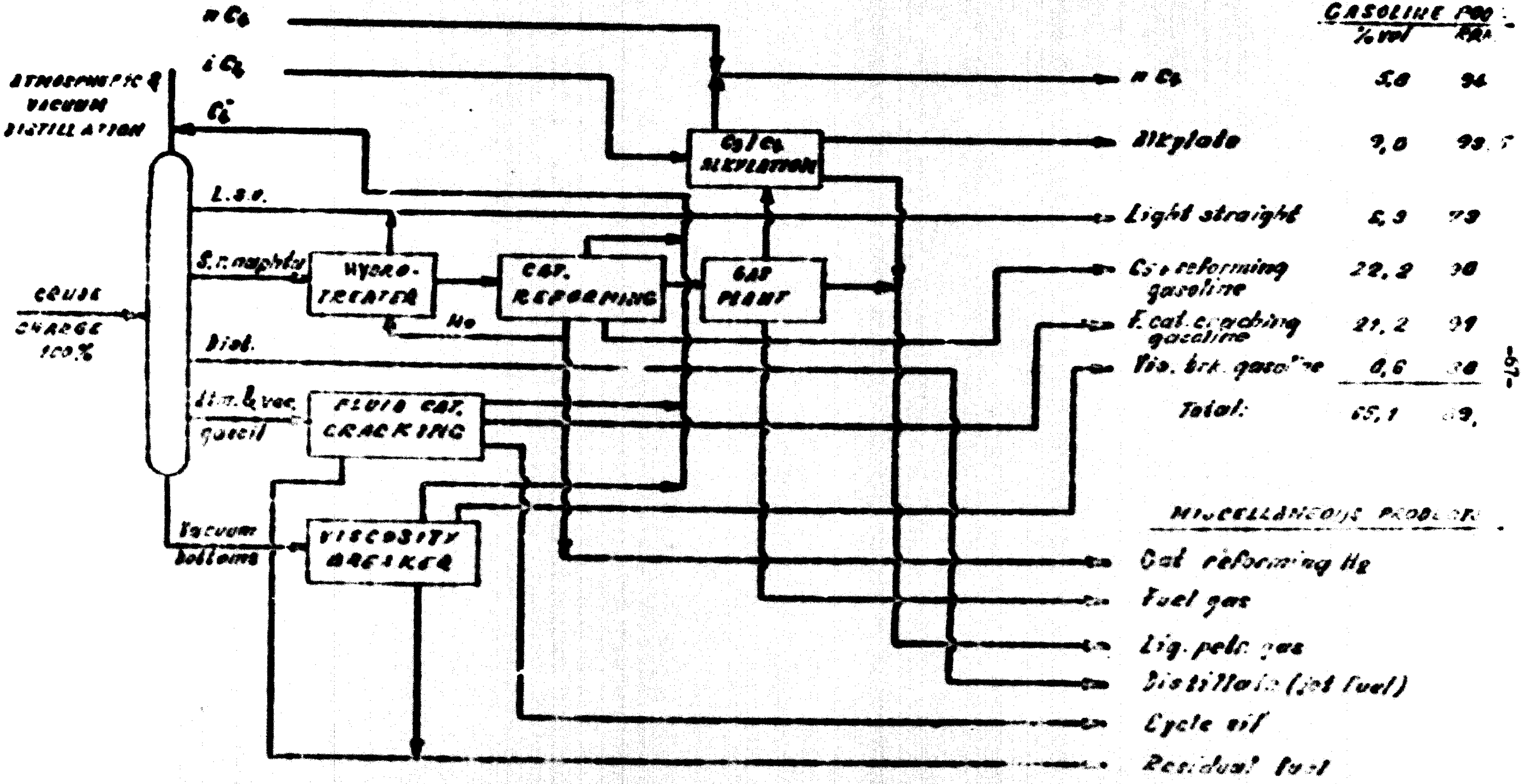


Fig.1. Refining yields
—— U.S.A.
- - - WESTERN EUROPE.

FIG. 2. GASOLINE PRODUCTION BASE REFINERY
FLOW SCHEME (4)



