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INSTITUT FRANCAIS DU PETROLE'S PROCESSES

FOR PRODUCTION AND TRANSFORMATION

OF AROMATIC HYDROCARBONS^{1/}

by

Institut Francais du Pétrole
Rueil-Malmaison France

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International Petrochemical Symposium on the
Development of the Petrochemical Industries in
Developing Countries

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SUMMARY

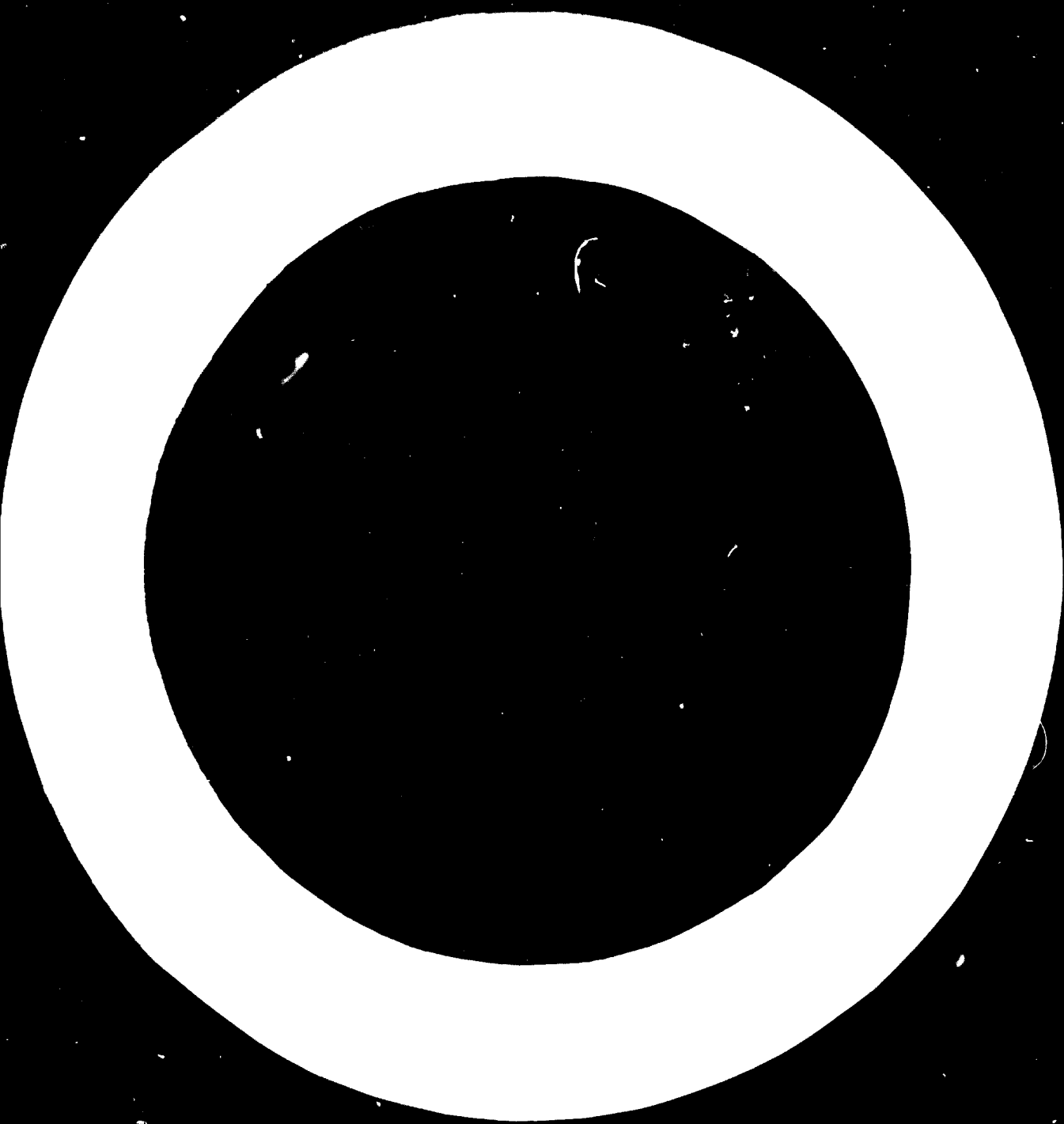
INSTITUT FRANCAIS DU PETROLE'S PROCESSES FOR THE PRODUCTION
AND TRANSFORMATION OF AROMATIC HYDROCARBONS^{1/}

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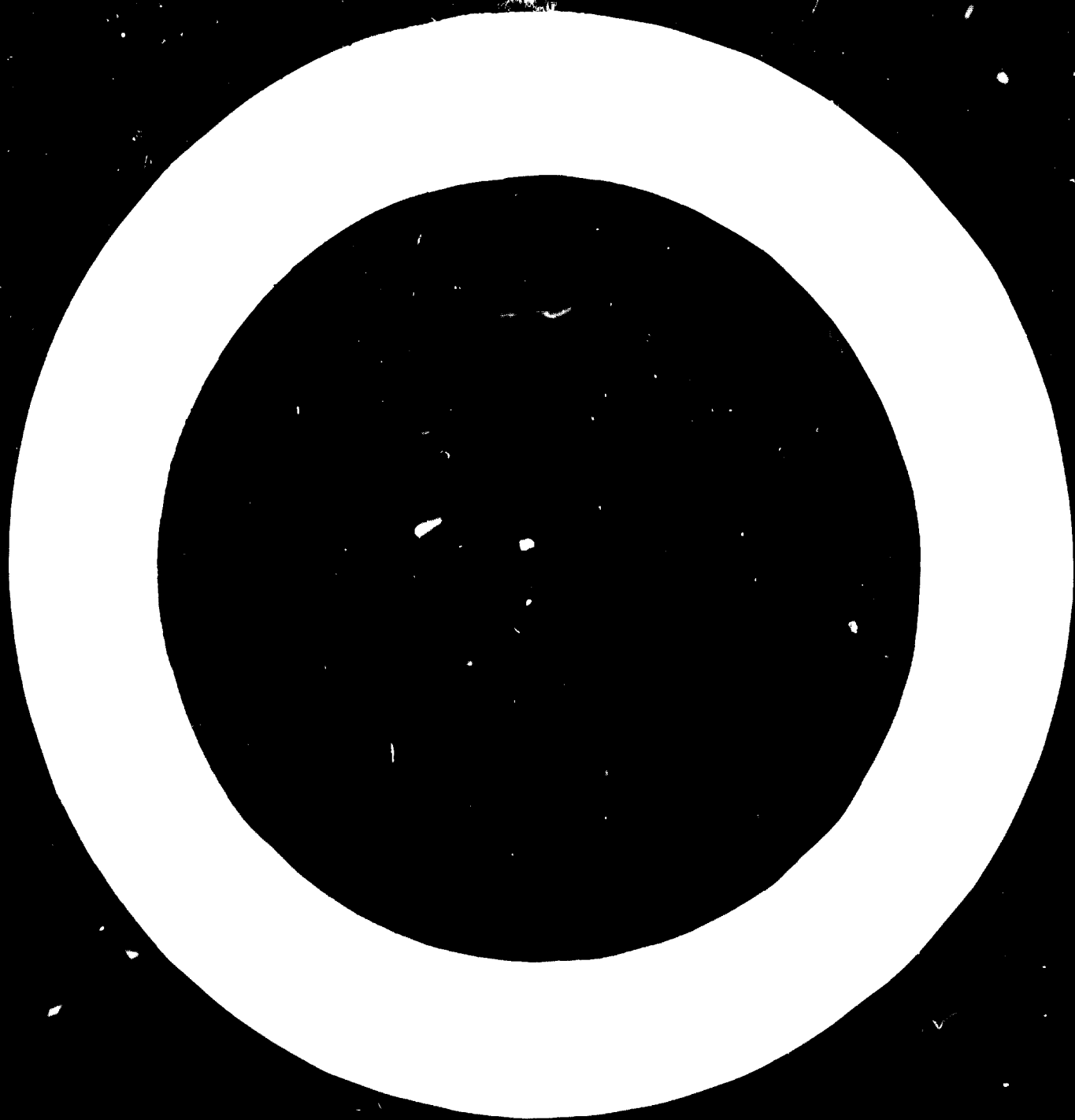
Aromatic hydrocarbons are together with olefins the leading raw material for the petrochemical industry. Nylons, polyester fibres, synthetic rubbers, resins and detergents production are based on products made from the basic aromatics produced from petroleum feed-stocks. The chemistry of the production of aromatics is first discussed, the conditions necessary for the dehydrogenation of cyclohexane and the conversion of five membered rings to six membered rings. An industrial process using platinum on a high purity alumina support as recommended by IFP is given in more detail showing that from a 100 parts of feed-stock 8 parts of benzene, 23 parts of toluene and 27 parts of xylenes can be produced. The various methods of extracting the aromatics are next discussed including the preliminary hydrogenation and the extraction of the aromatics with

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ethyl sulphoxide. By this method, 99.9 percent of the benzene, 98.5 percent of the toluene and 95 percent of the xylenes can be extracted from a catalytic reformate containing 10 percent benzene, 27 percent toluene and 18 percent xylenes. The hydrogenation of benzene to cyclohexane is next discussed, followed by the oxidation of cyclohexane to a cyclohexanol-cyclohexanone mixture. Various possibilities of using this mixture are mentioned. First the conventional use of mild dehydrogenation of the cyclohexanol to cyclohexanone as a raw material for caprolactam is described and then a process for more drastic dehydrogenation to phenol.

Besides the use of cyclohexanone to produce caprolactam there is the possibility of amination reaction to give cyclohexylamine which has an important outlet in the production of rubber accelerators and cyclamates. The process for dealkylating aromatics and naphthenes is next discussed. Finally, the use of paraxylene in the production of polyester fibres is dealt with and in particular processes for extracting paraxylene from mixed xylenes, a process for the isomerization of xylenes to reproduce the equilibrium composition and finally the oxidation of paraxylene to terephthalic acid. In all cases, the processes which have been developed or modified by the Institut Français du Pétrole are given in some details in many cases with detail figures, consumption of raw materials, process chemicals utilization etc.



ABSTRACT

Aromatic hydrocarbons are, with olefins, the leading raw materials for petrochemical industry. Nylons, polyester fibers, synthetic rubbers, resins and detergents productions are based on formation and separation of basic aromatics from petroleum feedstocks.

