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Development of the Petrochemical Industries in
Developing Countries

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Dakar, USSR, 21 - 31 October 1969

RECENT DEVELOPMENT IN PETROCHEMICAL INDUSTRIES SINCE 1964

AND THEIR INTEREST TO DEVELOPING COUNTRIES^{1/}

by

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SUMMARY

DEVELOPMENTS IN PETROCHEMICAL INDUSTRIES
SINCE 1964 AND THEIR INTEREST TO DEVELOPING COUNTRIES ^{1/}

by

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- I. Introduction
- II. New processes and technological developments
 1. Recent developments in petrochemistry
 - 1.1 Olefins
 - 1.2 Dioléfins
 - 1.3 Aromatics
 - 1.4 Oxygenated compounds
 - 1.5 Polymerization
 - 1.6 Protéines
 2. Process improvements and new processes developed since 1964;
 - 2.1 New steam-cracking units
 - 2.2 New processes and improvements in the field of polyolefins

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III. World economic studies

1. Economic characteristics
2. Economic factors and political factors influencing the market for petrochemical products.
3. Technical factors influencing the market for petrochemical products
4. Probable trends in the factors influencing the market for petrochemical product.
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Introduction

The dynamism of the petrochemical industry and the constant quest by manufacturing companies for lower costs of production has led, since 1964, to the appearance of numerous new techniques whose importance, which may vary with each particular case, can substantially transform production and the market for certain products. For this reason, although the new processes derived from these techniques have led so far to only a limited number of industrial applications, it seemed useful to describe their main characteristics, and to try to estimate their value.

An examination of the literature published since 1964 suggests a grouping of these new techniques on the basis of the products obtained:

- olefins
- diolefins
- aromatics
- oxygenated products
- polymers
- proteins

I - Production techniques for olefins and aromatics required by the petrochemical industry

To transform hydrocarbons obtained from petroleum so as to obtain the olefinic and aromatic compounds called for by the chemical industry, it must be had to the technique of steam cracking and catalytic reforming, the first of which is possible to obtain ethylene, propylene, butadiene and benzene in proportions which can be equated in most extent to the needs of the market while the second brings a complementary production in the form of aromatics and in particular, benzene and naphthalene.

I.1. Steam cracking

The first level steam cracking leads to the simultaneous production of a number of products which can be used in petrochemistry, and which have to be marketed either globally or locally in proportions which may be different from those in which they are produced by steam cracking, this led to research on methods of changing the relative proportions of these products so that production can be adapted to demand.

To achieve such adaptation, there are a number of possibilities:

Thanks to the ability of vapour-phase cracking to transform in and the most varied petroleum fractions, this process can be applied to any other of them according to their availability, in relation to industrial context. Thus it is, as is well known, that in the US where vast quantities of ethane and propane are available as a result of the development of energy production from natural gas, 70% of ethylene produced in 1970 will result from the cracking of ethane (representing 3.5 million tons/year) and 30% by the cracking of propane (representing 5.6 million tons/year).

In Europe (and in France in particular), 90% of ethylene produced in 1970 will come from the cracking of liquid hydrocarbons.

However, the yields of ethylene differ as we pass from one raw material to another, and as a result there appear real products - ethane, butadiene and aromatics - the recovery of which provides a source of profit to the operation.

Thus, given a higher yield of ethylene, i.e. 70-80% by weight; and also by weight, which may be multiplied, one finds only 3% of butane and about 10% of butadiene. As these products are of such great interest, there are provided only when it is possible to link the steamcracking plant with a other cracking plant which recovers in particular the cracking of propane for the production of propylene and butadiene.

Propane yields 40-45% by weight of ethylene, about 20% of propylene and 3% of butadiene, on a 90% - molar conversion of propane. If conversion is limited to 75%, the yield of propylene may reach 26% by weight.

Among the butanes, n-butane is a raw material of interest leading to 30-35% by weight of ethylene and 21-25% by weight of propylene, and 3% butadiene representing only 3% by weight. Iso-butane gives little ethylene (8% by weight only) and about 25% by weight of propylene.

Among the liquid fractions, naphthas (35° - 170°C) are the raw materials in greatest use at the present time. The yields of ethylene, propylene, butadiene and aromatic gasoline vary by notable percentages depending on the cracking conditions and also on the composition of the charge.

(a) by modifying the operating conditions which determine the severity of the treatment, viz. temperature and residence time, a given classical feedstock (Koudit naphtha 35° - 170°C) can be made to give yields of ethylene ranging from 25% to more than 30% - even to 35% - while, over the same range of operating conditions, the propylene yield goes through a maximum of 16%. As Table 3 shows, by varying the severity of the treatment, one can obtain either a maximum of ethylene or a maximum of propylene - the maximum being at a higher level according to the composition of the charge. The yields of butadiene and total aromatics are relatively unaffected by the severity of the cracking treatment and are around 4% and 20% respectively. As the severity is increased the concentration of feedstock in which the maximum yield of ethylene is obtained (Table 3) also increases and is obtained in which the total aromatics ranges from 25% to 35%, while the concentration of propylene and the C₆, C₇ and C₈ aromatics go from 25% to 35%.

However, the application of conversions of particular severity to a given feedstock is in some cases limited at the upper end of the severity range by the availability of materials of construction of the furnace, which have too short a life at high temperatures, or by the resistance of some of the former tubes and/or the structural equipment, leading to a subsequent stoppage of the plant. This effect is greater, at equal severities of treatment, for heavier than for lighter feeds, as shown in Table 2, the very high selectivities on gas-oil and associated with much lower yields of ethylene than on lighter feeds.

(b) By choosing a petroleum fraction consisting of hydrocarbons, the distribution of which favours the result sought after. Thus it is known that n-paraffins lead to a high yield of ethylene and a low yield of propylene: n-hexane can give up to 45.2% of ethylene and 14% of propylene (4). Transposing these results to a light naphtha, consisting in large part of n-paraffins, one obtains as shown by Table 1 (first column) up to 43% of ethylene and 13-14% of propylene.

Isoparaffins, on the other hand, give higher proportions of propylene with lower yields of ethylene: 2 - methyl - and 3 - methyl - pentane yield respectively 29.5% and 19.3% of propylene and 24.3% and 27.9% of ethylene (4).

Aromatics which are very stable at high temperatures, do not give light products. They undergo themselves to two main types of reaction, viz. dealkylation of substituted aromatics (which increases the benzene content of the product) and dehydrogenation of ethylbenzene, which yields styrene by a reaction of similar rate to that of the ethane-ethylene transformation. As a function to a large extent, and generally as shown in Fig. 1 shows that a correlation can be established between the aromatic content of gasoline and its yield of naphthalene. Although the majority of the naphthas were given yields of 2-5%, at naphthalene-contents of 15 - 20% by volume, Fig. 1 shows that by cracking feeds richer in naphthalene (20% or more), 7-10% of naphthalene can be obtained.