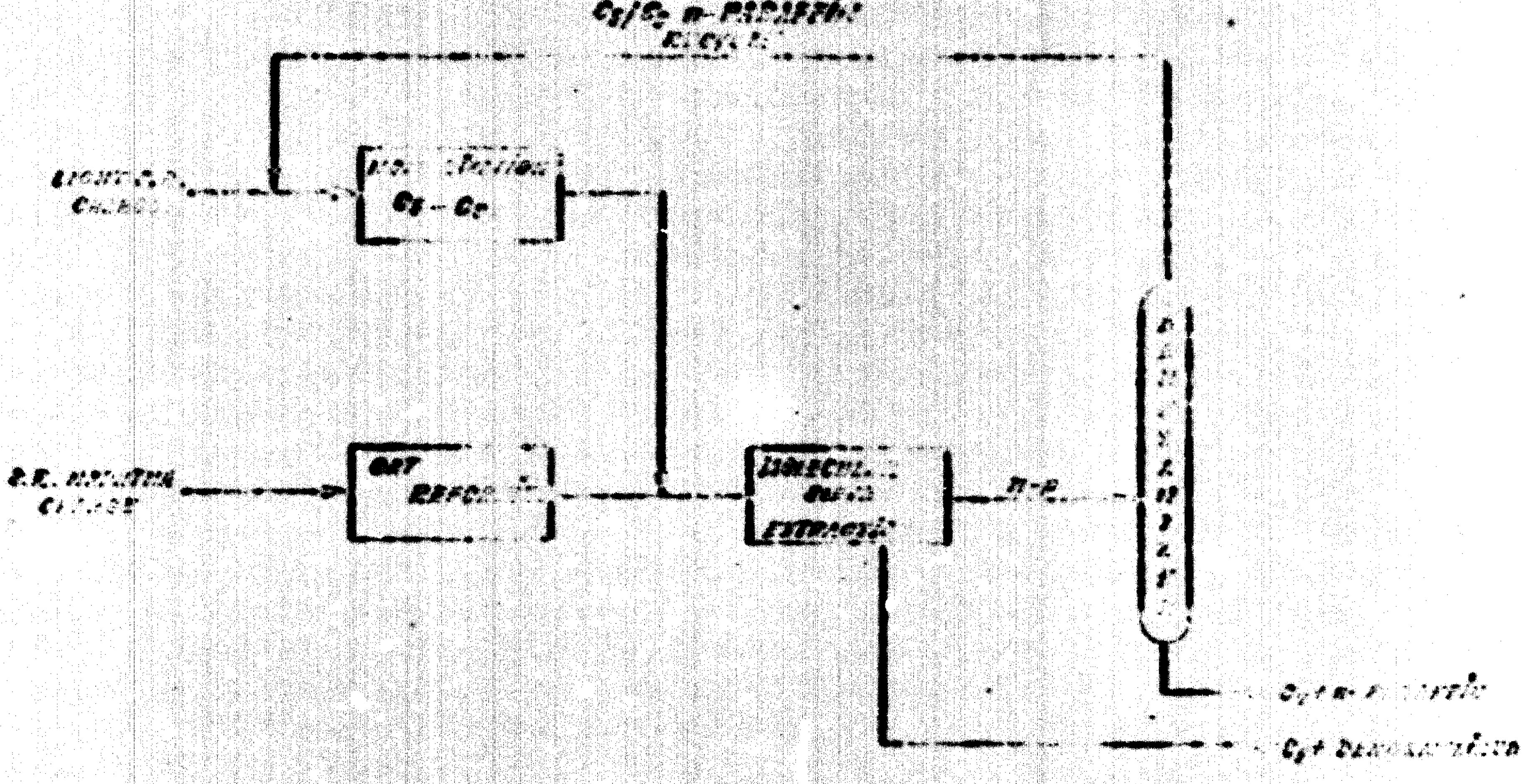
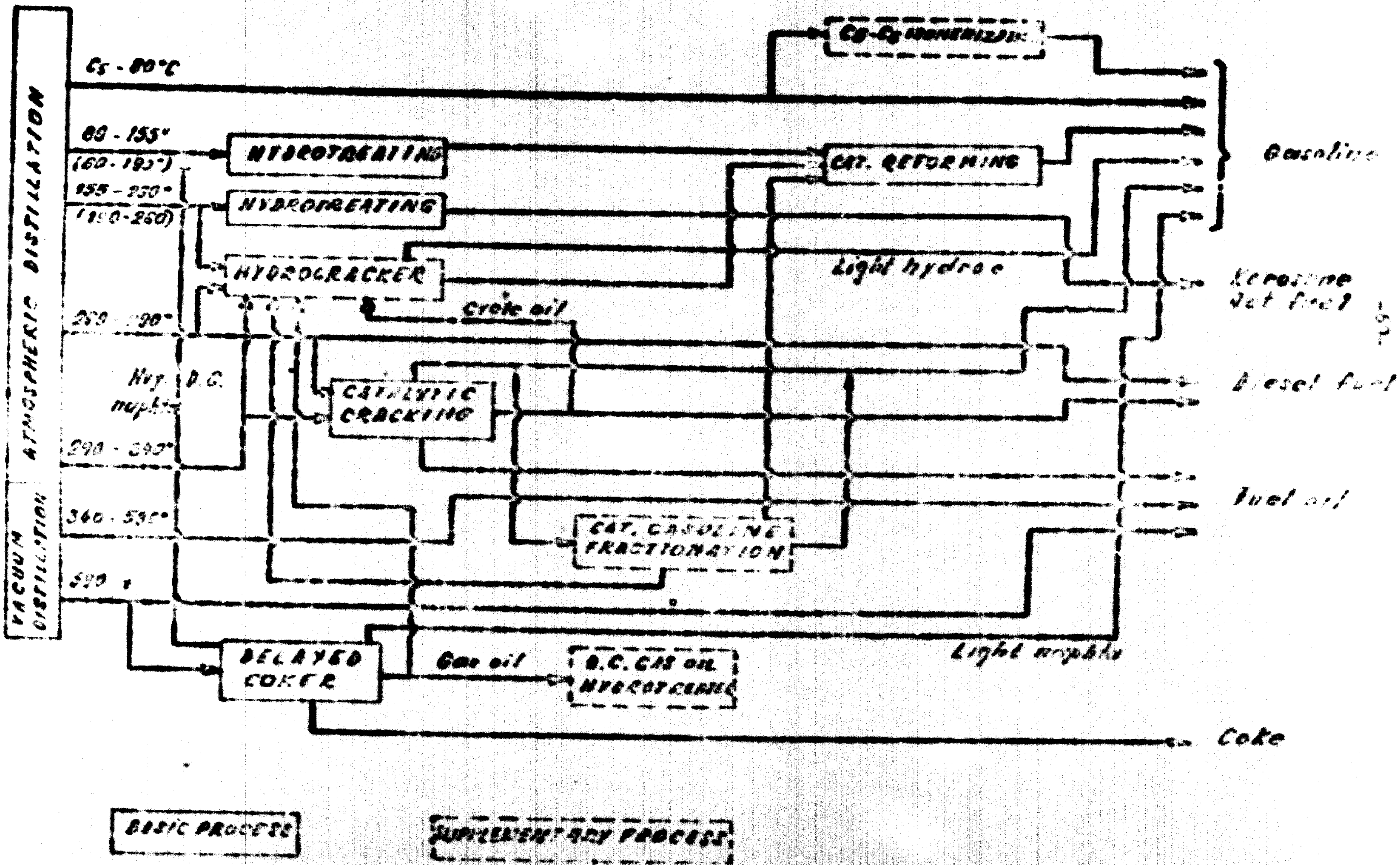


Fig 5. FLOW SCHEMATIC: CAT REFORMING COMBINED WITH ISOMERIZATION AND MOLECULAR SIEVE EXTRACTION

FIG.6. COMPLEX REFINERY FLOW SCHEME (7)