In recent years I.F.P. has developed and licenced a large number of refining and petrochemical processes. Part of I.F.P. activities has been directed towards development of technology for production and transformation of aromatic hydrocarbons. This paper presents Institut Francais du Pétrole achievements in this field. Process outlines, typical economics along with industrial references are described.

Contribution of Institut Français du Pétrole to development of new oil refining and petrochemical processes goes back to the very beginning of this organization. Industrial processes have proved competitiveness of processes like:

- hydrodesulfurization
- steam cracking gasoline hydrogenation
- catalytic reforming
- aromatic extraction
- benzene hydrogenation to cyclohexane

Such a background enabled rapidly I.F.P. to get an important place in the field of production and transformation of aromatics.

After having reviewed what are the present I.F.P. activities in the field of aromatics, we will describe in detail each I.F.P. process along with typical economics and technical performances.

Figure 1 shows a diagram for production and transformation of aromatics. I.F.P. processes appear according to the present stage of development of each one.

- 1° - Processes which are fully developed and proved by industrial experience
- 2° - Processes ready for sale, whose performances are backed by extensive studies in large pilot plants.

This general scheme shows that I.F.P. processes cover all basic processes for production of aromatics (hydrocarbons) and some processes for their transformation like paraxylene oxidation into TPA, whose the future appears to be very promising. Catalysts are manufactured and commercialized by TROCATALYSE, subsidiary of INSTITUT FRANÇAIS DU PÉTROLE and FICHTEY ST GOBAIN.

- Pretreating and Catalytic Reforming

1. . . process for pretreating and catalytic reforming has already appeared several times in the technical press. These papers reviewed fundamental reactions involved along with technical conditions of industrial applications. It is aromatic production feedstocks and operating conditions will be readily different from those recommended for octane boosting operations.

Benzene production, starting from 60-70% aromatic naphtha feedstocks, with conventional catalysts involves mainly transformation of cyclohexane and methyl-cyclopentane, and is carried out at pressure as low as 13 to 17 kg/cm². Xylene production, starting from 15-18% aromatic naphtha feedstocks is carried out at optimum pressure of about 15 kg/cm². Combined production of benzene, toluene, xylenes can be carried out with some an-

- either through a blocked out operation, processing each feed in optimum conditions and giving maximum yields for individual aromatics,
- or through an operation, carried out in a subsequently an aromatic production loss, compared with the blocked out operation, of 3 to 6%.

Increased production of benzene and xylenes are allowed by the use of new catalysts which, not only perform naphthenes dehydrogenation but moreover carry out transformation of naphthenes and naphthalenes into additional aromatics.

One of the most interesting features of aromatic scheme for xylenes manufacture in the past is possible, by reversing reforming severely, to obtain paraffin free xylene fractions. It is essentially difficult to separate pure xylenes by distillation being possible without aromatic extraction step.

Trend is to bring the operating pressure to lower values. This is possible with the improved stability of new generation of PROCELYSE reforming catalysts. PROCELYSE catalysts show a very high purity of the alumina support. According to the type of production (low or high severity, octane boosting, aromatic production) different types of catalysts can be recommended:

- 0.60% weight platinum on high purity alumina support
- 0.35% weight platinum on high purity alumina support
- new generation of catalysts with a lower platinum content.

These catalysts show an improved stability during reforming operation and one of them has already been selected for industrial run.

Table 1 shows typical industrial operation figures concerning a
 BTX production.

Table 1 - F.T. Reforming Process

typical yields in aromatics production

Feedstock

Temperature points °C	70 - 150
Feed analysis % vol.	
C ₅	66
C ₆	26
C ₇	8
<u>Operating pressure psig</u>	200

Yields wt %

C ₅	79
C ₆	2.0
vol % of C ₅	
Benzene	8
Toluene	24
Xylenes	27
C ₉ aromatics	5
C ₁₀ of C ₅	93

A 10,000 BPSD unit including pretreating section cost approximately
 \$3 Millions (erected in France).

Cost of catalysts (pretreating plus reforming but excluding platinum
 cost) ranges between 2 to 6 cts/bbl of feed.

11 - Steam Cracking

The high yield high severity L.S.C. process is presented in another paper in the same conference.

Steam cracking operation is a very important source of aromatics. C₅+ cut, with a final boiling point of about 200° C., contains high percentage of aromatics. A typical analysis of such a cut is the following:

C ₅ Paraffins		
Naphthenes	11 % weight	
Olefins		
Diolefins		
C ₆ Paraffins		
Naphthenes	5 % weight	
Olefins		
Benzene	50	"
Toluene	22	"
C ₃ Aromatics	3	"
Styrene		"
C ₉ Aromatics	4	"

III - Selective Hydrogenation and Hydrotreating of Steam Cracking Gasoline

Extraction of aromatics from steam cracking gasoline is not possible directly. Indeed all aromatics produced for petrochemistry have generally to be sulfur free. Since sulfur would go through extraction step and concentrated in aromatics, extraction feed is previously hydrotreated for sulfur removal. But it would be impossible to feed on the hydrotreating catalyst steam cracking gasoline because diolefins would polymerize and increase rapidly pressure drop on catalyst bed. Therefore a first hydrogenation step hydrogenates selectively diolefins to olefins, diolefins being particularly concentrated in potential B.M. cut, $6_4 - 150^\circ \text{C}$.

Sequence of operations is as follows:

- selective hydrogenation of diolefins to olefins
- sulfur removal (in order to get after extraction, sulfur free aromatics)

First step is carried out on a selective catalyst under hydrogen pressure from 20 to 60 kg/cm^2 of H_2 velocity from 1 to 2 m/sec, temperature from 80 to 200°C (R.S. 2).

Second step is also a hydrogenation on another type of catalyst on which sulfur is removed and subsequently bulk of olefins hydrogenated. Catalyst is selective enough to minimize hydrogenation of aromatics as shown in Table 2. Reactions are carried out at 150 to 200°C with space velocities between 0.5 to 3 and under 40 to 60 kg/cm^2 of H_2 pressure.

Table 3 presents an order of the stages reactions for a typical operation of aromatic extraction and preparation, all process flow sheet is shown in Fig. 3. F.P.F. process has been applied in 10 units. So far 5 are in operation representing 17,000 BPSD and 5 are under construction. Catalysts are commercialized by F.P.F. and life times are over one year.

Table 2 - Typical Performances of I.F.P. Process
for 2 stages hydrogenation of steam cracking gasoline

<u>Characteristics</u>	<u>Feed</u>	<u>Selective hydrogenations</u> <u>(one reaction stage)</u>	<u>Complete hydrogenation</u> <u>(two reaction stages)</u>
Specific gravity	0.811	0.800	0.795
NAV, mg/g	70	15	1
Bromine number, g/100 g	32	23	1
Induction period, minutes	-	360	960
Total sulfur, ppm	145	145	12
Aromatics content	62.5	62.5	60.5
Benzene	44	44	42.5
Toluene	13.5	13.5	13
C ₉ 's aromatics	2.5	4.8	5
Styrene	2.5	0.2	0

Table 3 - Typical Economics of I.F.P. Process
for 2 stages hydrogenation of steam cracking gasoline

	<u>Selective</u> <u>(one stage)</u>	<u>Complete</u> <u>(two stages)</u>
Investment (basis: 2,000 to 5,000 BPSD) per BPSD capacity	150 - 230	250 - 350
Typical utility requirements, unit per bbl feed		
Electricity kWh	0.9	1.8
Steam (230 psig) lb	100	154
Fuel MBtu	-	56
Cooling water (23 °C rise), gal.	660	1,190

IV - Aromatics Extraction

Main characteristics of L.S.F. extraction process have already been described in the technical press (3,4)

- 1° - Solvent is dimethylsulfoxide, which is an excellent and selective solvent for aromatics
- 2° - Good thermal stability of DMSO
- 3° - Good corrosion characteristics which allow the use of carbon steel
- 4° - availability and low price.

Process flow sheet (Fig. 4) is somewhat different from other liquid extraction process. Feed is sent counter-currently with solvent in the first extractor. In order to get high purity aromatics a backwash stream is injected at the bottom. Operating conditions - water content of solvent, solvent and reflux ratio - depend upon feed characteristics and aromatics recovery level. The solvent is regenerated in a second extractor by a reextraction with a paraffinic solvent. Conventional distillation columns eventually separate different aromatics hydrocarbons. A small fraction of DMSO, dissolved in raffinate and extract is removed by water wash and separated from water by vacuum distillation.

This process can treat every feed irrespective of boiling temperature. Selection of a good solvent makes possible recovery of light and heavy aromatics. Outstanding stability of DMSO enables the process to accept a wide range of feeds.

As an example, the extraction of aromatics from a catalytic reformate containing 10% benzene, 27% toluene, 18% xylenes will provide the following recoveries:

Benzene	99.9
Toluene	98.5
Xylenes	95

Design modifications will allow recovery of over 98% xylenes. Two units are in operation and several designs are being considered.

L.S.F. extraction technology can process feedstocks containing up to 15%

of olefins. In most of cases, sulfur removal in second hydrogenation step of extraction feed preparation involves subsequently hydrogenation of bulk of olefins. But in case of sulfur free feedstocks, the I.T.P. process acceptance of olefinic feeds leads to avoid second hydrogenation step.

Table 4 presents typical economics of the I.T.P. process

Table 4

Typical Economics of an I.T.P. Aromatics Extraction Unit

<u>Capacity</u>	:	170,000 t/y of feed	
<u>Investment</u>	:	1,400,000 U.S.	French basis erected cost but excluding engineering fee
<u>Utilities</u>	:		
		HP steam (260° C - 10 kg/cm ² gage)	0.95 t/t
		MP steam (210° C - 19.6 kg/cm ² gage)	18.56 t/t
		LP steam (145° C - 3.4 kg/cm ² gage)	4.17 t/t
		Cooling water (in = 10° C)	362 m ³ /t
		Electricity	162.7 kWh/t
<u>Solvent consumption</u>			
		25 t/y ar	

V - Benzene Hydrogenation

Main features of I.F.P. benzene hydrogenation process appeared very early in the literature (ref. 5). High purity of the product and low capital investment makes this process one of the most often used in the world. The inconvenience of using Raney nickel pyrophoric catalyst disappeared when I.F.P. developed a non pyrophoric type of Raney nickel with similar activity and resistance to sulfur. The use of this new catalyst led to considerable reduction in capital investment and business of operation.

Typical economics are shown in Table 6 and flow-sheet of the unit in Fig. 7.