These examples show that the yields from steam-cracking can be modified, not only by varying the operating conditions but also by selection of the treated feedstock (in which the chemical composition of the constituents can be of effect), so that they approach the desired proportions of ethylene, propylene, butadiene and acrolein. Table 1 and 2 illustrate these findings for selected starting materials: they show that the ethylene/propylene ratio can vary from 3.1 to 1.6 and that the yield of butadiene can range from 3.4 to 9.6. Such results provide steam-

Table 1

Steam-cracking of naphtha - Maximum chemical yields

Feedstock:	Light naphtha 40-97°C	Naphtha 34-117°C		
Specific gravity	0.663	0.713		
Origin	-	Kuwait		
<u>Analysis (% by weight)</u>				
n-paraffins	63.6	40.3		
iso-paraffins	25.1	32.2		
naphthenes	9.5	19.5		
aromatics	1.8	3.4		
% of cruds	5-8	22.5		
<u>Operation:</u>				
	C_2H_4 max.	C_3H_6 max.	C_4H_8 max.	C_5H_{10} max.
<u>Yield (% by weight)</u>				
C_2H_4	41.60	31.60	34.0	29.8
C_3H_6	13.30	18.55	13.50	16.15
C_4H_8	4.30	3.30	4.50	4.10
C_5H_{10}			(2.0% of total C ₅ and C ₆)	

Table 2

Steam-cracking of gas-oil - Maximum chemical yields

	Gas-oil 230-335 °C		Gas-oil 210-330 °C	
	Kuwait		Nigeria	
Yield	0.832		0.854	
<u>Yields (% by weight)</u>				
Hydrogen	17.7		8.7	
Acetylene	27.7		22.2	
Ethylene	23.0		41.6	
Propylene	31.6		27.5	
<u>Gas composition (% by weight)</u>				
	C_2H_4 max.	C_3H_6 max.	C_2H_4 max.	C_3H_6 max.
	28.80	24.30	20.10	18.0
	10.35	13.75	8.35	11.45
	4.35	5.65	3.45	4.45

(S.B. Zlotnik et al., 1967)

NAPHTA STEAM-CRACKING BUTADIENE YIELD

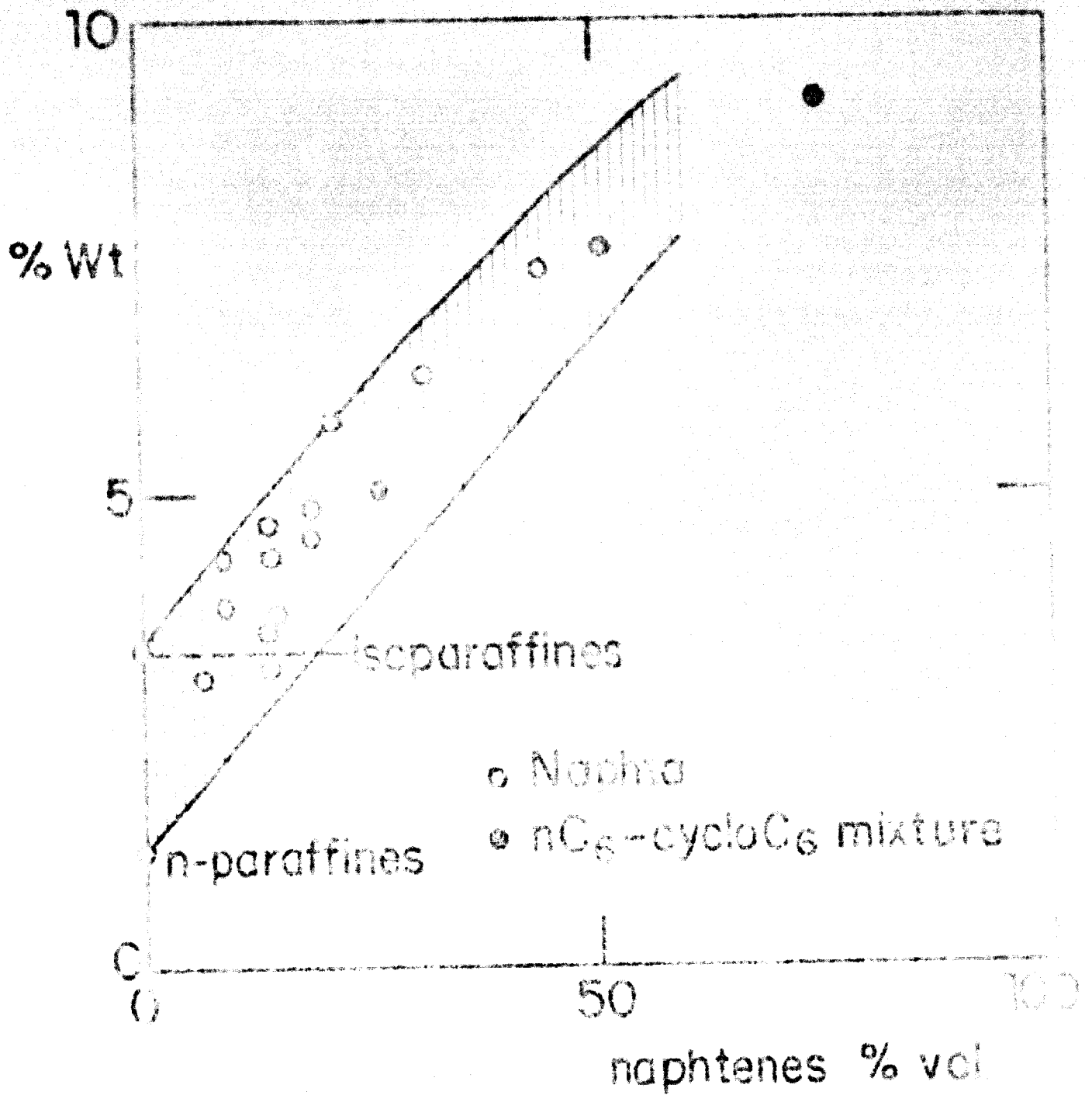
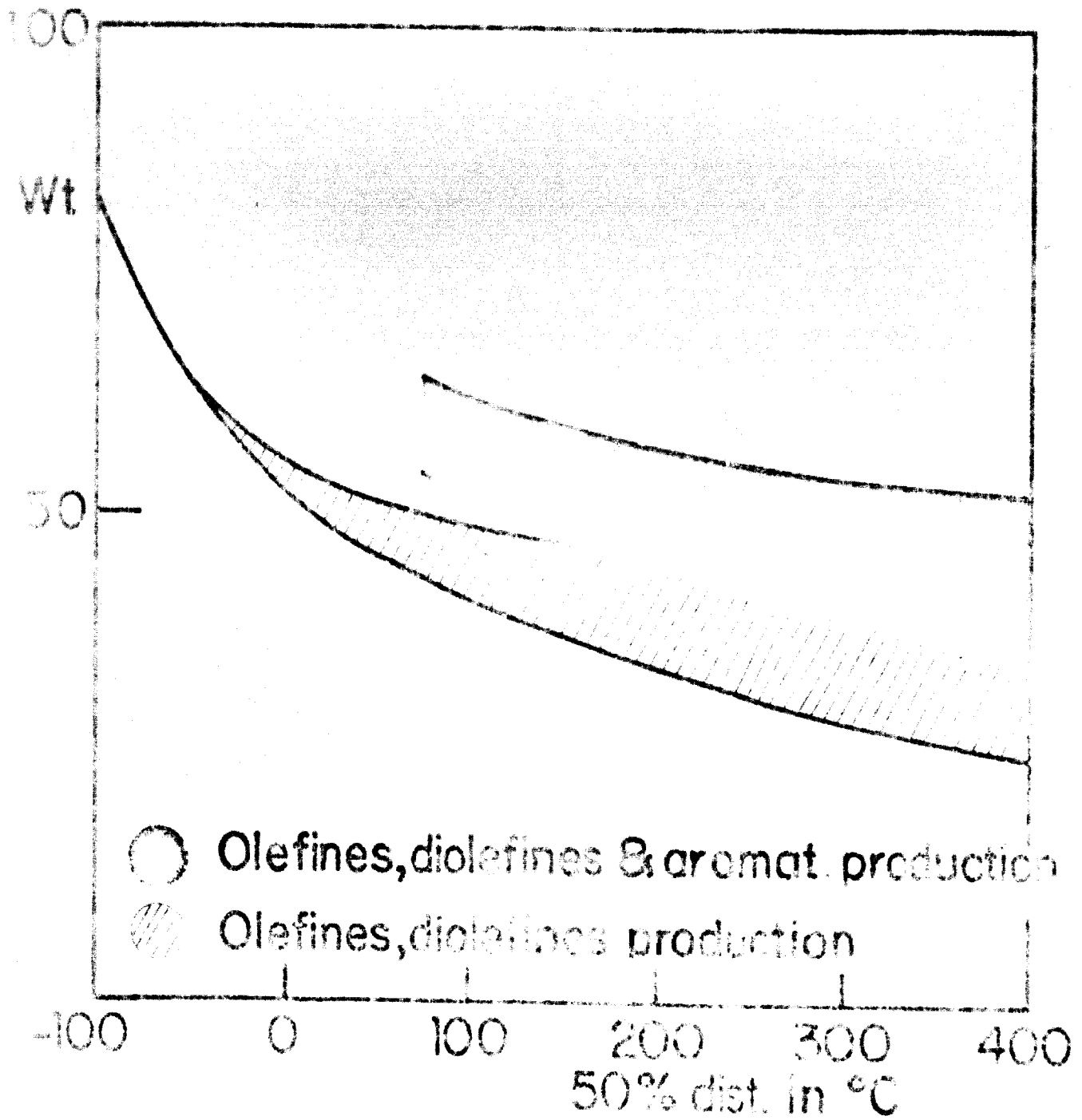