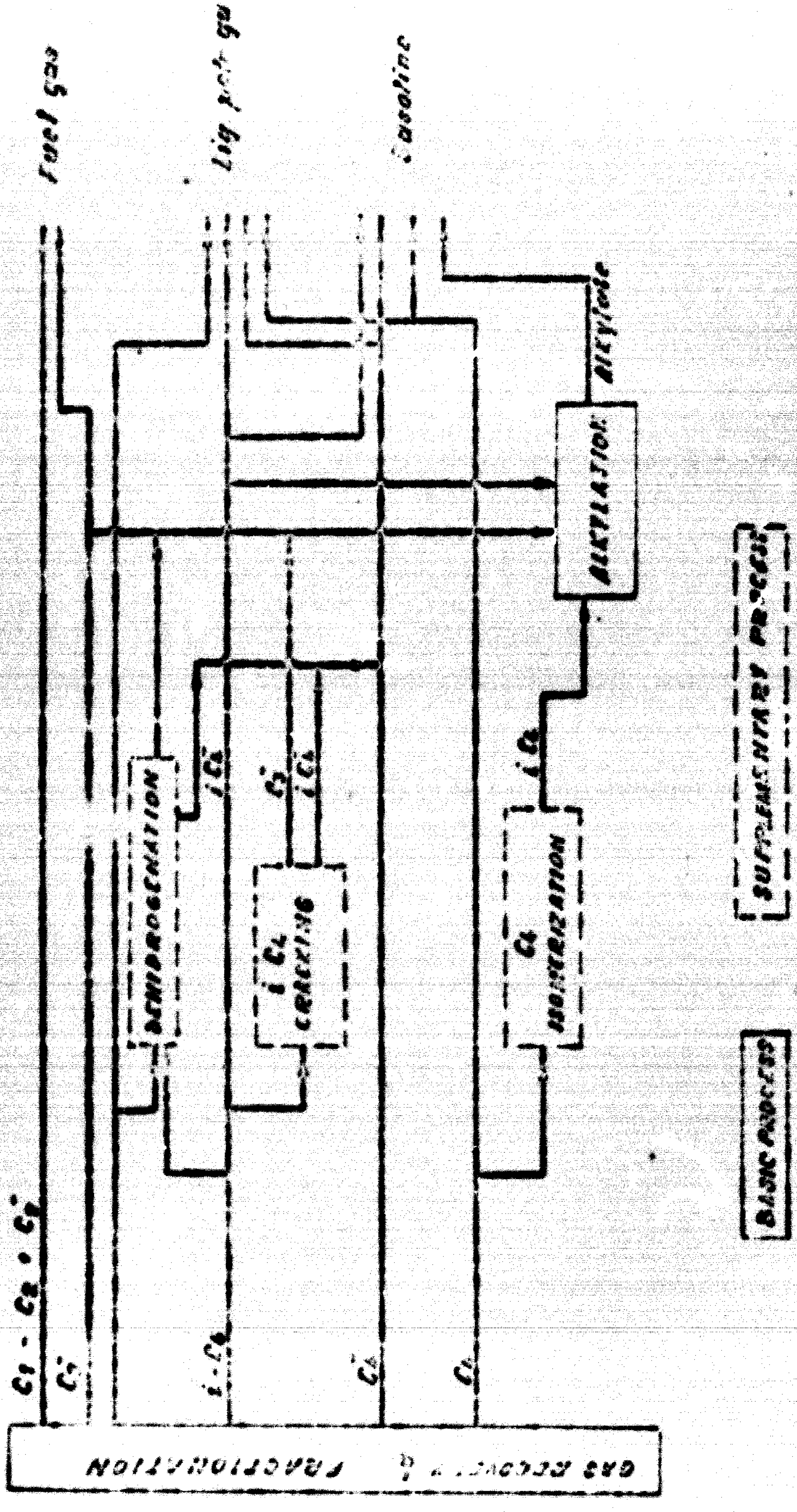


FIG. 6. GAS PROCESSING POSSIBILITIES (7)

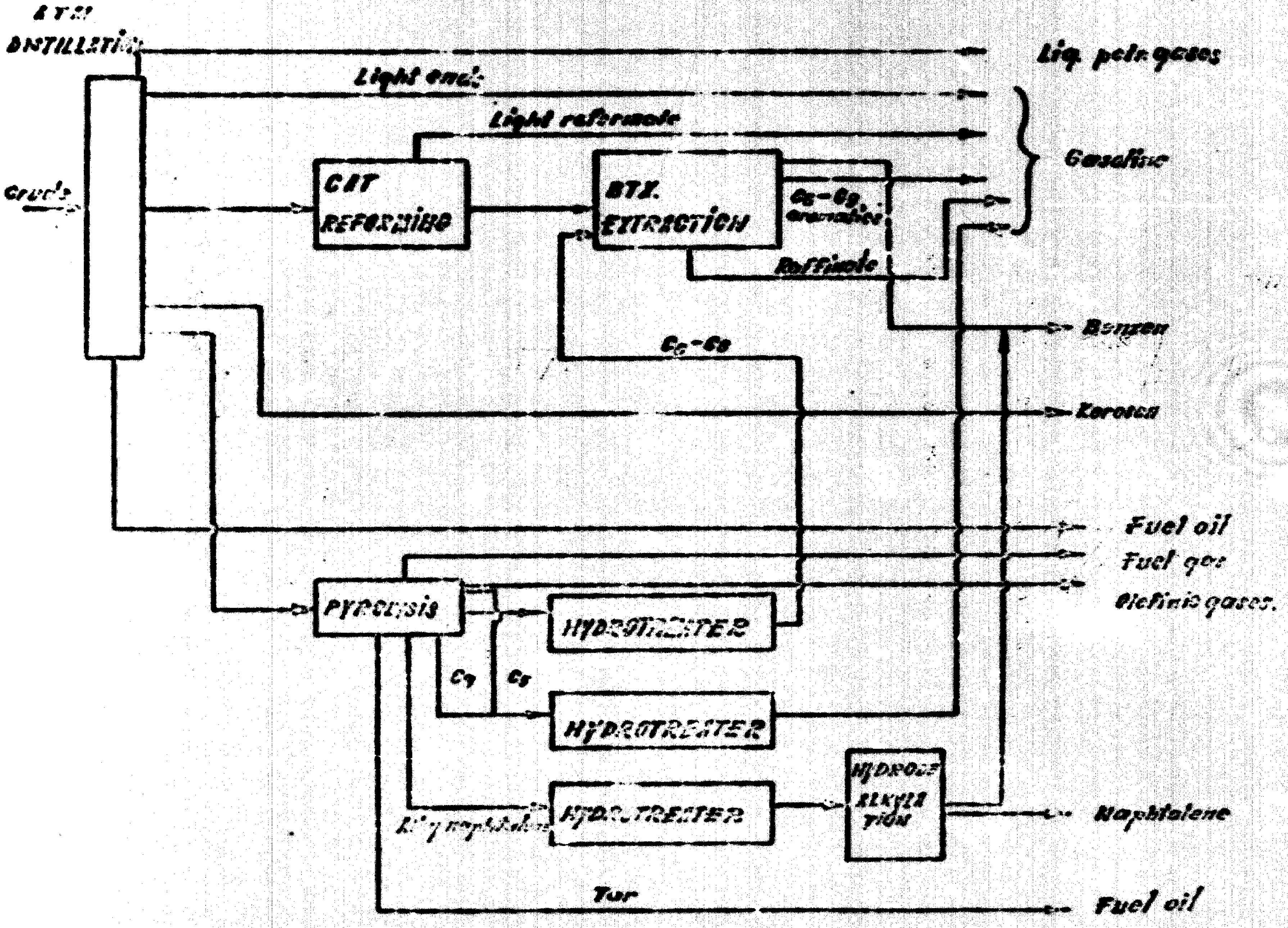


Fig. 6. FLOW SCHEME FOR A CHEMICAL REFINERY.