Hydrogen rich gas is compressed up to the operating pressure and is introduced into the hydrogenator reactor, together with fresh benzene feed. The hydrogenation is virtually completed in one reactor pass. The reactor contains a liquid phase suspension of Raney nickel catalyst. Vigorous stirring of the reacting phase is performed by external forced circulation of liquid through an exchanger which simultaneously removes the exothermic heat of reaction and permits close control of the thermal equilibrium. The vapor reactor effluent receives a finishing treatment in a second reactor. The effluent is condensed and the liquid phase separated. The liquid effluent, still under relatively high pressure, goes into the stabiliser which removes light dissolved gases and inert gases from the cyclohexane product. So far 8 units are in operation and total licensed capacity amounts to 550,000 t/y.

Table 5

Typical Economics of I.P.M. Benzene Hydrogenation Process

The following data apply to a 100,000 metric tons/year cyclohexane unit under U.S. conditions, using a 72% hydrogen gas (catalytic reformer off-gas) with no recycle.

<u>Investment</u>	\$ 1,100,000
(battery limits, including gas pretreatment section and engineering)	
<u>Catalyst initial load</u>	24,000
<u>Annual consumptions:</u>	
Catalyst	\$ 48,000
Steam	35.3 MM lb
Power (*)	1,500 KW/HR
Cooling water	658 M gal
Boiler feed water	22.7 MM gal
Labor	1 op/shift
Benzene	207 MM lb
Hydrogen gas	4,130 MM SCF
Credit LP steam	186 MM lb
Fuel gas	1,170 MM SCF

(*) without make-up compressor and air coolers

VI - Cyclohexane Oxidation

Oxidation of cyclohexane to cyclohexanol-one mixture is the basic step for the production of synthetic fibers through nylon 6. Moreover cyclohexanol-one mixture can be starting raw material for some other chemicals preparation like phenol, cyclohexylamine, cyclohexane...

I.F.F. presents a liquid phase oxidation by air of cyclohexane Fig. 6 shows a simplified flow sheet of the unit. The oxidation section comprises essentially the continuously operated reactor with its auxiliary equipment for heat exchange and gaseous effluent treatment. A specially designed reactor allows very high selectivities to be attained whilst controlling very closely the operating temperature. Efficient heat recovery has permitted a considerable saving in overall heat requirements. The reactor effluent consists of unconverted cyclohexane, cyclohexanol, cyclohexanone and of by-product acids and organic esters of cyclohexanol. The reactor effluent is flashed and the vaporised cyclohexane is recycled. The product is then water washed and caustic washed to eliminate acids and decompose the esters. It is then sent to a distillation and fractionation section where residual cyclohexane is separated and recycled and the alcohol-one mixture is obtained at over 99.5% purity. One unit has been successfully operating in Japan.

Product has been successfully tested by fibers manufacturers, who recognised the suitability of the cyclohexanol-cyclohexanone mixture for caprolactam manufacture.

Table 6 shows typical economics of a 40,000 MT/Y unit. As a result of collaboration between I.F.F. and DSM/Holland the complete technology from cyclohexane up to caprolactam can be offered. The combination of I.F.F. cyclohexane oxidation step with Stanicarbon processes for hydroxylamine, caprolactam production and purification leads to an optimum economy.

Table 6

Typical Economics of I.T.P. Cyclohexane Oxidation Plant

<u>Capacity</u>	40,000 lb/Y
<u>Investment</u> (battery limits unit, erection and engineering included)	3,500,000
<u>Chemicals annual load</u>	20,000
<u>Annual consumptions</u>	
Raw materials :	
cyclohexane	82 MM lb
caustic soda (100%)	2.9 MM lb
chemicals	0.44 MM lb
Utilities :	
steam 147 psig	353 MM lb
368 psig	132 MM lb
power	12 MM kWh
cooling water (inlet = 10° C)	2,960 MM gal
process water	21 MM gal
brine (5° - 15°)	9,520 MM Btu
Labor : 2 operators per shift	

VII - Cyclohexanone

I.F.P. process for vapor phase dehydrogenation of cyclohexanol-one mixture to cyclohexanone leads to a product of more than 99.7 weight % purity.

Following process description refers to Fig. 7. The cyclohexanol-one mixture is partially vaporized. The vapor phase, preheated to reaction temperature by thermal exchange with molten salt, is sent to the reactor section. The endothermic dehydrogenation reaction is performed in a multitubular reactor. The use of an isothermal process allows close control of reaction temperature, resulting in high yields and low catalyst volume.

The reactor effluent is cooled and partly condensed. Hydrogen is evolved and can be sent to a benzene hydrogenation unit. The liquid phase is separated in a distillation section where unconverted cyclohexanol is recycled and pure cyclohexanone is obtained.

Table 7 shows typical economies for 20,000 K/Y unit.

Table 7

Economies of Cyclohexanone Unit
of 20,000 K/Y Capacity (Gulf Coast Basis)

<u>Investment</u> (battery limits plant, erection and engineering included)	\$	580,000
<u>Initial catalyst charge</u>	\$	6,000
<u>Annual consumption:</u>		
Raw material: ol-one mixture	46.3	MM lb
Utilities: steam 147 psig	71	MM lb
368 psig	25	MM lb
power	360	MM KW
cooling water (4.4 - 10° C)	32	MM gal
brine (5° C - 15° C)	1,590	MM Btu
fuel	38,100	MM Btu
Labor: 1 operator per shift		

VIII - Phenol

Conventional route to phenol is the catalytic oxidation of isopropyl benzene. Decreasing prices of by-product acetone made, during past years, this route less and less attractive.

Among other alternative routes I.P.P. has chosen the dehydrogenation of cyclohexanol-one mixture. Fig. 8 shows a typical flow sheet of the process. The cyclohexanol-cyclohexanone mixture is vaporized and then dehydrogenated over a noble metal catalyst. The two main reactions are endothermic and therefore the feed needs to be heated as soon as the temperature drops below a certain limit. Hydrogen product is partly recycled in order to maintain the catalyst activity. The reactor effluents, after cooling, are stabilized and then phenol is separated from the phenol-cyclohexanol azeotrope which is recycled. Phenol purity is over 99.5 wt %. Table 8 presents typical economics.

Table 8

Economics of I.P.P. Phenol Process

Capacity: 60,000 TP/Y

Estimated cost in Lattery limits, Calif Coast conditions	\$ 3,100,000
Initial charge of catalyst	\$ 100,000
Raw material: cyclohex mixture	1.08 ton/ton
By-product : hydrogen	26,000 SCF/ton
Electricity :	805 KWH/h
Fuel Oil (17,500 Btu/lb)	2,320 lb/h
Steam (35. psia)	16,350 lb/h
Cooling water (: t - 30° F)	69 US GPM

IX - Cyclohexylamine

Cyclohexylamine is the main raw material for production of cyclamates and accelerators for vulcanisation of certain types of synthetic rubbers. Demand follows the growing market of ethylene propylene rubber and was around 8,000 MT in 63 for United States.

Process developed by I.F.P. includes two steps:

- a liquid phase amination step of cyclohexanone
- an azeotropic distillation step to separate water
- a purification step by distillation.

X - Dealkylation

When prices structure justifies a dealkylation process, potential user is to choose between the two routes available: thermal or catalytic. I.F.P. oriented research towards the catalytic route because use of catalyst makes possible lower operating temperature and subsequently higher selectivity in desired aromatics. I.F.P. process dealkylates toluene into a high purity benzene (Fig. 5).

The charge mixed with toluene and gas recycle reacts over a specific catalyst. A quench is needed to prevent secondary reactions. The quenched reactor effluent is flashed and then sent into a stabilizer to eliminate the light hydrocarbons from the benzene stream. The hydrogen rich recycled gas must be purified: first elimination of all traces of water and benzene and then separation of CH_4 in a cold box.

The stabilizer bottoms are clay treated and benzene is separated from toluene and higher aromatics which are recycled.

Table 9 shows typical economics of I.F.P. processes.

Table 9

Typical Economics of F.I.P. Hydrodealkylation Process

Investment for treating 20,000 tons/year of pyrolysis gasoline to produce 70,000 tons/year of benzene.

Erected cost in battery limits, including the cold box: \$ 1.6 MM

Utilities:

Electricity	465 KWH/h
Steam produced	2.5 tons/h
Cooling water (at = 13°V)	1,320 US GPH
Fuel gas absorbed	16.5 MM Btu/h
Hydrogen consumed	2,800 S. H

Methylnaphthalene can be dealkylated into pure naphthalene through a similar technology.

XI - Paraxylene into Polyester Fibers

Polyesters demand in the United States has been rapidly growing since 1955 as it is shown in the following table:

Year	1955	1963	1966	1970
Polyester demand in the states	17,000 MM/y	100,000	250,000	420,000

In Europe the demand was of the same order in 1966 (195,000 MM/y) and is increasing of about 60,000 MM/y.

It seems reasonable to plan that this market will go on increasing and there will be more and more polyester plant coming up.

Conventional route to polyesters is through dimethyl terephthalate because that was the easiest way to obtain a pure fiber grade product. Few processes to obtain fiber grade terephthalic acid have appeared and process licensors claim to present a more economic route. Nevertheless the question is far to be settled because conventional route is constantly improved and fiber grade DM faces less problems in the subsequent fiber technology. Since F.I.P. is having

technology for aromatic production by reforming and extraction by the DMSO process, the complete chain to terephthalic acid has been completed by developing:

- a process for paraxylene crystallization
- a process for xylenes isomerisation
- a paraxylene oxidation process to crude PTA.

XII - Paraxylene Crystallization

High purity paraxylene can be obtained by crystallization of the mixture meta and paraxylene containing or not orthoxylene and ethylbenzene.

Paraxylene recovery by crystallization is limited by the eutectics between paraxylene and the isomeric xylenes. It will be necessary to cool the feed mixture down to a temperature slightly higher than the eutectic temperature without reaching it. Fractional crystallization cannot extract more than 65% of paraxylene in single pass. The conventional processes for paraxylene recovery use two steps:

- 1 - First a crystallization step in which the liquid is cooled either by expansion of prechilled gas in the liquid, or by indirect contact transfer. Crystal separation is then performed mostly by centrifugation.
- 2 - Then a purification step which consists either of a second crystallization with separation by centrifuging or filtration and a series of crystal washings with pure paraxylene.

The I.F.P. process in the other hand, involves following successive steps: (ref. 6)

- crystals formation by consequent contact with a non miscible liquid
- filtration from the mother liquor
- countercurrent washing of the moving crystal layer by melted paraxylene crystals
- crystal melting.