Fig.1.

AMOUNT OF PRODUCTS FOR CHEMICAL USE IN STEAM-CRACKING



C₂ C₃ C₄

↑ naphtha ↑ light gas-oil ↑ heavy gas-oil

Fig.2.

cracking with a special flexibility, but cannot be applied to obtain high ethylene yields unless a profound study of the operating conditions shows that new difficulties do not arise to offset the advantages of the high yields and thereby cancel out their effect. Particular points are the amounts of steam required by the process, and the behaviour and rate of fouling of the tubes.

To adjust the relative proportions of the products of steam-cracking, one might also consider recycling some of them. Although this type of operation is not applied in practice except in the case of ethane resulting from cracking of liquid fractions, the recycling of a gas rich in hydrogen has been considered. The proportion of ethylene can be raised in this way with a reduction in the tendency of coke formation in the tubes; the amount of styrenic compounds in the C_2 , C_3 and C_4 fractions can also be reduced, but the yield of ethylene is much lower than in distillate cracking - 1.5-2% instead of 4-6%. Even in the present state of our knowledge the advantages of a reduced tarolene production outweigh the other advantages, this procedure cannot be adopted at the present time.

Attempts have also been made to recycle the napthalene (6): this gives a slight rise in the yield of ethylene but a notable increase in the C_3 fraction which might be of interest if a maximum production of aromatics were desired.

1.2. Catalytic reforming

Catalytic reforming is a prime example of better utilization of raw materials. Among the various technical possibilities available for applying this process to the production of aromatics, we appear particularly attractive:

- the first consists in increasing the yield of benzene by using particularly active catalysts which, under the operating conditions chosen, favour its yield while at the same time favouring not only the dehydrogenation of naphthenes but also cyclization of the iso-paraffins.

Apart from this, and thanks to new catalysts (Mobil "Selectoforming" catalysts) based on crystalline aluminosilicates (molecular sieves), it is possible to obtain a concentration of aromatics in the product by selective cracking of the untransformed paraffins (2). In this way, in this circumstances, extraction of these aromatics by solvents can be carried more economically thanks in particular to improved marketability of the refined product.

The second consists in modifying the operating conditions in such a way that treatment of the fraction containing C_8 aromatics is simplified. In fact it is known that one proceeds generally, after reforming, to solvent-extraction which eliminates the non-aromatic compounds thus making it possible to recover by distillation the benzene and a C_8 fraction which, in its turn, yields ortho-xylene by distillation and para-xylene by crystallization.

This sequence may be simplified by not separating the C_8 fraction by solvent-extraction: this fraction found free from non-aromatics, can be treated in some cases by direct distillation of the product of the reforming process.

Table 2 shows Table 3, which shows the outcome of the catalytic cracking of a heavy petroleum gasolene under high severity conditions and compared in comparison with the normal value of the same material under less severe conditions (first column), it can be seen that only traces of C_8 paraffins and isoparaffins, the boiling points of which are very close to those of the C_8 aromatics, are present in the reformate. As a result, there is obtained directly, on fractional distillation of the reformate, a C_8 fraction with a high content of aromatics from which the individual xylenes can be separated, in particular suitable for later chemical use, by a series of distillations and/or crystallizations. In this way, the solvent-extraction unit is concerned only with the $C_8 - C_{10}$ fraction and, in fact, with the C_8 fraction alone since there is not a sufficient market for toluene as a chemical product.

III. Selective methods of producing olefins

III.1. Polymerization and polymerization

In early 1964, numerous publications and, in 1965, the World Oil Conference in New York City introduced new methods for the production of ethylene, propylene, butadiene, and styrene, these methods being designed to produce specific products, through the use of special catalysts. The catalysts used were based on zirconium or hafnium compounds. The catalysts used in the field of stereoregular polymerization are of the type $ZrCl_4 \cdot 2THF$ and $HfCl_4 \cdot 2THF$, where THF is tetrahydrofuran. The catalysts used in the field of stereoregular polymerization are of the type $ZrCl_4 \cdot 2THF$ and $HfCl_4 \cdot 2THF$, where THF is tetrahydrofuran.

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These catalysts, in particular, are used in the production of ethylene, propylene, butadiene, and styrene. The catalysts used in the field of stereoregular polymerization are of the type $ZrCl_4 \cdot 2THF$ and $HfCl_4 \cdot 2THF$, where THF is tetrahydrofuran.

Table 3

Products of catalytic reforming

<u>Crack (naphtha)</u>		65 - 152°	
Gas		8	
Light ends		32	
Gasoline and iso-paraffins		60	
<u>Gasoline (3 per weight)</u>			
		1.8	2.0
		17	19
		7	7
Paraffin aromatics		11	9
		8	8
Non-aromatics		6	4
		13	13
Paraffin aromatics		3	1
Paraffinatics *		25	29
Non-aromatics		1	Trace
Paraffinatics		7	7
<hr/>			
o-xylene		22	
m-xylene		45	
p-xylene		17	
ethylbenzene		16	

This selectivity of coordination catalysts has also been used advantageously to produce straight-chain hexenes, which are possible intermediates in the synthesis of straight-chain dodecenes to be used in the production of biodegradable detergents.

11.2. Dehydrogenation of n-paraffins of C₁₀ - C₁₃ series

The most direct way of producing C₁₀ - C₁₃ olefins is by dehydrogenating n-paraffins resulting from extraction by molecular sieve. This technique has been used by many companies and has been applied in practice by U.O.P. under the name "Profil", in a 750 - S.P.S.T. unit in Japan. The dehydrogenation is carried out with a limited degree of conversion (probably 20 - 40%) and in a selectivity factor of 90% or more. The feed is a mixture of unreacted n-paraffins and olefins, which can be used directly for the production of detergents by classical methods using noble metal catalysts (hydrofluoric acid, titanium chloride).

Such a method, leading to a straight chain alkylbenzene, which gives thorough and persistent detergent action to liquid, mostly detergent, is used with the following system (U.S. Pat. 3,111,111) which consists in promoting the paraffin dehydrogenation with a catalyst containing a hydrogen halide, an aluminum chloride, a metal chloride, and a metal chloride, as an inhibitor. The first method used is to use a catalyst consisting of a primary chlorine such as ethyl, and of the metal as an inhibitor equivalent quantity of hydrochloric acid for each mole of metal from the synthesis of metal chloride, it is difficult to find a particular use.