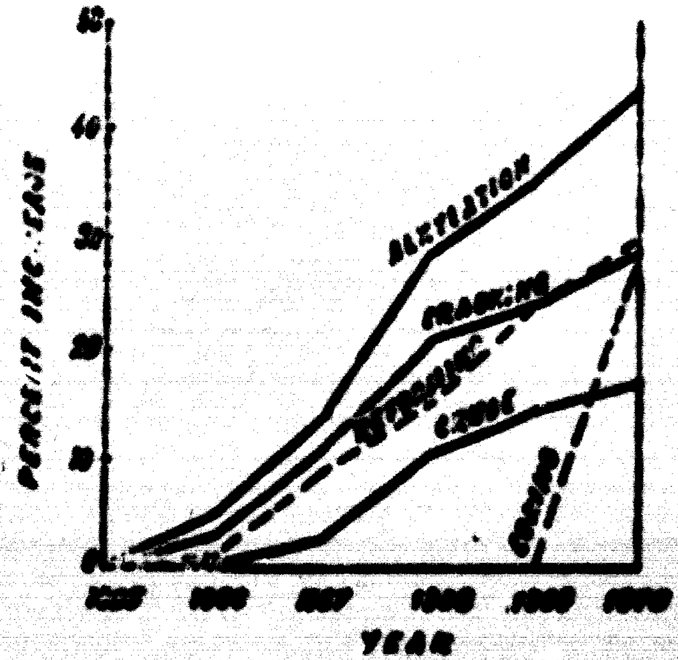


FIG. 7. PROCESSES EXPANSION IN USA.

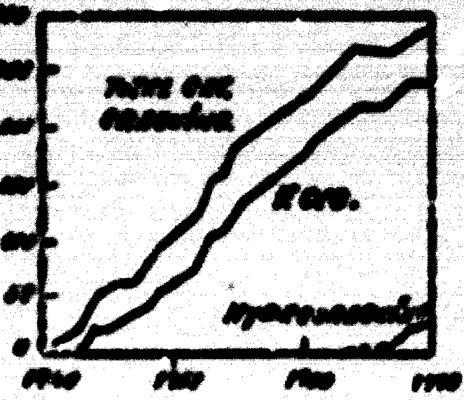


Fig. 8. CATALYTIC CRACKING IN THE USA

FIGURE 9

EFFECT OF OPERATING VARIABLES ON ZEOLITIC PERFORMANCE

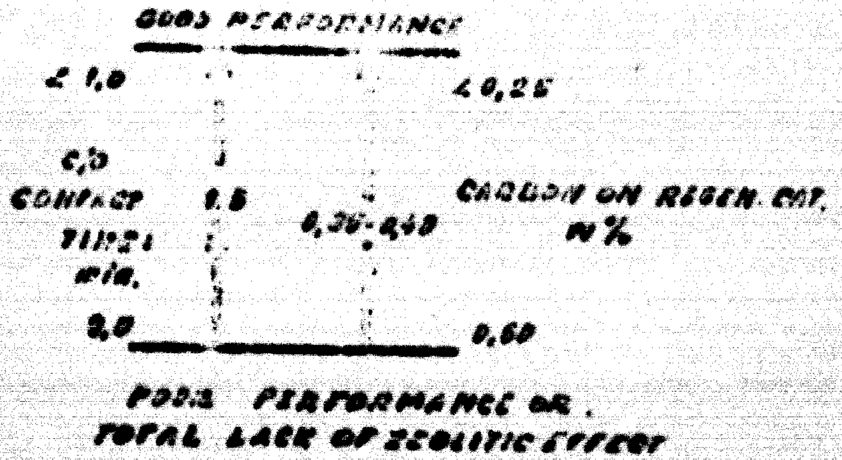
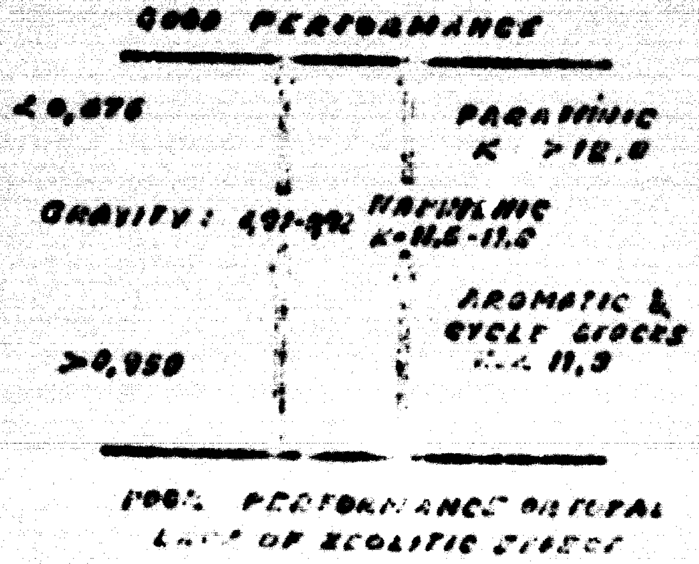