Fig. 10 shows a simplified flow sheet of the process.

This very inventive I.F.P. technology allows a significant gain on refrigeration expense (about 30%) and leads to markedly lower investment

and operating costs (at least 25%). The process uses only one stage crystallization, and no pumping of crystal rich streams. It also eliminates the use of scrapers chillers and centrifuges.

Recently announcements have been made of a process involving absorption technology showing recovery yields close to 100%. Nevertheless economic studies show that I.P.P. process, whose typical economics are presented in Table 10, is very competitive. This is mainly due to the fact that I.P.P. process involves simple equipment and does not have to take in account costly materials like absorbents.

Table 10

Typical Economics of I.P.P. Process for Paraxylene Crystallization

Product	:	99.8% pure paraxylene	
Capacity	:	35,000 MT/yr of paraxylene	
Feed	:	20.6% of paraxylene in C ₈ aromatics	
Paraxylene recovery	:	63%	
Investment in battery limits, refrigeration and cond engineering included			MT 1.75
Utilities, by metric ton of paraxylene product			
H ₂ steam		0.3 ton	
Power (assuming air cooling)		230 kWh	
Process water		2.5 m ³	
Chemicals		0.70	
Labor	:	2 men per shift	

An 11,000 lb/day ferronitrolic plant was put in operation in early 1969.

XIII - Xylenes Isomerisation

I.P.F. xylenes isomerisation is a newly developed process based on extensive studies on bench scale and large pilot plants. Over a period of ten years I.P.F. has accumulated know how in reforming reaction of hydrocarbons on dual function catalysts containing noble metals. This knowledge has led to the development of new catalyst system for xylenes isomerisation. Isomerisation unit is generally coupled with a xylene crystallization unit. Feed is the mother liquor produced by isomerisation unit containing about 10% of paraxylene. Isomerisation occurs on a promoted platinum catalyst.

Products are:

- small quantity of high octane gasoline
- small quantity of C₈ aromatics stream
- over 90% weight of isomerisate containing about 20% of paraxylene

Process flow sheet, extremely simple, involves a single fixed bed down flow reactor. Small hydrogen circulation is required to maintain activity of the catalyst at high level. Hydrogen rich gas from high pressure separator may or may not be recycled according to make-up hydrogen availability.

Capital investment (erected cost including engineering fee) for a 10,000 BTP is around 1.2 million.

Utilities consumptions are the following:

- Fuel 13.2 x 10⁶ Kcal/h
- Electricity 2,100 KWH/h (assuming maximum air cooling)

Catalyst life time is over one year.

XIV - Terophthalic acid

In spite of new fibers grade TP material coming up on the market, 1,4 route to polyester remains at the most important mainly because the technology for processing TP has not been as fully tested commercially as the 1,3 technology.

I.P.F. chose, as a first step, to develop a new process for oxidation of paraxylene into grade TP (99.5% purity). In commercial applications, I.P.F. oxidation step will be linked to one of the available TP technology to produce polyesters.

Paraxylene is catalytically oxidized into TPA by air in an acetic medium. Paraxylene is first oxidized into paratoluic acid which is further oxidized into TPA. TPA is insoluble in reaction medium. Crude TPA is separated by centrifuging from water and acetic acid.

Vapor effluent from reactor is cooled and water washed in a column for acetic acid recovery. Solvent from centrifugal machine is sent to a solvent recovery section where acetic acid is concentrated and recycled to reaction section. Spent catalyst is continuously purged and replaced.

A 15,000 TPA/year plant requires a capital investment of around \$10 million and following consumption of chemicals and utilities:

Per ton of crude TPA

Electricity	270 KWH
Steam	3.8 T
Cooling water (at = 13° C)	230 m ³
Process water	0.3 T
Catalyst	1
Acetic acid	2.4

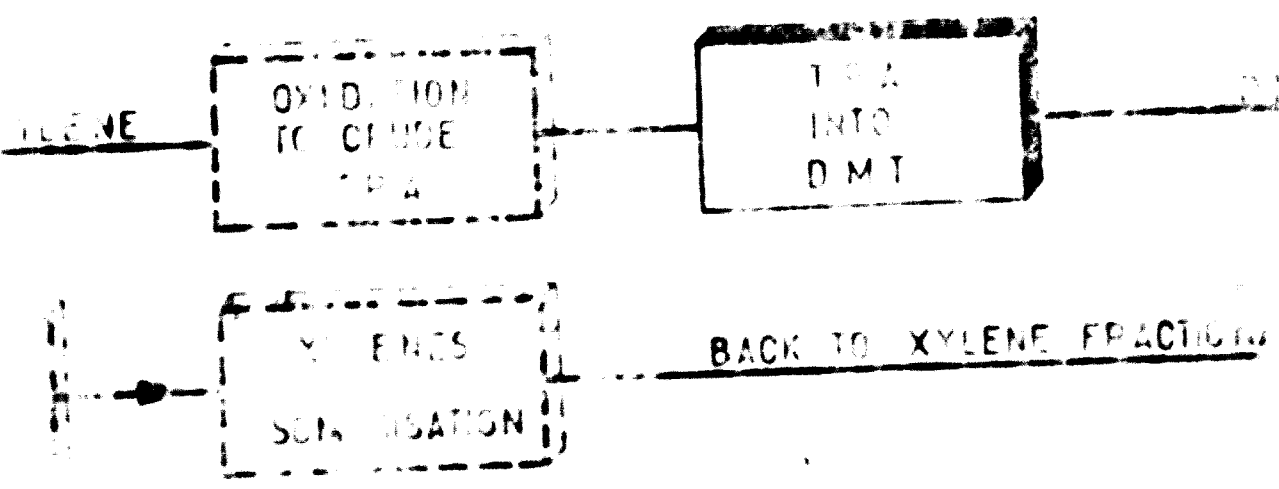
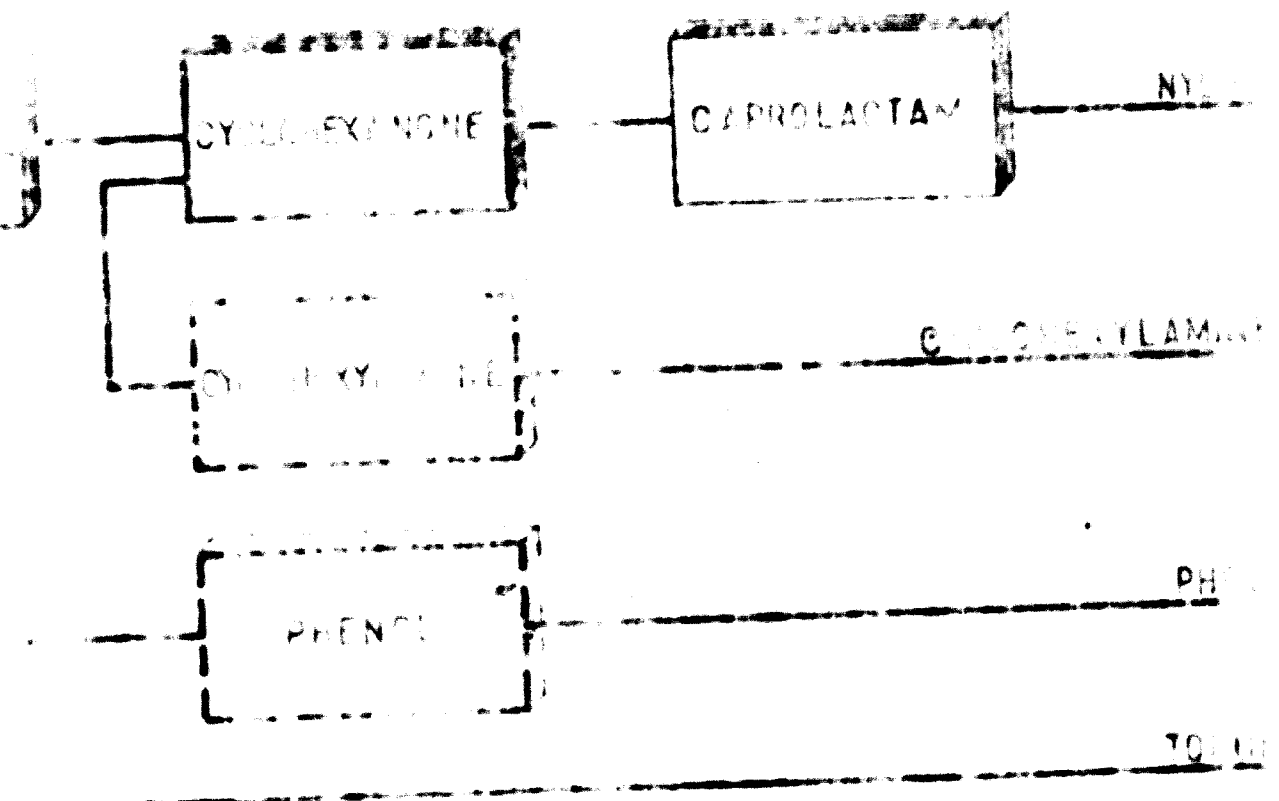
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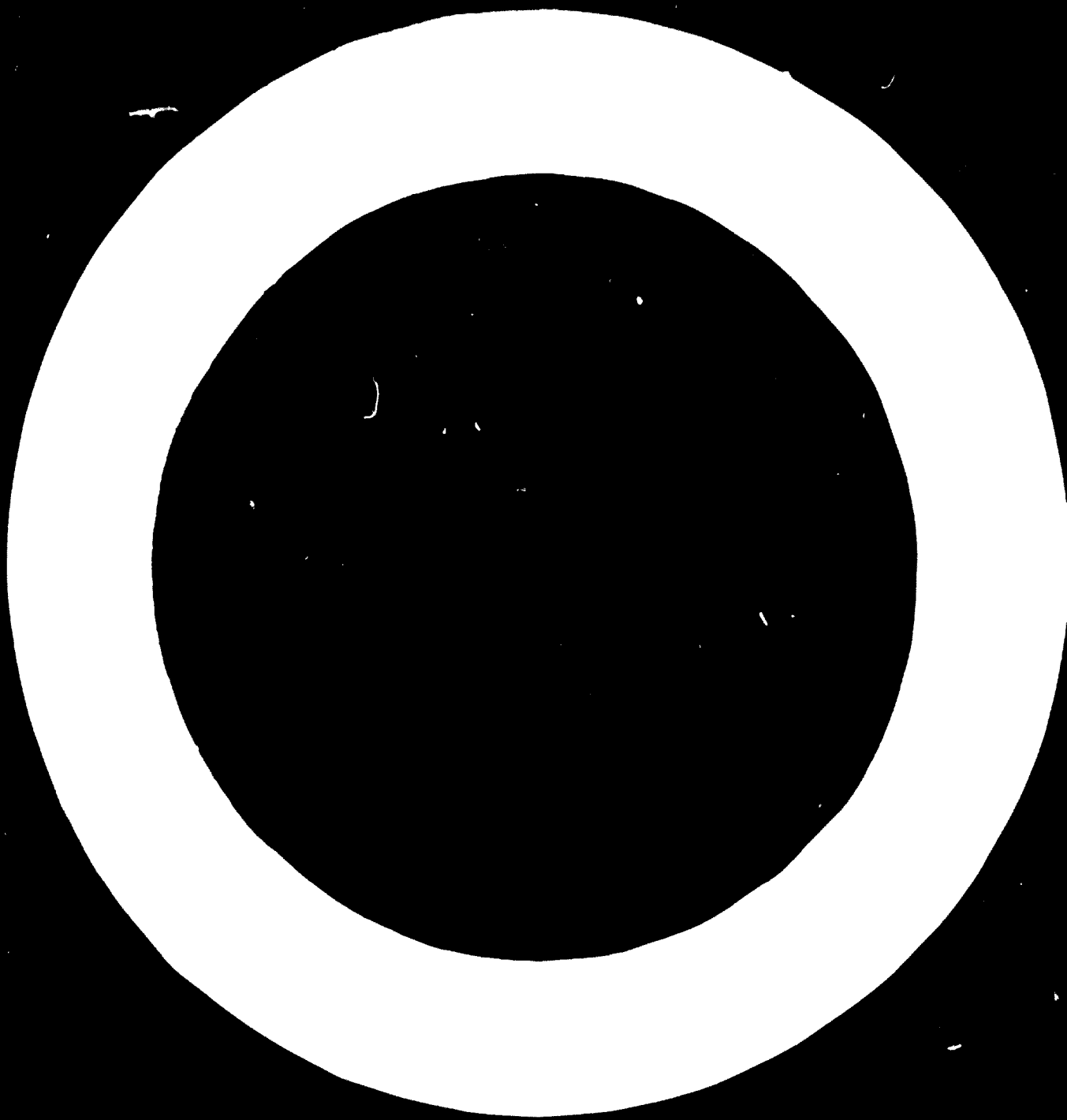
PRODUCTION AND TRANSFORMATION