As it is desired to obtain the olefins in the pure state either because immediate reaction or alkylation is not possible or because the olefins are used as intermediates for uses other than detergents (polyamides, alkyl sulfonates), the olefins can be separated by absorption on a selective solid substrate. Benzene is selected by a dehydrogenation carbon which has a boiling point lower than that of the feed and which, after separation of the olefins, is recycled. The unreacted paraffins are then returned to the dehydrogenating reactor. The technology employed

achieve this separation is related to that used in the "Molex" process for separating n-paraffins.

The combination of the two techniques, for a capacity of 33,000 tons/year, entails an operating cost of about \$ 40 per ton of olefins. The elements and calculation are given in Table 4.

Olefins

The production of butadiene has been appreciably modified by the development of steam-cracking methods, which produce this compound at an average rate of 4% of m. feedstock. Therefore the main improvement has been in the solvent extraction process. Alongside the older processes based on acetone/trile (Wall) or furfural (Phillips), new solvents became available, such as dimethylformamide (Geac), N-methyl-pyrrolidone (SASOL-Burgi), and acetamide (Imperial Chemical).

Two of these solvents, dimethylformamide and N-methylpyrrolidone, are able to extract olefins from the C_4 fractions from a naphtha-cracker.

In order to obtain olefins of a sufficient purity for polymerization, these also employ separation techniques which utilize the selective action of a solvent: thus, selective distillation in presence of a solvent, extraction by a solvent, and even liquid-liquid extraction (in the case where olefins are recovered from C_4 cuts poor in olefins), are used. The olefins are distinguished from one another by choice of solvent and management of the separation conditions to give a product of high purity.

The C_4 steam-cracking fractions contain in fact, in addition to olefins, not only C_4 saturated and olefinic hydrocarbons but also a smaller or less amount of light n-alkane hydrocarbons which must be rigorously eliminated. The combined operations of extractive distillation, solvent stripping, and washing lead to the elimination of these impurities one after another. In addition, the solvent must be completely separated from the product and must be recovered. As it is difficult to draw up a useful economic comparison between the various existing processes, because the results depend too much on the special circum-

Table 4

Capacity:	33,000 T/year		
Capital cost *			
(Battery limit)	\$ 4,558,000		
Feed: n-paraffins C ₁₂ - C ₁₅		(T/T)	1.05
By-products: hydrogen		(m ³ /T)	140
light ends		(T/T)	0.035
Utilities: fuel		(10 ⁶ cal/T)	6.25
cooling water		(m ³ /T)	210
power		(kWh/T)	600
labour		(men/shift)	3
Catalyst and adsorbent		(\$/T)	12.5

* Including material and labour, design, engineering and contractors' charges, and initial charge of catalyst and adsorbent.

stances of each project, we are submitting for discussion (Table 5 below) the economic data which have been already published.

Aromatics

Owing largely to the development of synthetic fibres (nylon and poly-ester) and to a smaller extent to that of resins (polyesters and phenolics), the chemistry of aromatic hydrocarbons has made substantial progress in the last few years.

The greater part of the research work has been directed to increasing available quantities of benzene and para-xylene at the expense of other aromatic hydrocarbons derived either from reforming or from steam-cracking, and has led to the advent of the new processes:

1. Solvent treatment

In the field of extraction, substantial progress had already been achieved when sulpholane (I.C.I. - Shell) had replaced glycol as an extraction solvent for aromatics; since then, the value of new solvents has been confirmed by the building of industrial plants: dimethylsulphoxide (DMSO), and methylcyclohexane (Lurgi).

Alongside this technique leading to the production of all aromatics C_6 to C_{10} various techniques specific to a single compound have gained increasing interest: in particular, extractive distillation or azeotropic distillation, which leads to benzene from a rich fraction C_6 derived, for example, from very low pressure cracking.

A new solution was brought (Japanese Chemical) to the treatment of xylene which in past years comprised, alongside a distillation step designed to produce ortho-xylene and possibly ethylbenzene, the crystallization of para-xylene, associated with the isomerization of the xylene liquors (mixture of para- and meta-xylene). This solution is a new technique in which the extraction of meta-xylene is carried out with an acid solvent consisting of hydrofluoric acid and boron trifluoride (12). As a result, it is no longer necessary to employ crystallization, and each of aromatic hydrocarbons can be made available in the pure state. This process appears particularly attractive for the future, mainly in the case

Table 5

Capacity 50,000 T/yr	B.A.S.F.	U. T. C.	Green
Capital Investment (Battery limit) 10^6	1.62	2.17	1.85
Utilities (per ton of butadiene)			
Steam (t)	2.1	3.6	3.9
Power (kWh)	250	210	170
Cooling water (m^3)	110	160	150
Solvent consumption (kg)	0.2	1.5	0.25
Yield and recovery (%)	96	98	98
Labour: 1 man per shift			

market for pure meta-xylene: it is known, indeed, that the development of the market for this product through its oxidation product, isophthalic acid, and the resulting polyesters has been limited up to now by the high cost of production at a high purity.

2. Crystallization

Production through crystallization has however made significant advances both as far as the overall economy of this technique and the purity of the products obtained are concerned. While existing processes were continuously being made more efficient (Phillips, Amoco), a new technique of crystallization through direct contact with a cold solution was developed by the Institut Français du Pétrole. Furthermore this technique has the advantage of crystallization and washing counter-current systems which permit the production of high-purity meta-xylene (99.5 + %) while reducing expenditure on refrigeration.

3. Selective adsorption on Zeolite

This technique, which has already been applied to the production of n-paraffins thanks to the use of synthetic zeolites and to the use of n-dioxane (Olex - see above), has found a new application in the separation of para-xylene from the constituents of the C₈ aromatic stream. This method, developed by IFFI, and marketed under the name "PAREX", uses a solid having selective adsorption and a technology similar to that already used by the same firm for the Polox and Olex processes. Apart from an economic advantage which cannot be correctly estimated until it is applied commercially, the process permits the recovery of practically the whole of the para-xylene present in the feed. The crystallization processes mentioned by the composition of the mixture of para-xylene and the other aromatics. Furthermore, if this process has to be combined with the one which is a function of the other aromatics and of ethylbenzene, the amount of material to be treated in the separation plant is reduced with a resulting drop of about 40% in the capacity which that unit must have. The details of the economics of the process are not known in detail, but the following table gives the available data:

Table 6

		50,000 T/year
Capacity		50,000 T/year
Capital Investment		\$ 1,800,000
Catalyst and adsorbent inventory		\$ 836,000
Direct operating cost	\$/T	10
Indirect operating cost:		
Depreciation (10 years)	\$/T	3.6
Interest (6.5% of Investment)	\$/T	1.7
Total		15

23.4. Chemical Transformation of products

However, the management of primary hydrogen was not sufficient to meet increasing demand, which could be satisfied only if production methods were improved or new conversions invented.

At the beginning of the 1960s, which provided an energetic oil in which benzene production had led to an improvement in the availability of this compound. In order to improve production of solvents, catalytic reforming operating conditions were modified and led to a 10% increase in existing quantities of aromatic hydrocarbons only, thus eliminating the necessity of the solvent extraction.

Other methods have been worked out for the conversion of 11 aromatic hydrocarbons of lower value: toluene and xylenes (mainly para-xylene).

Alongside the techniques already known, hydroalkylation and isomerization, the dimerization of toluene to benzene and a mixture of xylenes (Peyo - Ryan (8) Atlantic Richfield (13)) is now available. This process

As the first industrial plant is under construction, increases, in the expense of toluene, the availability of benzene and xylene mixtures in association with isomerization and crystallization of para-xylene leads to the production of additional quantities of ortho-xylene and para-xylene without requiring the construction of large capacity special reforming plants.