FIGURE 10

EFFECT OF FEEDSTOCK QUALITY ON ZEOLITIC PERFORMANCE



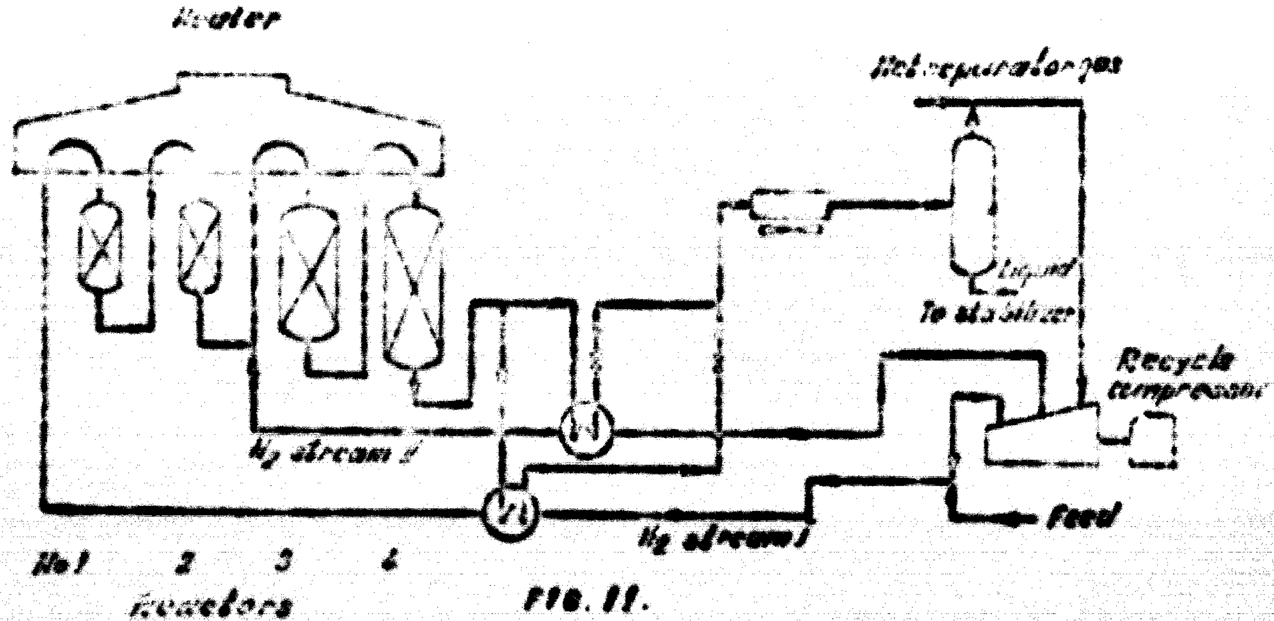


FIG. 11.

MAGNAFORMING PROCESS.

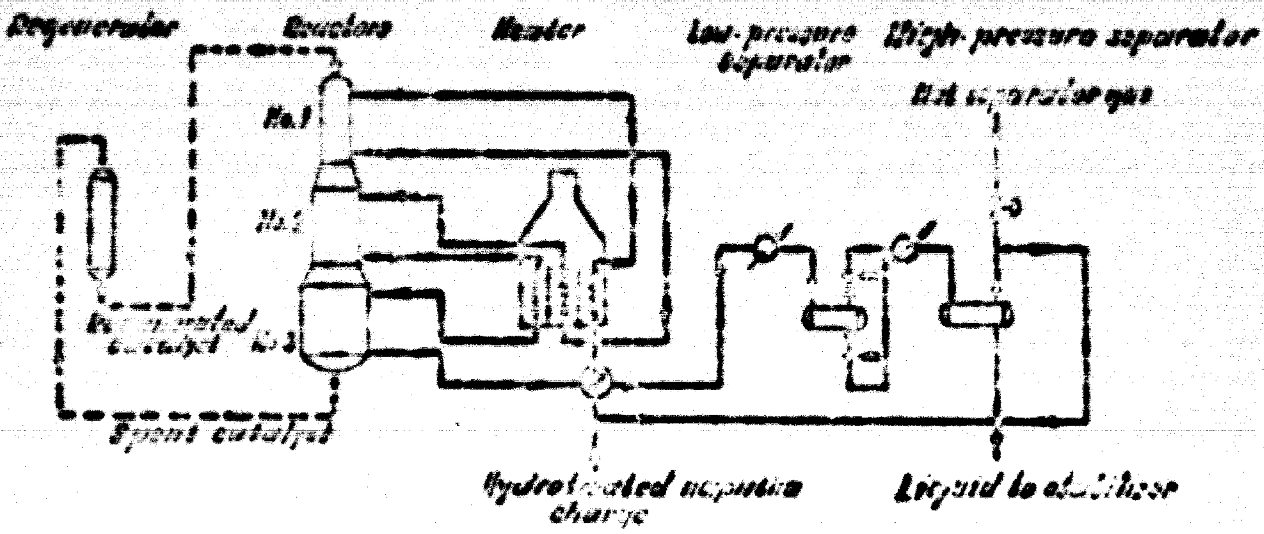


FIG. 12.

U.O.P CONTINOUS REGENERATING REFORMING PROCESS.

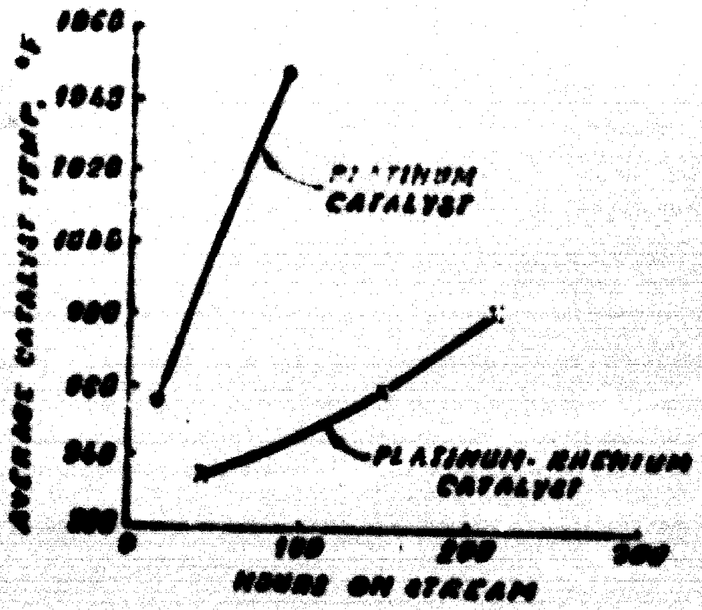


FIG.13. REFORMING FOR 100 R.O.N. NAPHTA WITH Pt. AND Pt-Re CATALYSTS.