NAPHTHA C5-150

NAPHTHA C6-200

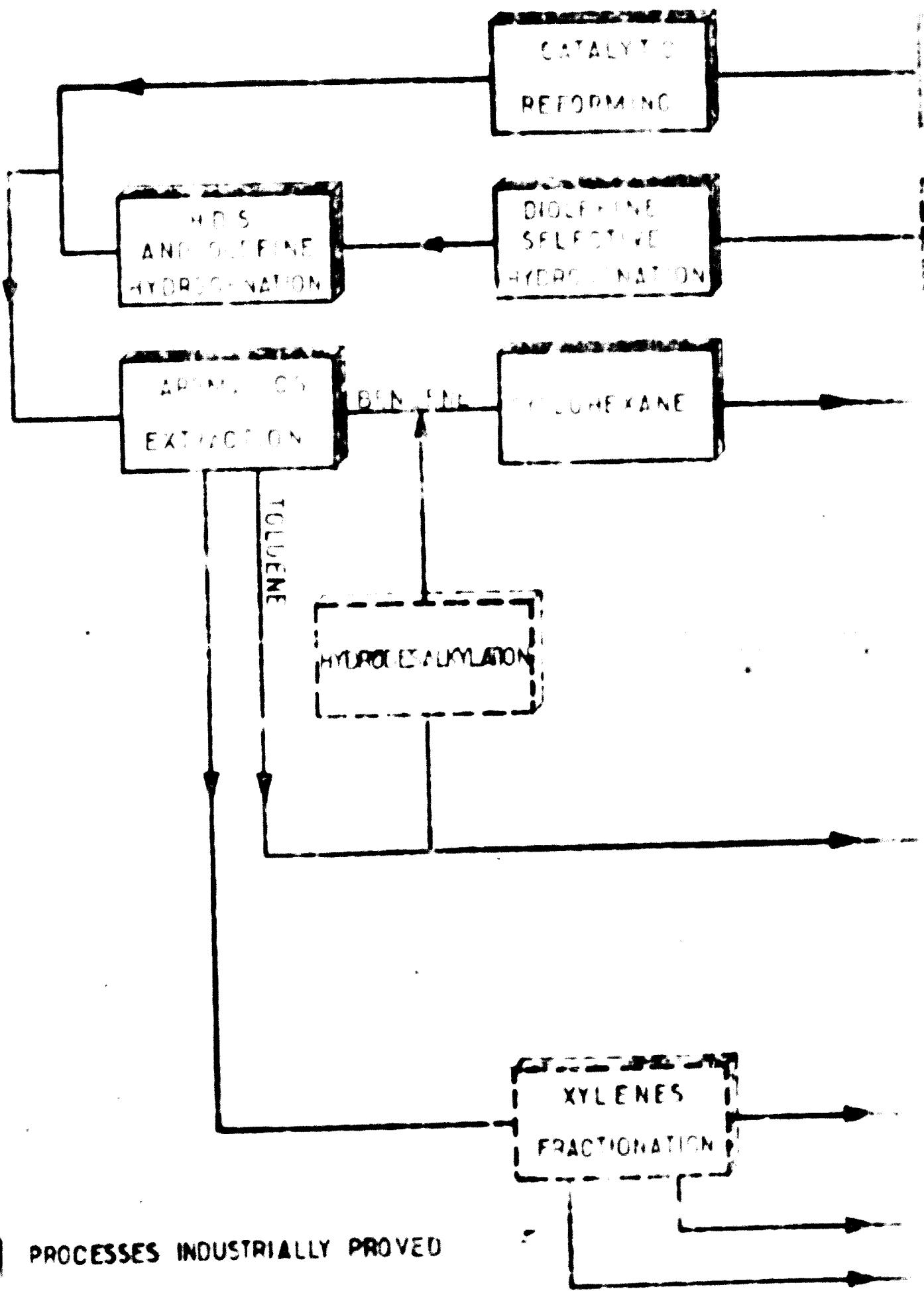


ETHYLBENZENE



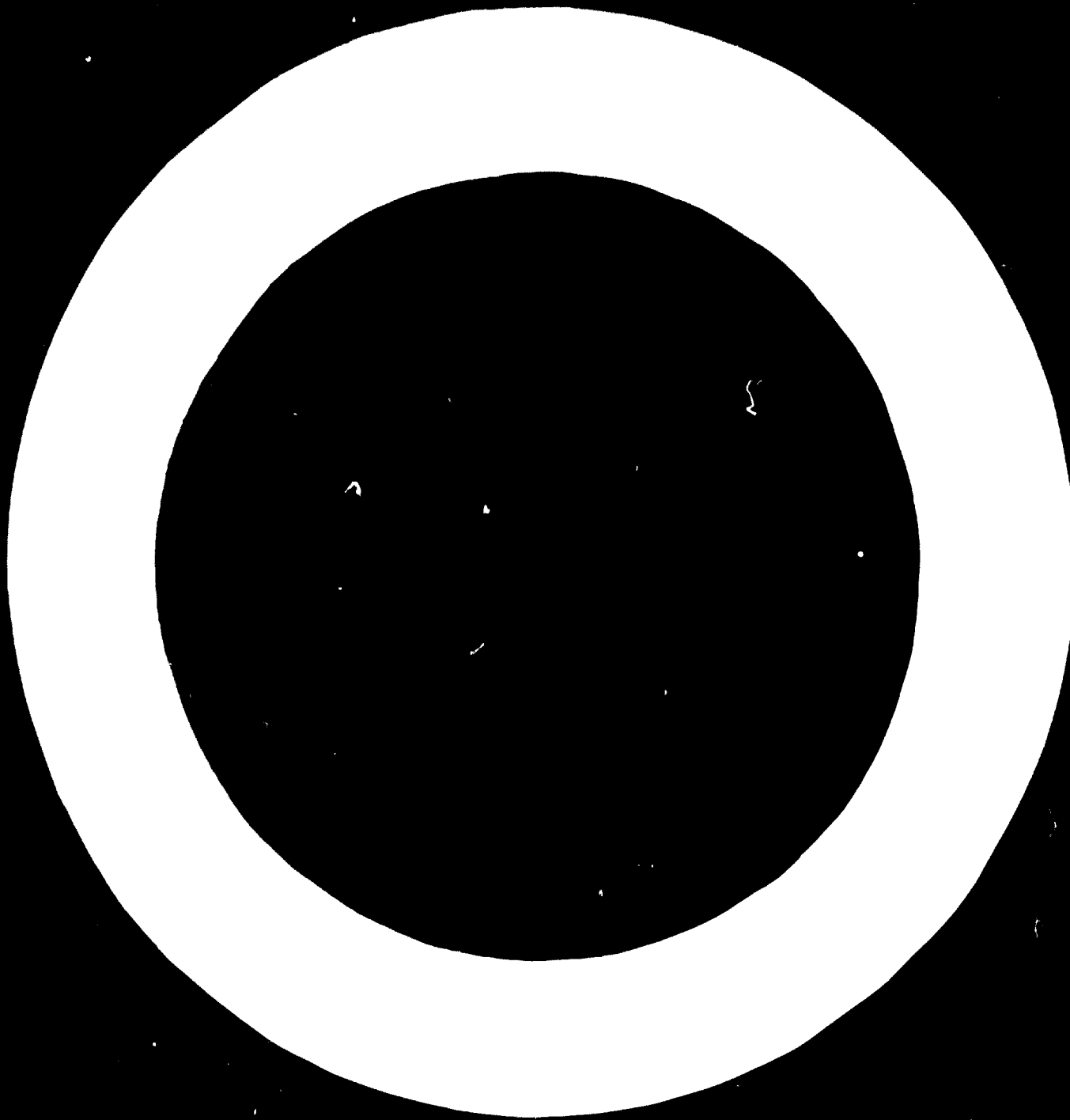
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FRANCAIS DU PETROLE'S PROCESSES IN THE FIELD