Table 7

Atlantic Richfield data (xylenes - plus process)

	50,000 T/year (xylene)
Investment (battery limit)	\$ 1,900,000
Working inventory	85,000
Material: toluene (T/T)	1.82
benzene (T/T)	0.68
light product (10^6 kcal/T)	0.4
heavy products	3.09
fuel (Kcal/T)	3.2×10^6
cooling water (m^3/T)	200
power (KWh/T)	125
Heat consumption (T/T)	0.33
Losses (mm/air)	

Operational experience

It would be presumptuous, in this report, to try to quote all the research work that has led to improvements of existing processes. We should mention only that related to the most important products as far as savings or increase in consumption are concerned.

V.1. Methanol

The synthesis of methanol has been improved (ICI) through the use of new catalysts which have permitted a reduction of operating pressures from 300 atm. to 50 atm. while at the same time, the temperature has been reduced from 350 - 400°C. to 250 - 300°C. The value of this new process can be seen from two main standpoints:

- at low pressures and large capacity (150 - 200,000 T/yr) it becomes beneficial to use centrifugal compressors whose use was already advantageous in the synthesis of ammonia.

- owing to the lower pressures, it is possible to design a methanol synthesis plant where the cost of gas compression is minimal. It is known indeed, that naphtha steam reforming, which produces the H_2 - CO mixture, can be carried out at pressures of 20 to 30 atm.; the separation train can, taking pressure losses into account, operate advantageously at the same pressure, and it is then only necessary to bring out the effluent at the synthesis pressure with a compressor having a compression ratio of approximately 2.

From the point of view of compression costs this beneficial situation can be still more significant if partial extraction is used (Tosco, Shell) which can be carried out at 50 atm. and higher. In this case, the overall operation is at the same pressure: oxygen alone has to be compressed. Typical condenser data are shown in Table 6.

V.2. Acetic Acid

In the synthesis of acetic acid, the oxidation of light oil (Distillers) has not eliminated other oxidation methods: this is because of its low selectivity (1.5% of naphtha per ton of acid) and the large production of by-products which have to be valorized (formic acid, propionic acid and succinic acid).

Table 8

Methanol Production

Capacity : 180 T/day	65,000 T/year	
	High pressure process: Reciprocating compressor	New I.C.I. low pressure process. Centrifugal compressor
Capital investment		
Energy limits 10^6 C)	5.4	4.6
Materials	natural gas	natural gas
Work and fuel (10^6 kcal)	9.15	8.60
CO ₂ (t/day)	725	60
Water feedwater (m ³)	1	1
Hot water (m ³)	210	215
Chemical and chemical (%)	0.26	1.88
Loss (ton/shift)	4	4

Among the new routes, the oxidation of butenes (lower) is a high activity, due to an indirect route through butyl acetate. In this case indeed, butyl acetate is first synthesized, and then oxidized to acetic molecules one of which is recycled and returns to the ester synthesis stage. In this way, a yield up to 1.2M T of acetic acid per ton of butenes is obtained.

Following a completely different route, acetic acid may be produced by the reaction of methanol and carbon monoxide under high pressure (D&W). Although this method appears to be costly, on account of the high pressures (100-700) it can take advantage of the low price of methanol obtained in large capacity plants operating according to ICI's technique.

V.3. Vinyl acetate

The synthesis of vinyl acetate from ethylene is the subject of numerous investigations, in which attempts have been made to obtain the most direct synthesis of vinyl acetate from ethylene. Although this objective has not in fact been reached, one of the most recent developments consists in oxidizing ethylene, in the presence of acetic acid, into vinyl acetate and acetaldehyde. This latter product, required for the operation. In this way, it is no longer necessary to use an external source of acetic acid.

By way of illustration, Table 9 gives economic data for the process developed by Demal.

Table 9

Capacity (T/year)	50,000
Capital investment (latterly limited) (\$)	3,000,000
Raw materials:	
Ethylene (T/T)	0.845
Oxygen (T/T)	0.6
Utilities: Steam (lb./T) (T/T)	1.4
Steam (lb./T) (T/T)	2.4
Cooling water (T ³ /T)	580
Power (kW/T)	310
Catalyst and chemicals (t/T)	3.8
Labour (man/shift)	6

V.4. Propylene oxide

The direct oxidation of propylene to propylene oxide, in spite of a good deal of research, has not yet been carried out in a satisfactory manner. However, the use of organic peroxides or oxidizing agents (Scientific Organic Area), has led to particularly high yields related to propylene. However, the decomposition of the organic peroxide leads to the formation of by-products whose quantity is detrimental to the economy of the process. Solutions appear to be particularly promising prospects:

the organic peroxide is obtained from ethylbenzene which subsequently is a mixture of acetophenyl ketone and methylphenylcarbinol. Hydrogenation followed by dehydration gives styrene. Although it is possible, to obtain extra, to adjust the prepolymer oxide-styrene ratio, 2.5 T of styrene per ton of prepolymer oxide are usually produced.

The organic peroxide is prepared by oxidation of isobutane and, by means identical to that used with regular cases, tertiary butyl alcohol is added and then hydrogenated into isobutane. In this case, 1.6 T of styrene is produced for each ton of prepolymer oxide.

Phthalic anhydride

The plant catalytic oxidation of acetylene had already been improved. The technique of dilution was adopted, leading to greater homogeneity of temperature and a more efficient control of operating variables. It remains to improve the catalyst and, possibly, it will be possible to increase the concentration of acetylene from 2% of phthalic anhydride from 0.8 to 0.9 %.

This new process, although promising very well, as far as capital investment is concerned, must in the first analysis be preferred especially for large plants, on account of the economy of raw materials.

Acrylonitrile

Acrylonitrile

Simultaneously with the appearance of new polymers or copolymers, production techniques were being modified and improved. Among these improvements, those involving the polymerization of ethylene should be noted as a result of recent progress made in organometallic catalysts (Ziegler-Natta type) which make it possible to produce high density polyethylene with very low catalyst consumption.

Styrene-propylene rubber

Styrene-propylene rubber, development of which has been slowed down by difficulties in vulcanization and blending with other rubbers is expected to take a larger part in the rubber market with the introduction of a new copolymer, ethylacrylate neoprene which, while making possible the vulcanization of this rubber, also makes it compatible with the other synthetic rubbers.

VII - Proteins

The fermentation of hydrocarbons, which in principle can find numerous applications in the synthesis of complex organic molecules, has found its first major application in the synthesis of protein concentrates (BP, IFF, Esso, Phillips) for animal feeds. Two solutions are now under study, the first of which uses gas-oil as a source of paraffinic hydrocarbons, and the second involves pure paraffins or paraffinic concentrates.

Although it is still difficult to measure the impact of this process on the animal feed market, it may be estimated that, after the initial product and process, testing phase, plants with a capacity of the order of 100,000 T/yr will make it possible to obtain essential constituents of animal feeds by a synthetic means.

Typical economic data are shown in Table 10.