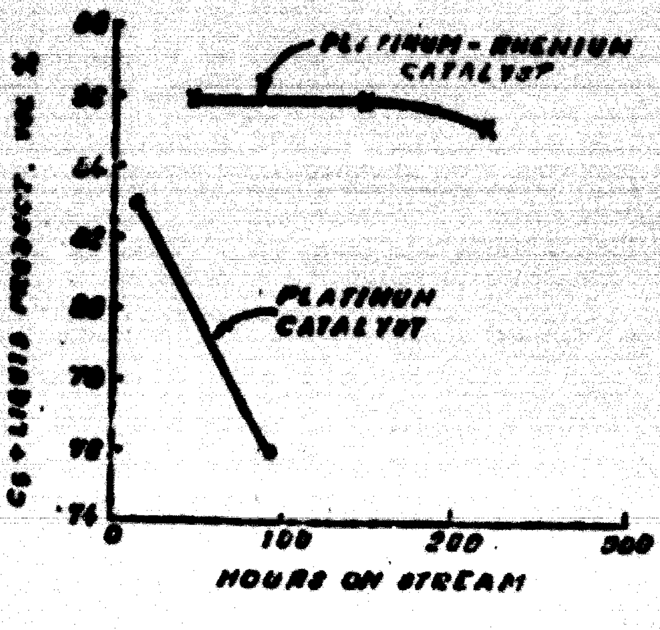


FIG.14. REFORMING FOR 100 R.O.N. NAPHTA WITH Pt- AND Pt-Re CATALYSTS

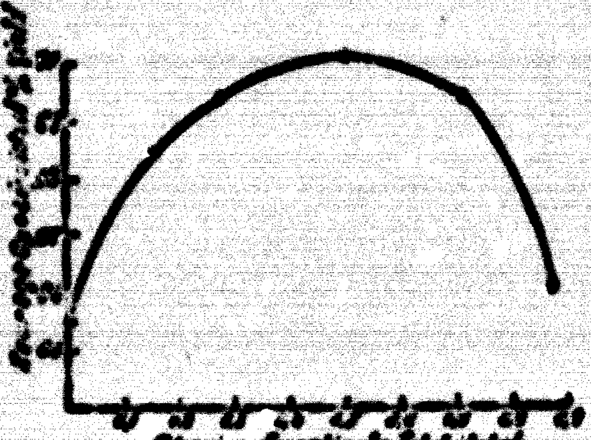


Fig.15 — Pt-rhenium-alumina catalysts—effect of metal composition on C_5^+ yield.