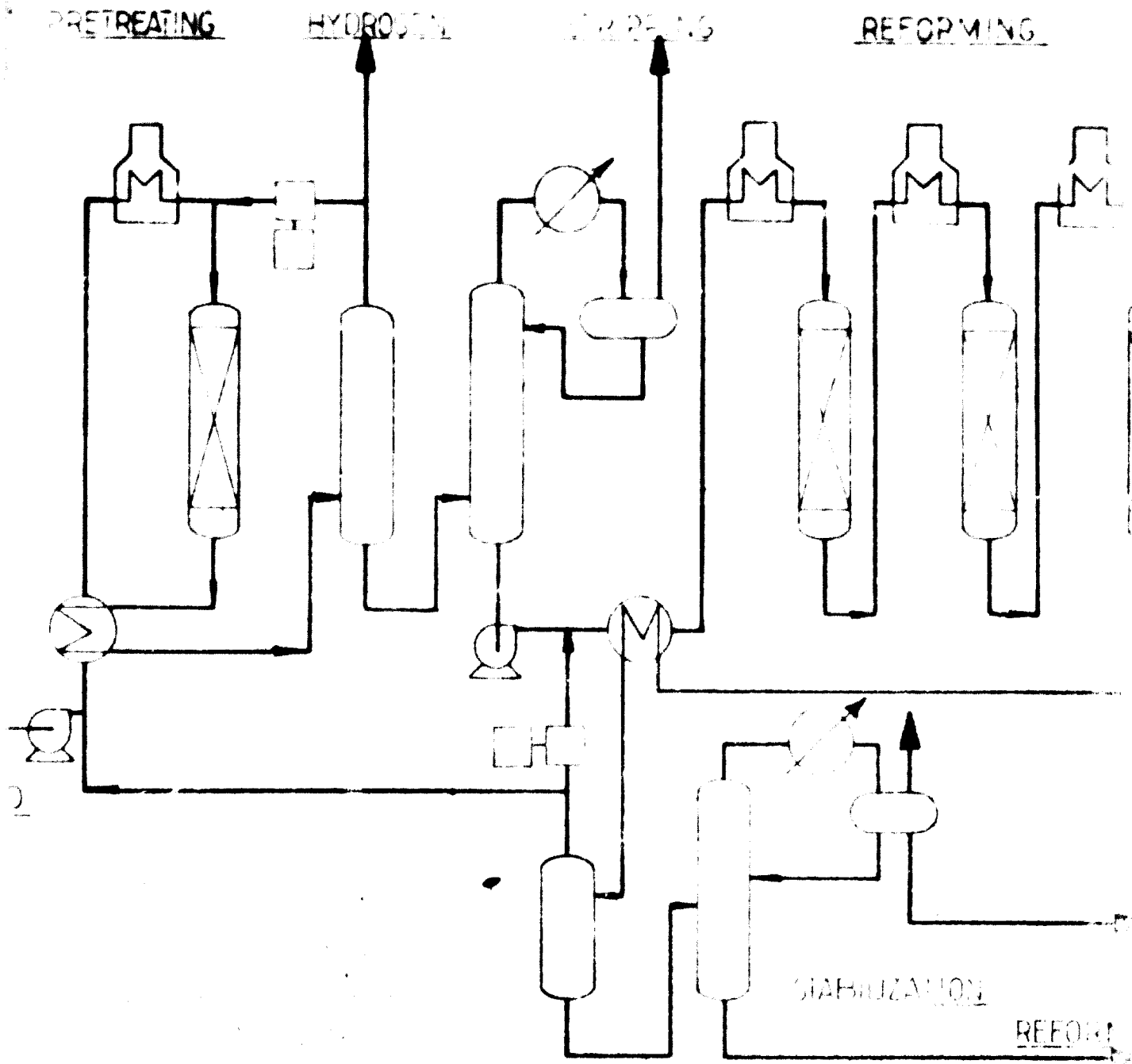


PROCESSES INDUSTRIALLY PROVED

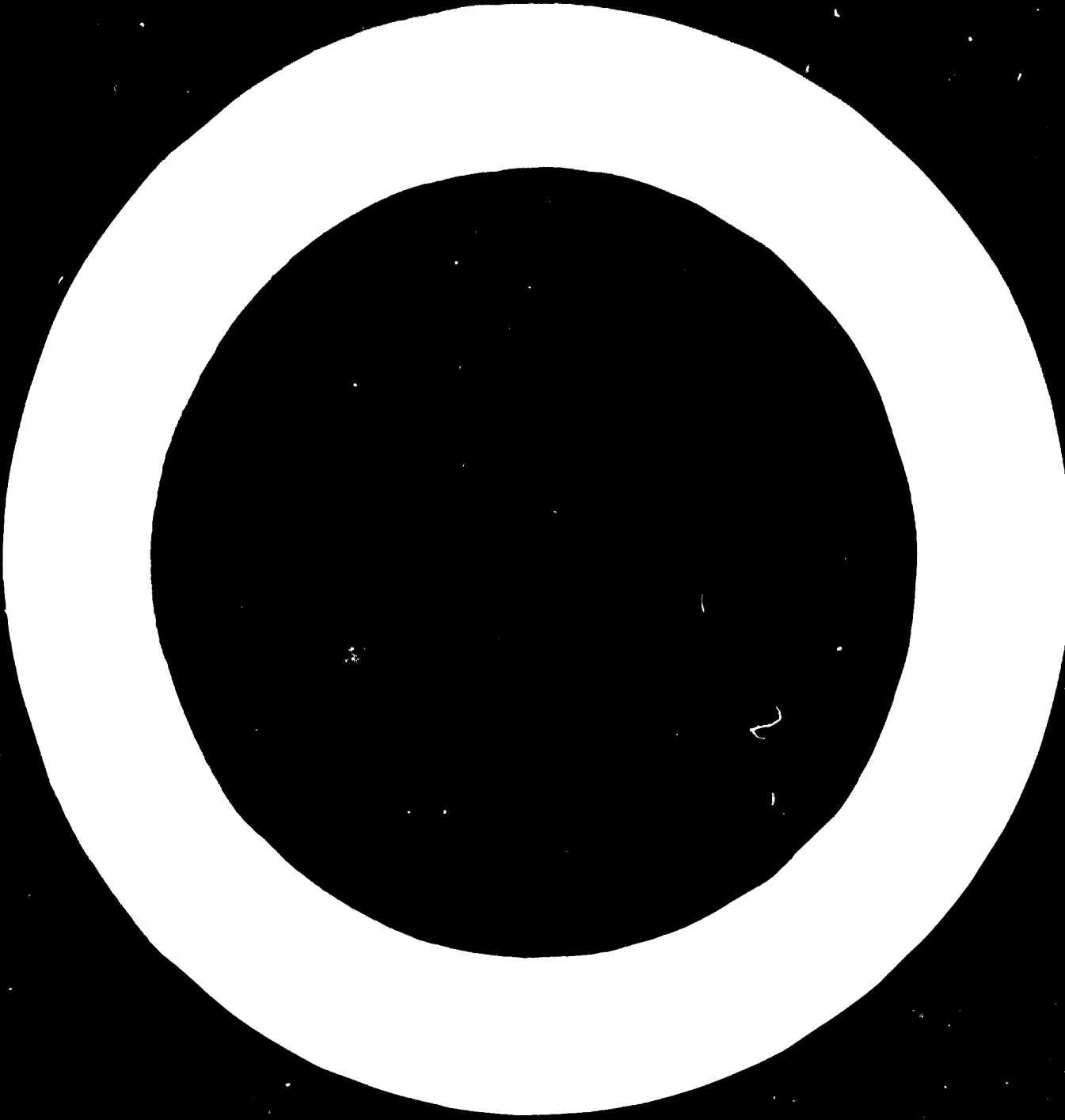
PROCESSES READY FOR SALE



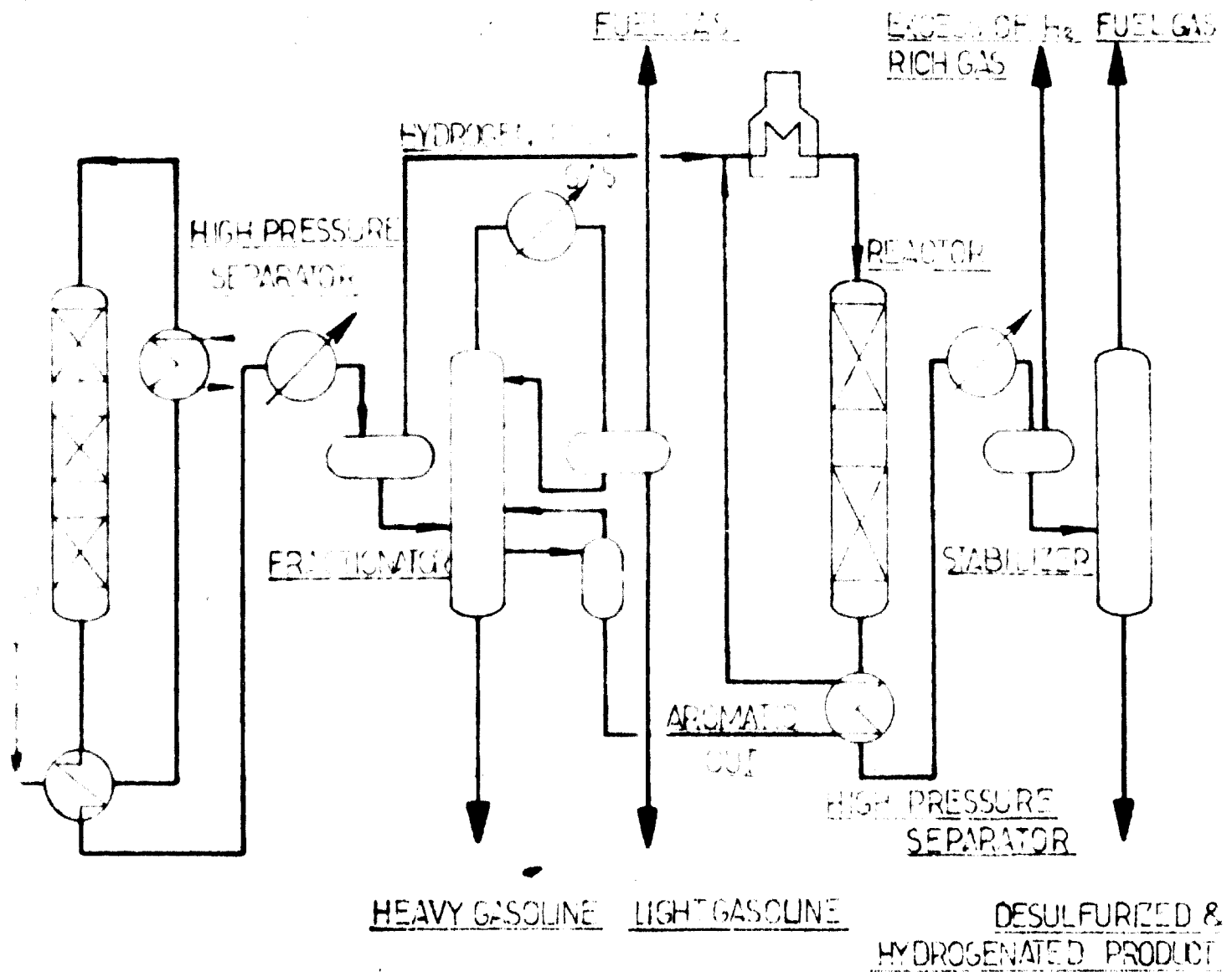
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2. TYPICAL FLOW SHEET OF L.F.P. REFORMING UNIT ALONG WITH
PRETREATING SECTION