Table 10

Capacity (T/year of yeast)	60,000
Capital investment * ($\$/10^6$)	8.5 to 11.0
Feedstock (T/T)	1.13
Utilities ($\$/T$)	20 to 30
Chemical products ($\$/T$)	25 to 30
Labour (men/shift)	10
Credit for dewaxed gas-oil ** ($\$/T$)	25

* Process units: auxiliary units

** \$ 2 per ton of dewaxed gas-oil.

Conclusions

These new processes, together with those resulting from improvements in techniques already known - improvements of which a full account cannot be given here, and which are in some cases profound - have helped, thanks to their performance, to reduce the manufacturing costs of chemical products, whether by savings in capital cost or in power consumption or savings on raw materials. However, on examining a petrochemical plant it is seen that the problem of valorizing secondary products is still a number of points. To illustrate this and to understand the difficulties attending this problem, which many are trying to solve, it is better to examine one or two basic petrochemical processes - steam-cracking and catalytic reforming - from the point of view of utilization of secondary products, bearing in mind the new techniques that have become available.

Case of steam-cracking

Fig. 2. shows that in steam-cracking an increasing part of the output is made up of chemical products as the starting material becomes more complex. The shaded areas, defined by two limited curves, represent valorization of paraffins (lower area) and of olefins, diolefins and aromatics (upper area).

When steam methane, raw material which gives ethylene most selectively, is cracked, the percentage generally recovered varies from 80% down to 50% when 30%.

Let us see first what these products are which, in the absence of a chemical outlet, serve as constituents of motor spirit or as fuels. Paraffins, which go by side with a gaseous mixture of methane and hydrogen, used on the one hand in certain selective hydrogen operations (C_2 , C_3 , C_4 , motor spirit) and on the other as fuel in the cracking plant, there are found.

- normal butenes which have only special uses resulting from certain limited initiatives, butyl alcohol, polybutenes.

- isobutene, which finds various uses in the chemical industry (additives to motor spirit, polymers, paints)

- the C_5 fraction, rich in diolefinic compounds, isoprene, piperilene and cyclopentadiene, which finds use in the production of certain types of resin (Escorez). However, the resolution of the mixture into its constituents and in particular the recovery of isoprene and cyclopentadiene, have not yet been systematically achieved. So far as concerns isoprene, the reason for this lies in the limited supplies of the C_5 fraction available which are insufficient to feed economic units of a size commensurate with the needs of the market. For example, a steam-cracking unit treating one million tons of feedstock a year (250/300,000 t/year of ethylene) yields only 8,000 - 10,000 tons a year of isoprene. An extraction unit of this capacity is generally considered to be uneconomic. To reach an acceptable profitability level and to meet the requirements of the elastomer industry, capacities would have to be 40/50,000 t/year. To do this, it would be necessary to combine the outputs of several neighbouring steam-cracking units; and it appears that it is an attempt of this sort that must have been undertaken by the Japanese industry, where the concentration of steam-cracking units is a favourable factor.

So far as concerns cyclopentadiene, which is extracted by thermal dimerization as dicyclopentadiene, the market remains limited to certain insecticides and to the co-monomer used in ethylene-propylene rubber; but it should be noted that cyclopentadiene meets certain serious competition in this latter application from cyclo-octadiene and ethylidene norbornene.

The C_8 aromatics, among which is ethylbenzene, are not recovered since they are too small in amount unless they can be treated in admixture with a larger feed derived from a catalytic reformer: ethylbenzene itself is largely derived from the hydrogenation of styrene when pyrolytic fractions are stabilized by hydrogen.

Fuel-oil, which has a high aromatic content, is sometimes used in a mixture with other residues as a raw material for the production of carbon black. The remainder is used for industrial heating.

Thus, whether because of the market being too limited or because the amounts are too small, a large proportion of the products of steam-cracking does not appear to find ready outlets other than industrial heating or the manufacture of petrol; but in certain special cases, which could progressively increase in number chemical uses for these by-products may develop thanks to the application of new techniques.

III.2. Cases of catalytic reforming

In order to study, in this case, the quantity and origin of compounds which have no use in the chemical industry, account should be taken of the variants which may be found in the structure of a plant-complex producing aromatics.

The first diagram (Fig. 3, case 1) shows a classical installation in which, following the catalytic reforming plant, solvent extraction yields a mixture of C_8 and C_9 aromatics, and the latter are thereupon separated from each other by distillation and, in the case of para-xylene, by crystallization. If 1,000 represents the reforming feed, 21% of aromatics are obtained viz. benzene 30, toluene 125, ethylbenzene 35, para-xylene 23, and ortho-xylene 50. The rest of the feedstock used comprises hydrogen (20), light combustible products ($C_1 - C_4$) (240), non-aromatic liquid fraction (230) and $C_8 - C_9$ aromatic fractions (213). The total (663) represents products which have no use other than in the refinery.

Table 11

	Benzene	Toluene	Ethylbenzene	m-xylene	p-xylene	o-xylene	Total
Case 1	30	125	35	-	23-38	50	317/332*
Case 2	80	125	35	-	96	96	452
Case 3	152	-	37	-	141	141	446
Case 4	80	125	39	110	41	53	467

* This figure can be increased to 332 thanks to a process for the total recovery of para-xylene (38 instead of 23) by adsorption on solid (7).

AROMATICS PRODUCTION

CAS 1

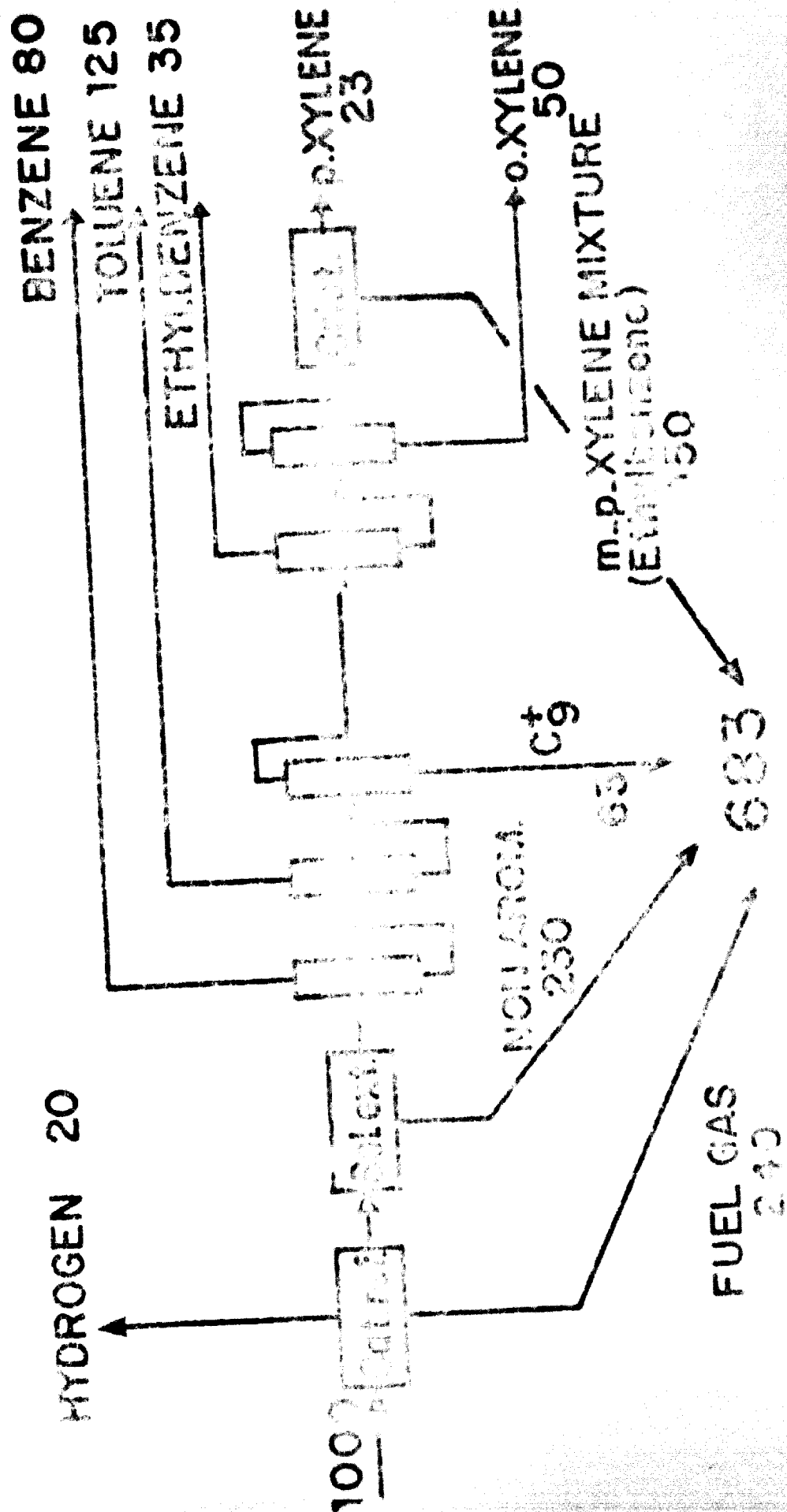


FIG. 3.