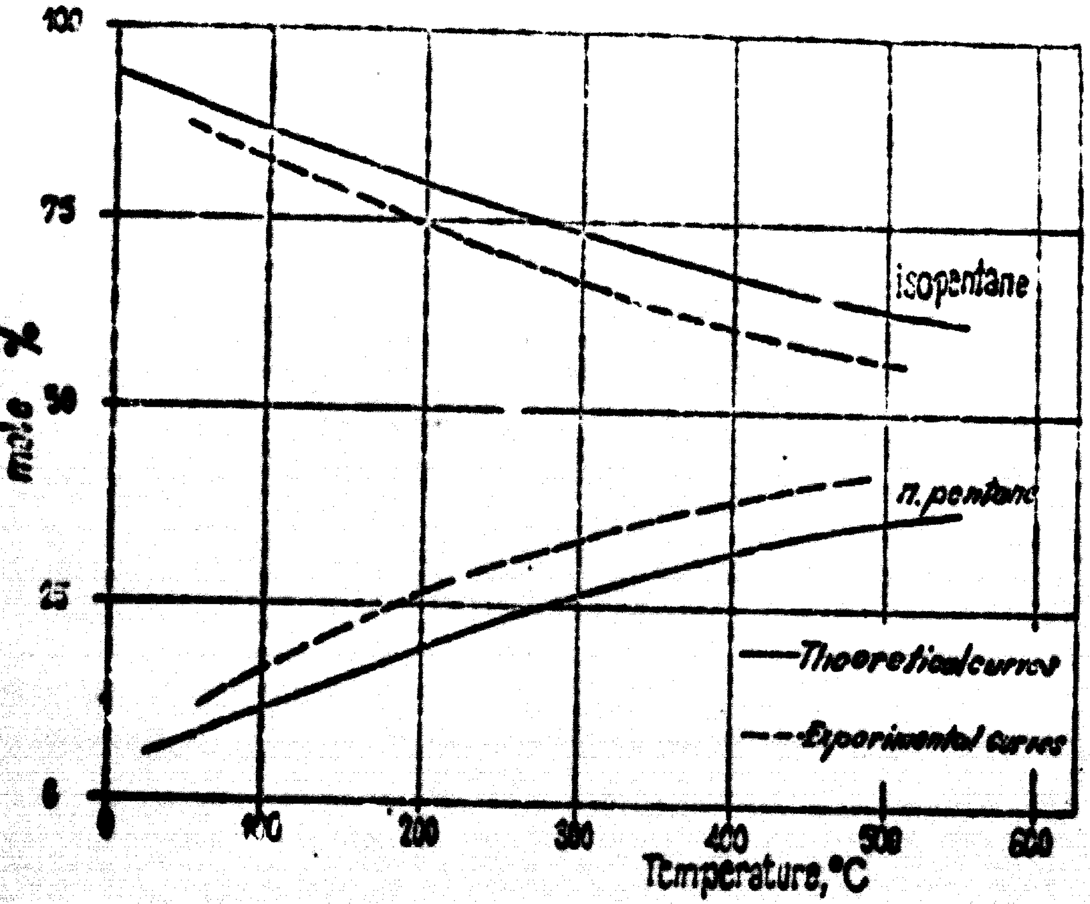


Fig.16. Isopentane and n-pentane equilibrium

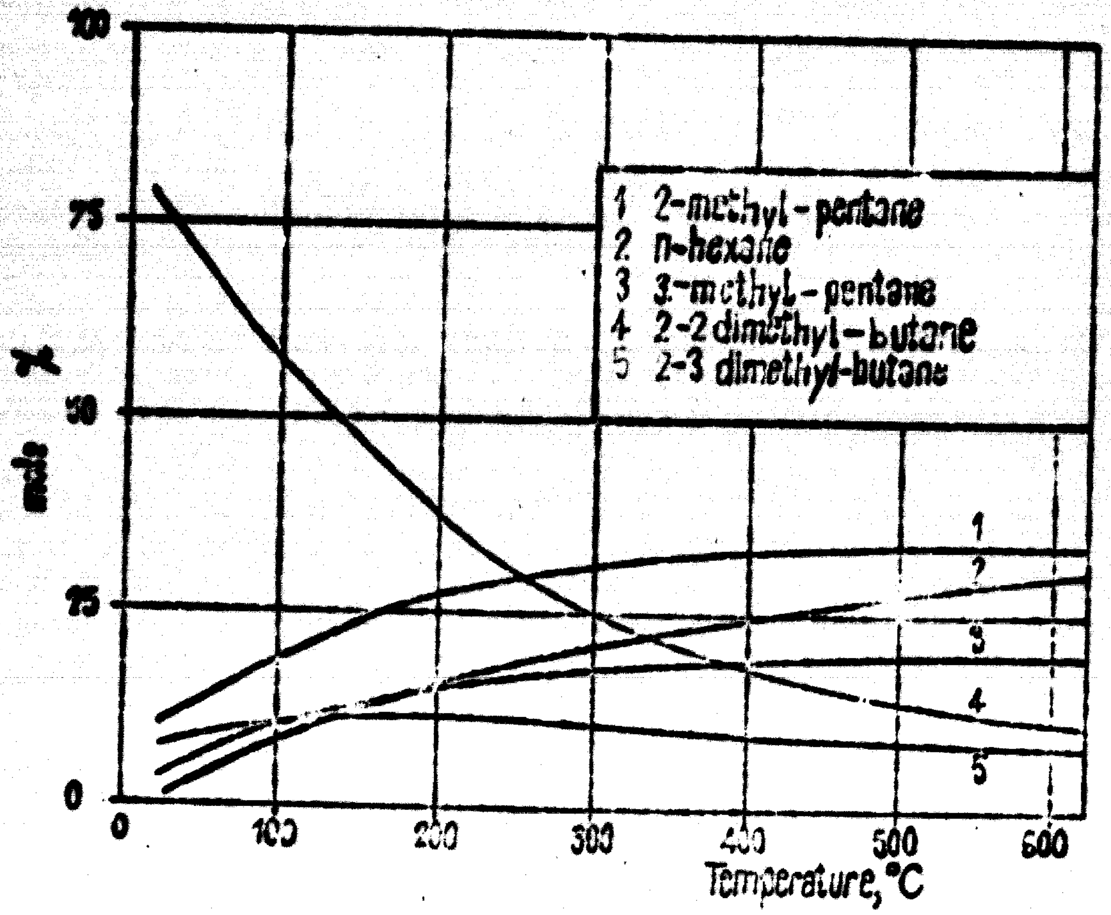


Fig. 17 C_6 isomers equilibrium

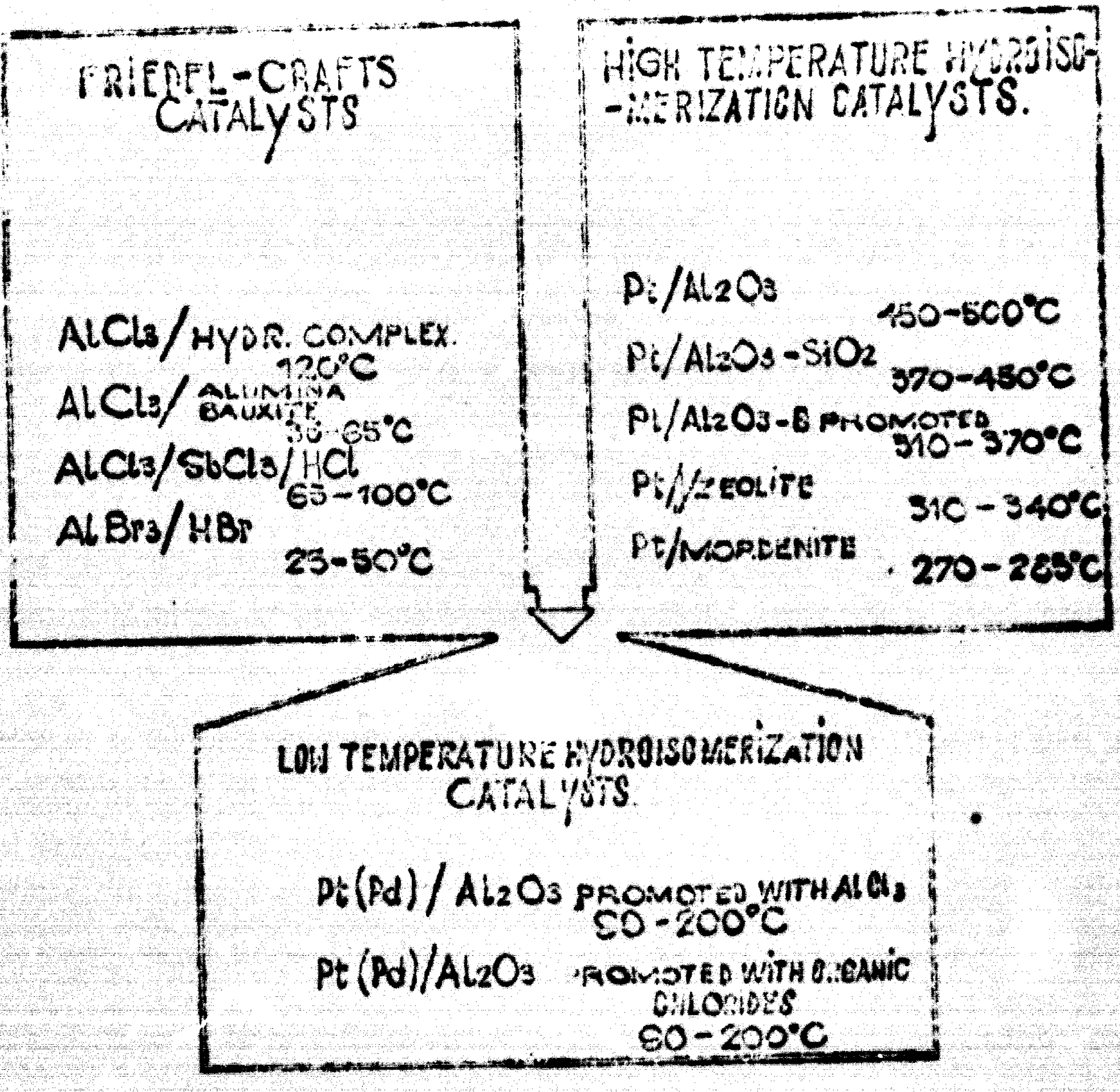


Fig. 13.

Isomerization catalysts development.

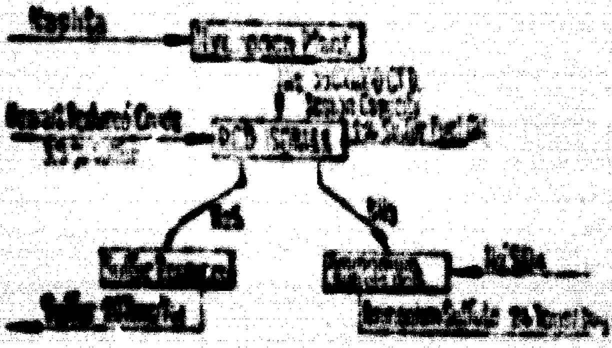


FIG.19 BLOCK FLOW DIAGRAM OF RCD COMPLEX.