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TYPICAL FLOW SHEET FOR L.P. 2 STAGES STEAM CRACKING GASOLINE
HYDROGENATION PROCESS



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EXTRACT AROMATICS • RAFFINATE DISTILLATION
EXTRACTION REEXTRACTION WATER WASH

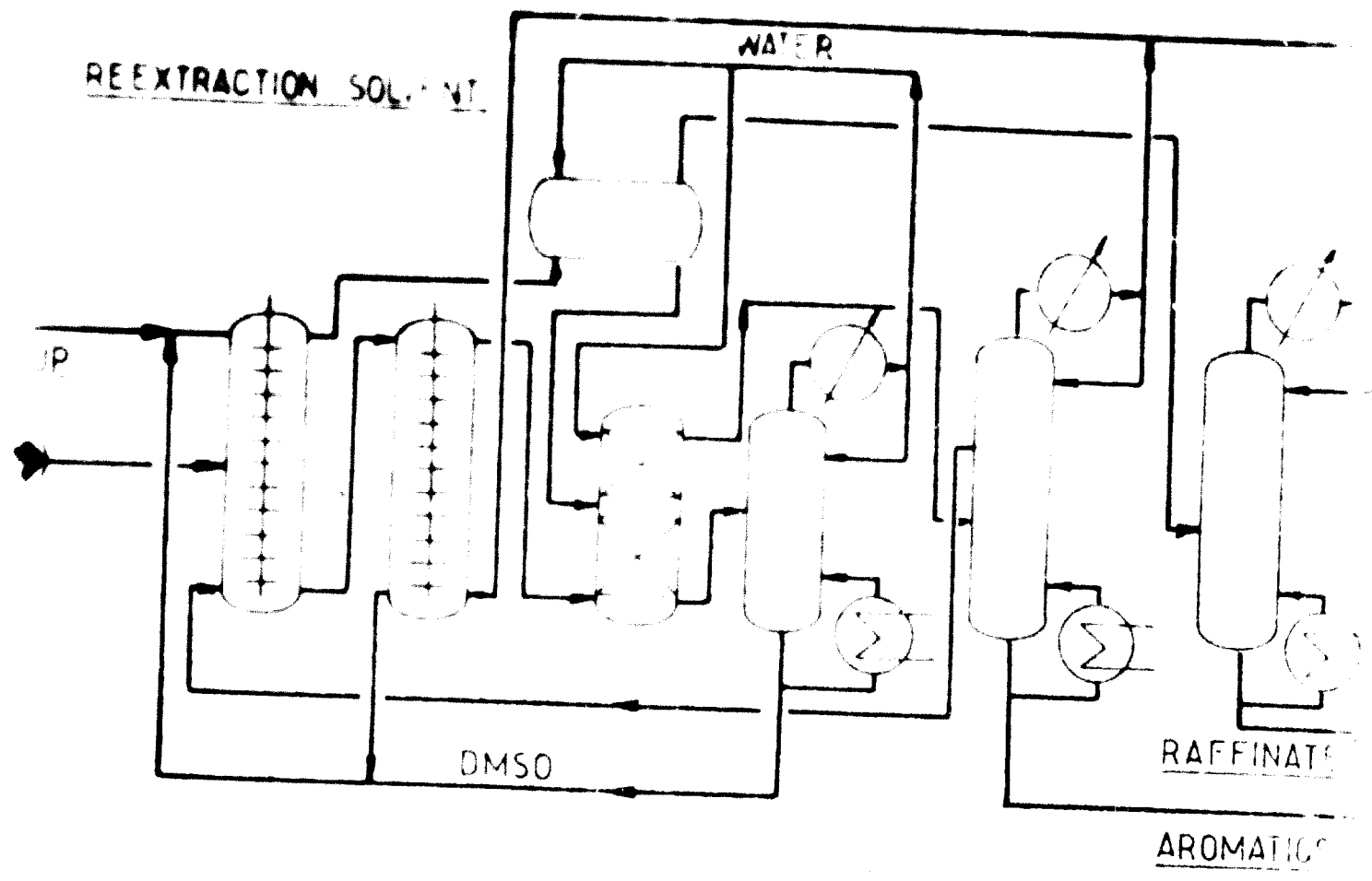
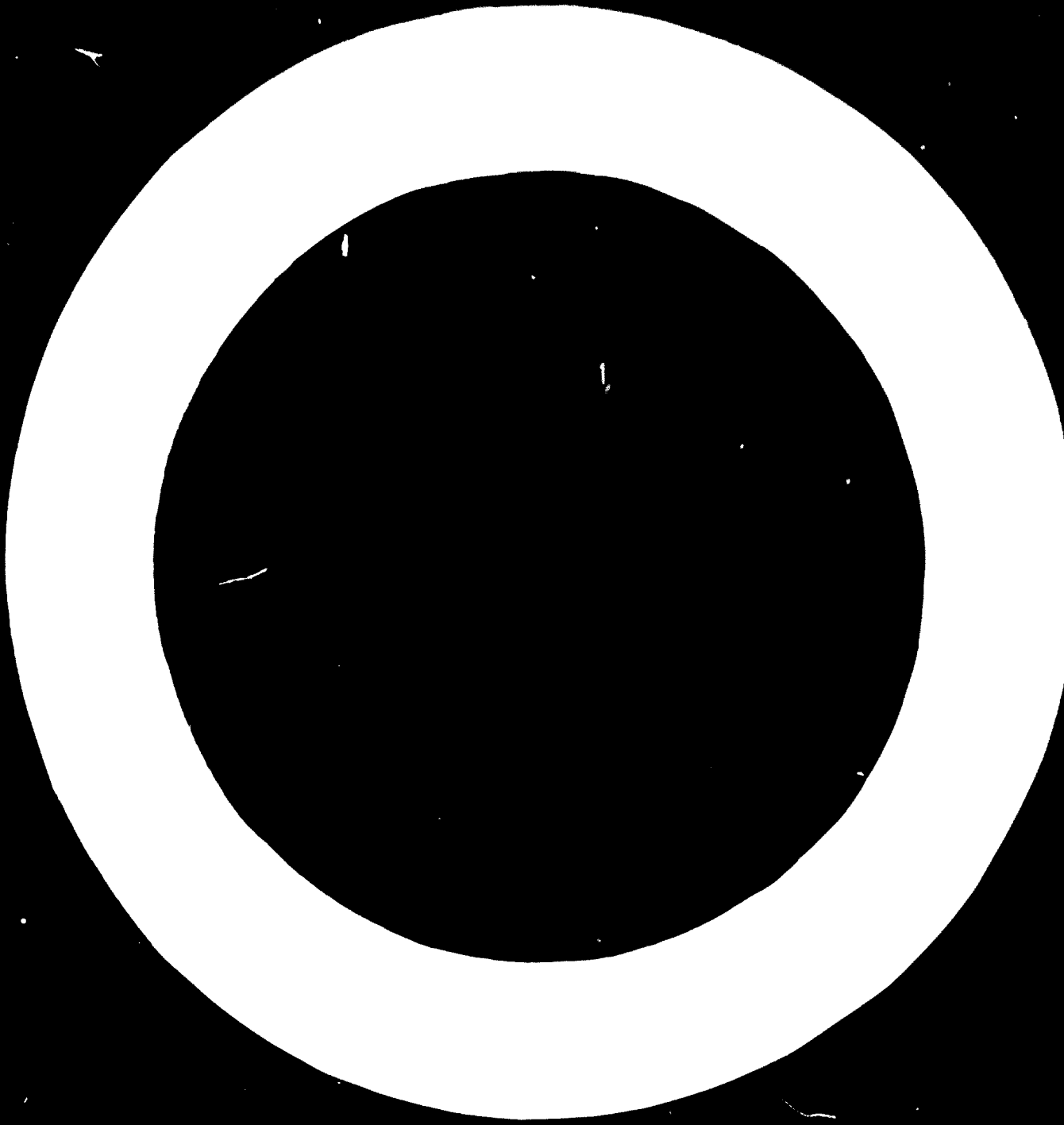
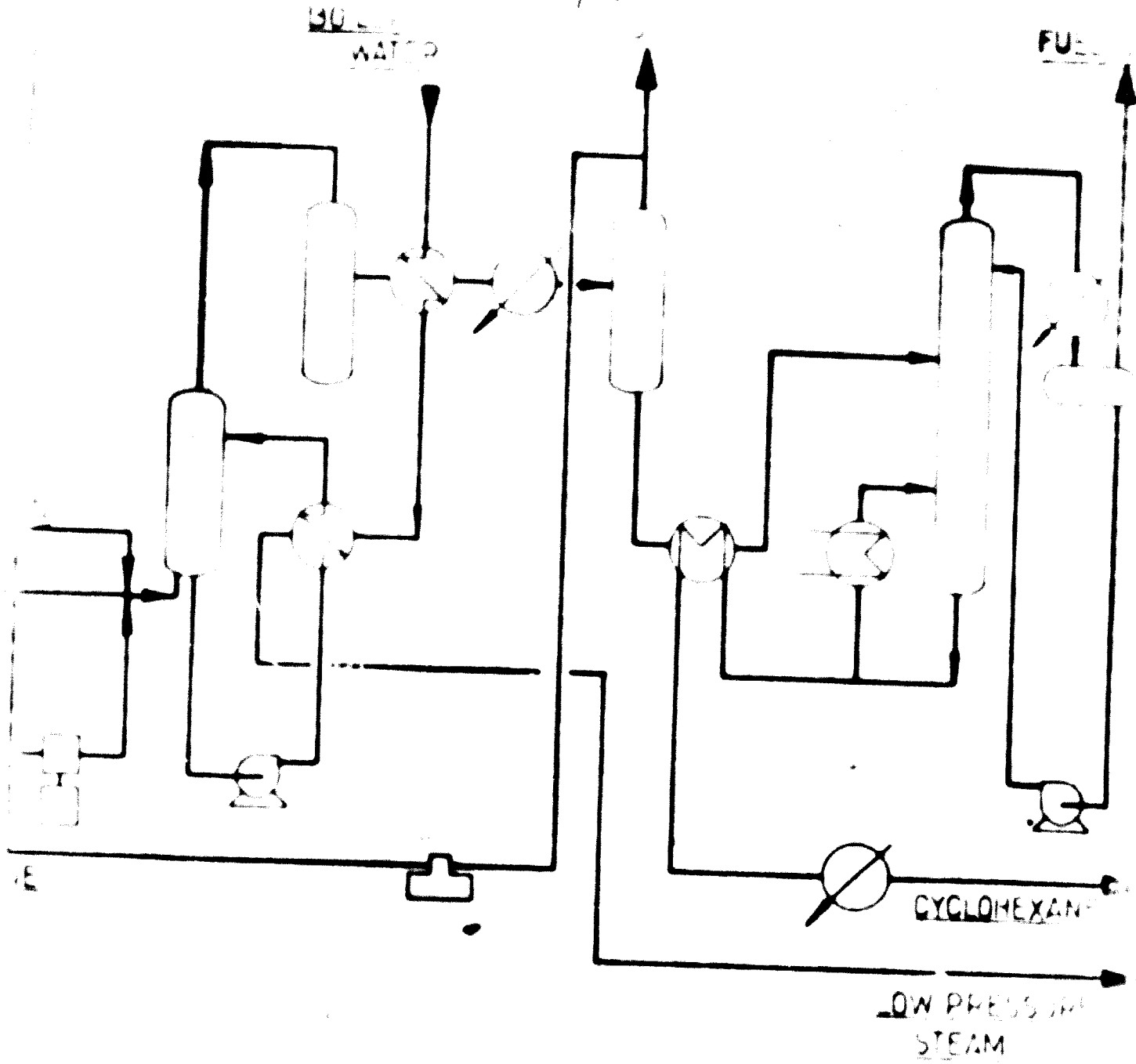