AROMATICS PRODUCTION

CAS 2

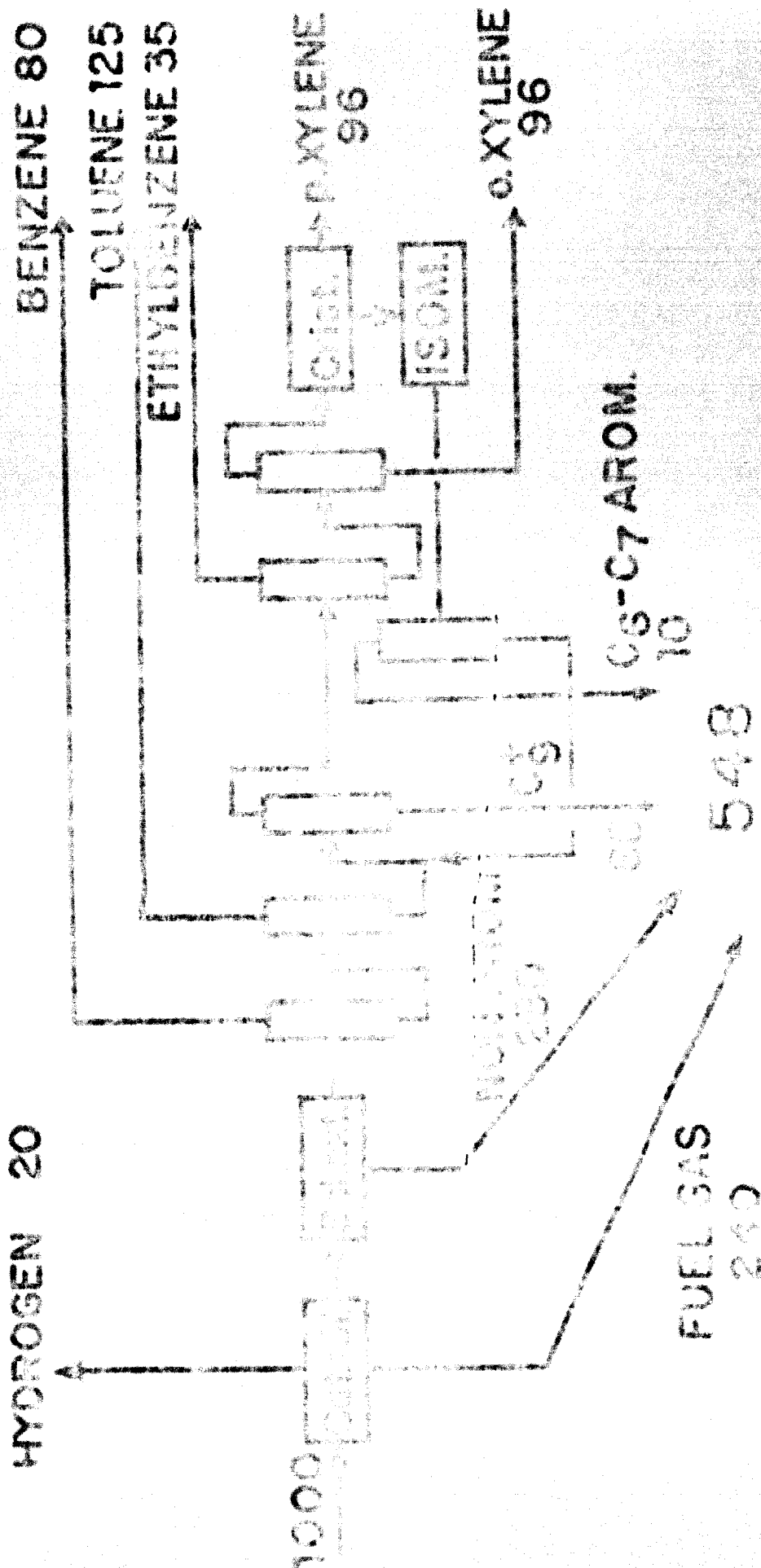


Fig 3

HYDROGEN SULFIDE POLYMERIZATION

CAS 3

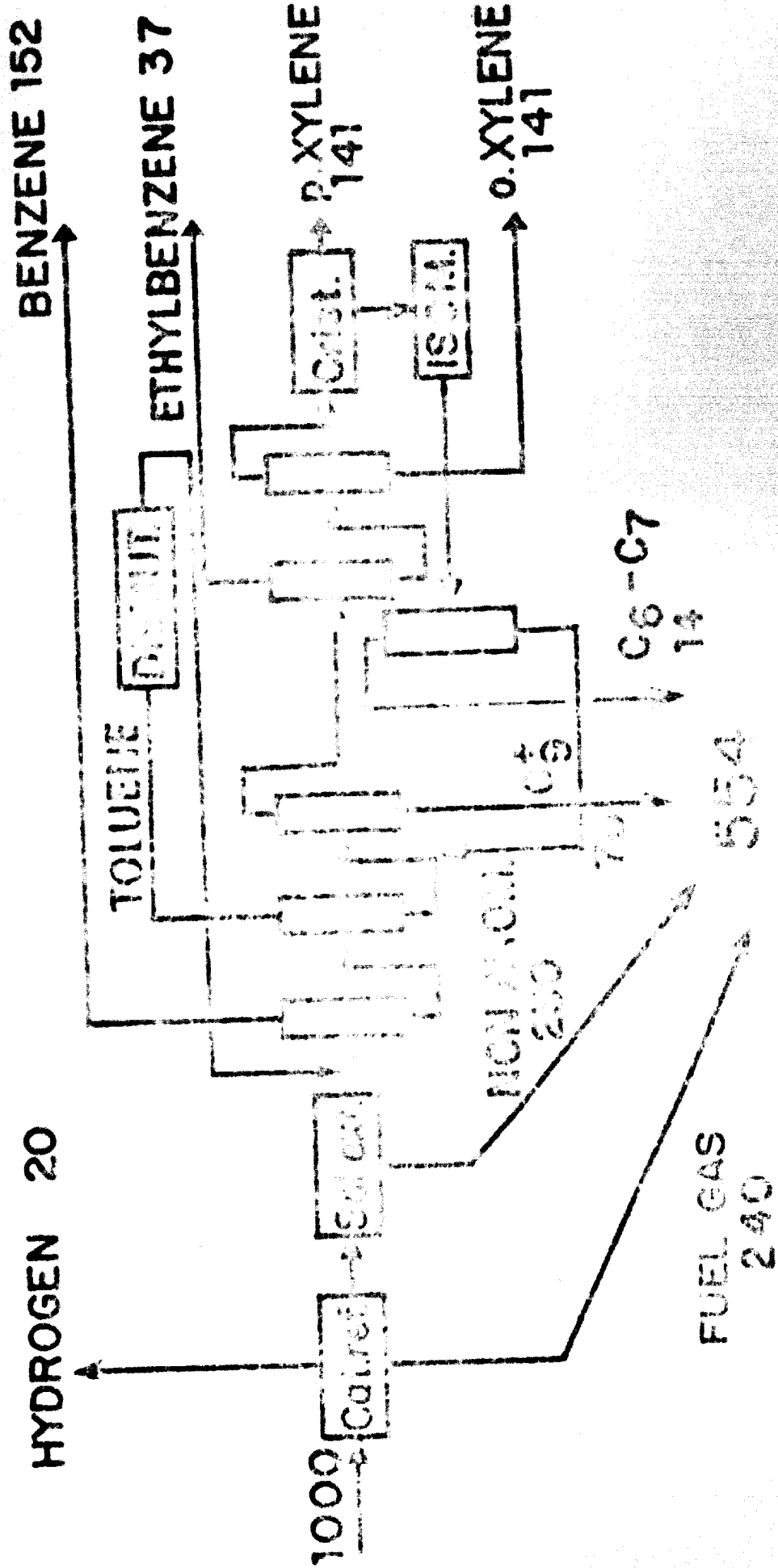


Fig. 3.

AROMATIC PRODUCTION

CAS 4

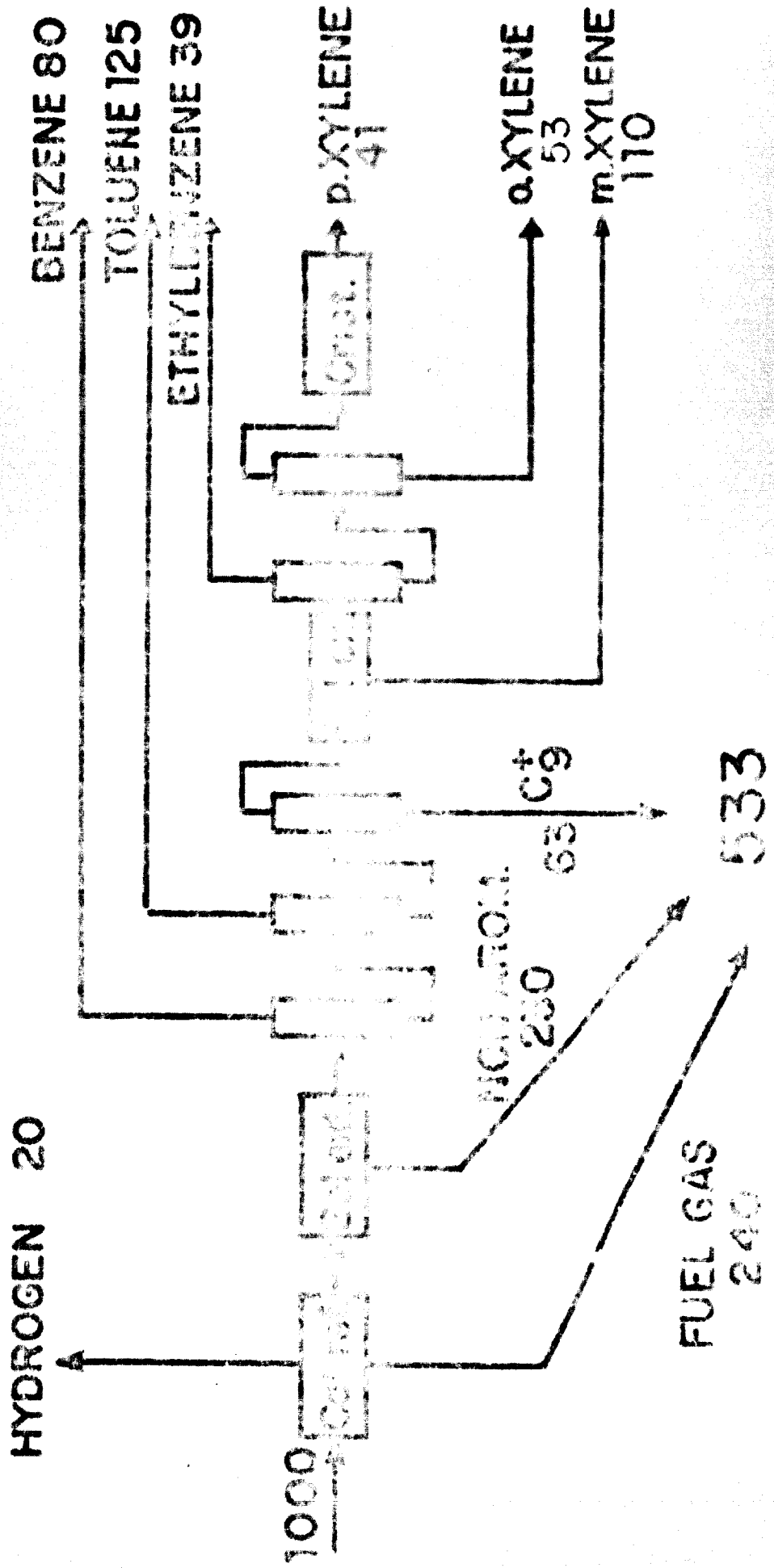


FIG. 3.

This situation can be modified, however, by adding conversion processes which increase the proportion of products which can be valorized in the chemical industry. Case 2 in Fig. 3 and Table 11 show the case in which, by adding an isomerization unit which treats the para-xylene crystallization mother-liquors, the quantities of para-xylene and ortho-xylene produced are raised to 96, thereby reducing to 54% the amount of products which are not valorized chemically. This reduction occurs at the expense of the mixture of C₈ aromatics, which represents 34% of the entire residual liquid fractions and has the highest octane number.

Case 3 shows the effect of converting toluene by dissipation, into benzene and C₈ aromatics⁽⁸⁾. This operation does not appreciably change the total yield of aromatics but makes it possible to increase substantially the amount of benzene (15% instead of 8%) and - often more valuable - that of para and ortho-xylene to 44% instead of 36.

Finally, in Case 4, an attempt has been made to extract ortho-xylene also by enclosing an extraction unit in a selective solvent for meta-xylene. The latter has become available in a high degree of purity, so that its use in polymers chemistry can be visualized. If the market, too small today, does not develop to a sufficient extent, the mother-liquors will have to be subjected to dissipation in relation to ortho and para-xylene. The materials balance diagram in the case of Case 4 can be like the one in Fig. 2, which differs from it only in energy values.

These four examples, which will be referred to as "Case 1" through "Case 4" (working or planned), show how the proportion of compounds that can be valorized chemically can be reduced and what are the main technical implications.

- * Case 1: classical case
- Case 2: raising the most recent till line 80
- Case 3: Topy Kroyon
- Case 4: Japan Gas Chemical.

It can be seen that, even if new techniques are required, the total yield of aromatics from such a complex does not exceed 45%.

Thus, whether we are considering steam-cracking, which produces
olefins, diolefins and aromatics, or catalytic reforming, which produces
aromatics only one-half of the raw material is converted into products
which can be used in the chemical industry. This situation can be
changed, to be sure, by a still larger combination of diverse plants,
leading to a greater number of products (paraffins, olefins, acetylene, etc.)
and having to provide their own power requirements. This we arrive
at the idea of a petrochemical refinery in which schemes have been
developed, and some plants approach this idea (Sartre, Rio, Triello,
Lindell, etc.). It would appear that the question whether this type
of installation is profitable or not can only be answered by
a careful economic study, taking into account the particular site under
consideration.

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