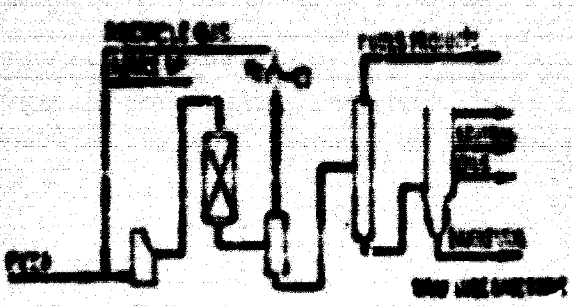


FIG.20 SIMPLIFIED PROCESS FLOW DIAGRAM FOR LUBE HYDROCRACKING

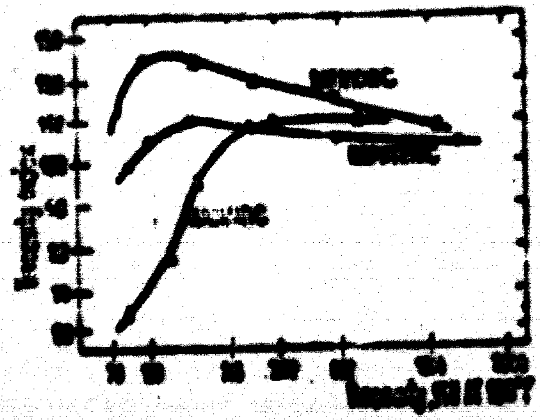


FIG.21 EFFECT OF FEED COMPOSITION ON VISCOSITY INDEX-VISCOSITY DISTRIBUTION

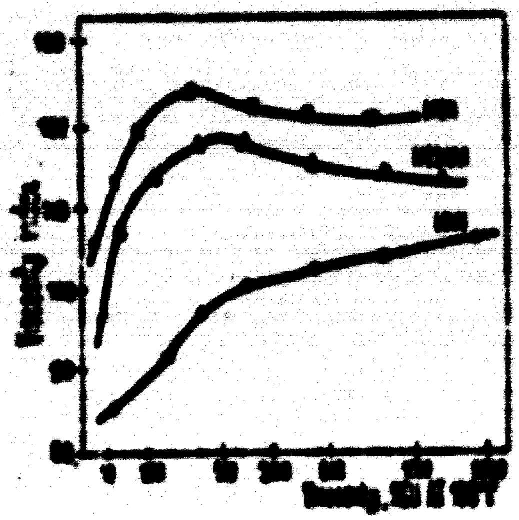
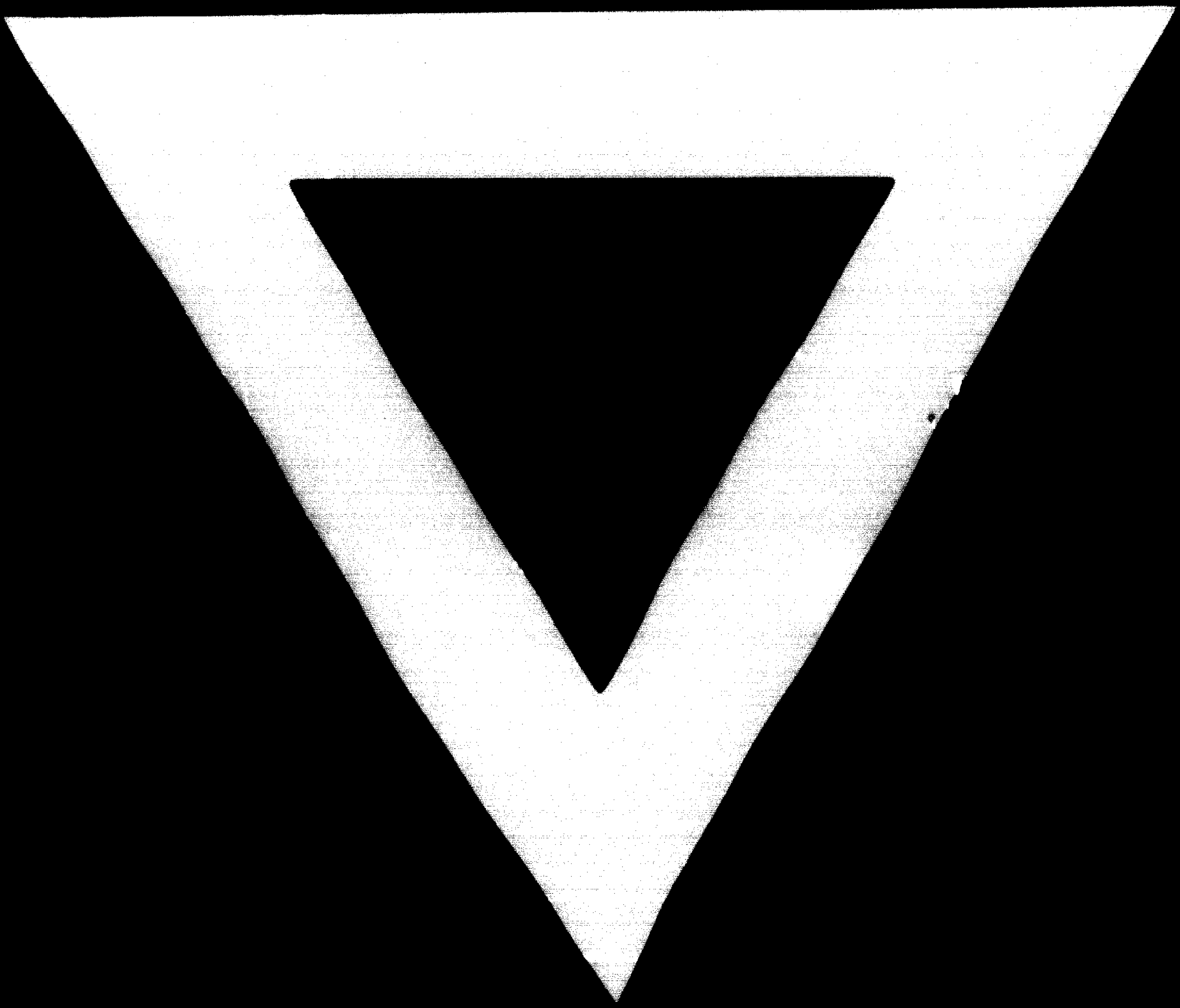


FIG.22 EFFECT OF HYDROCRACKING SEVERITY ON VISCOSITY INDEX - VISCOSITY DISTRIBUTION FOR AROMATIC FEEDS.



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