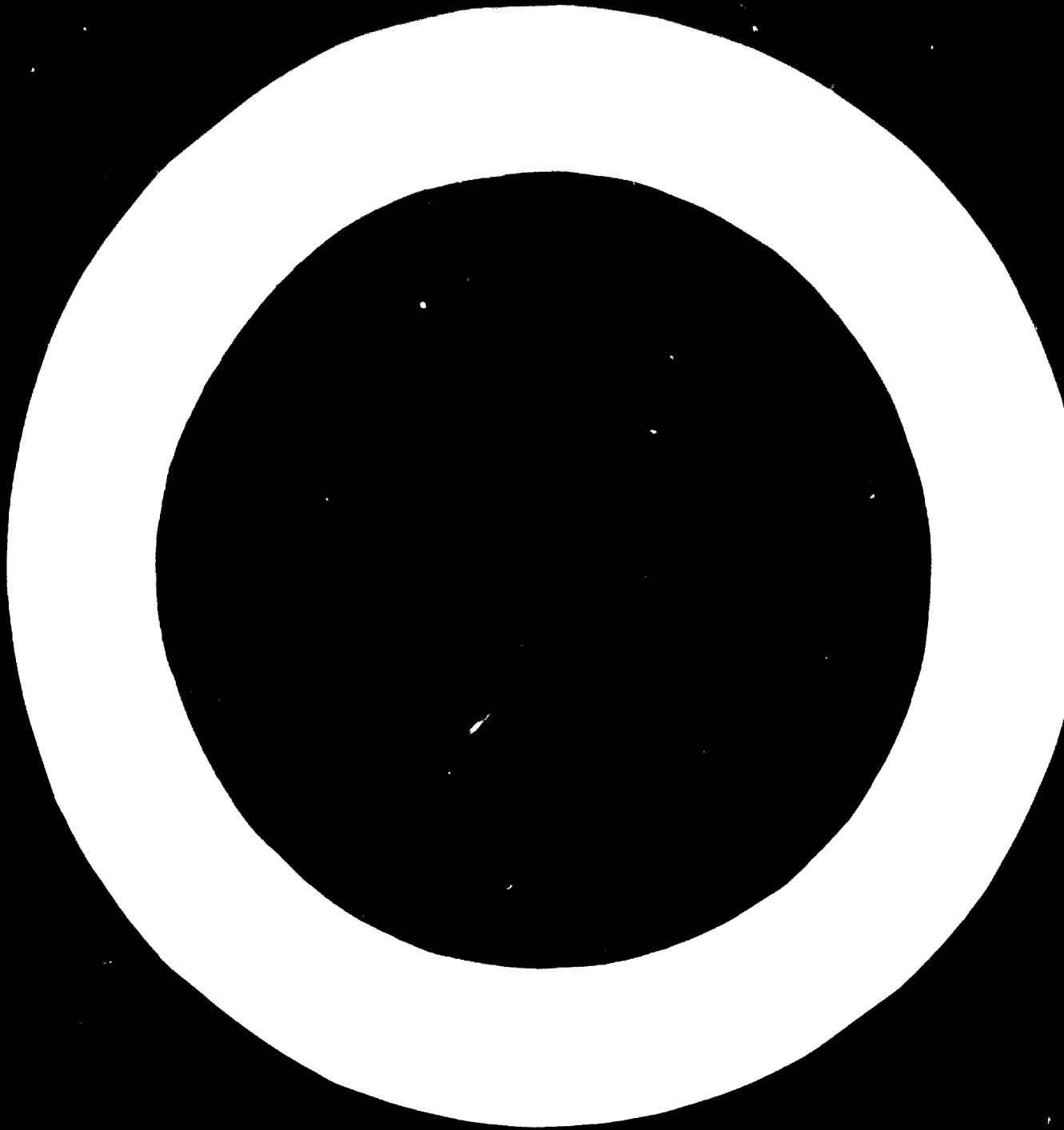
FIG. 4 — TYPICAL FLOW SHEET OF I.F.P. AROMATIC EXTRACTION PROCESS



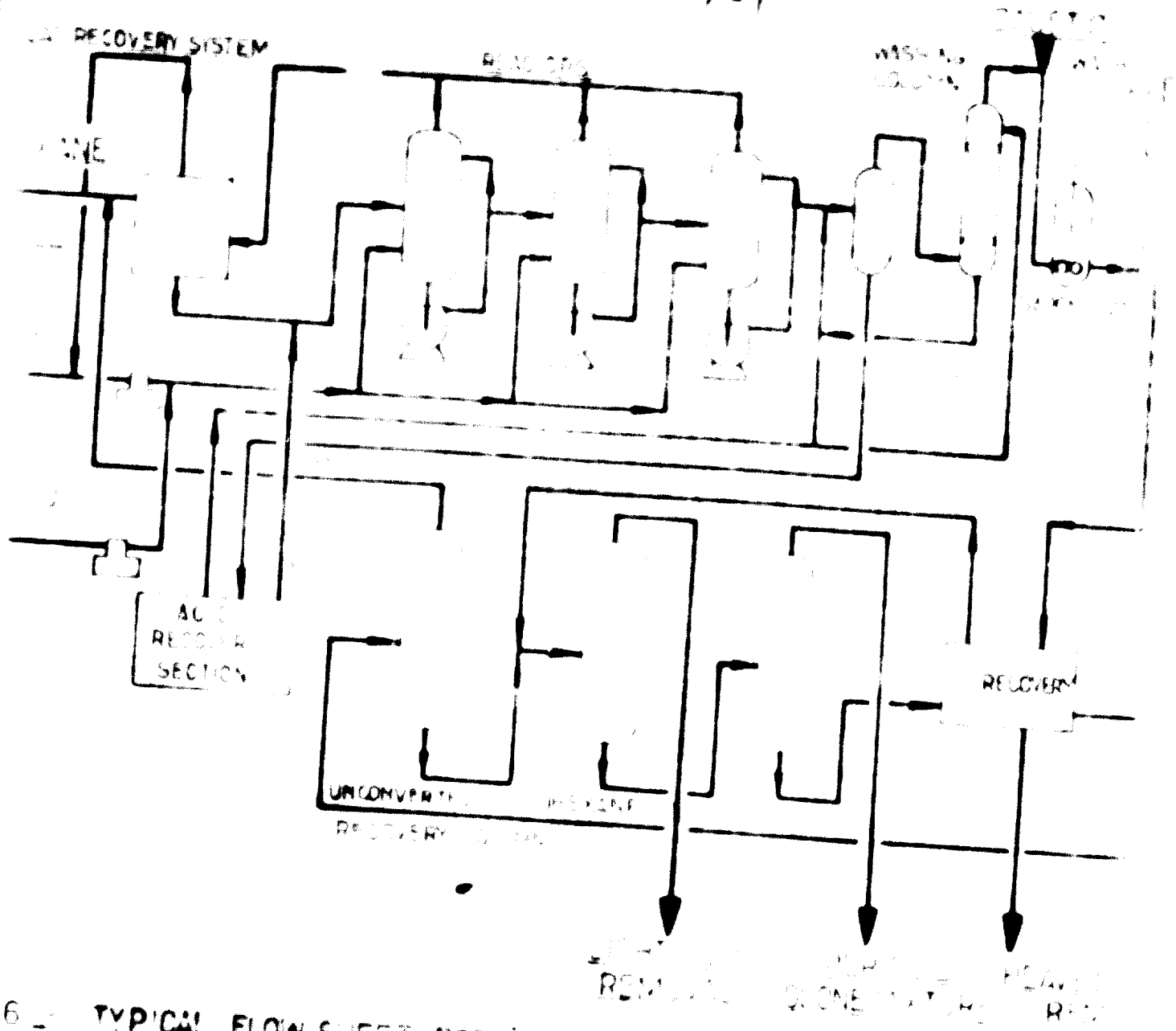
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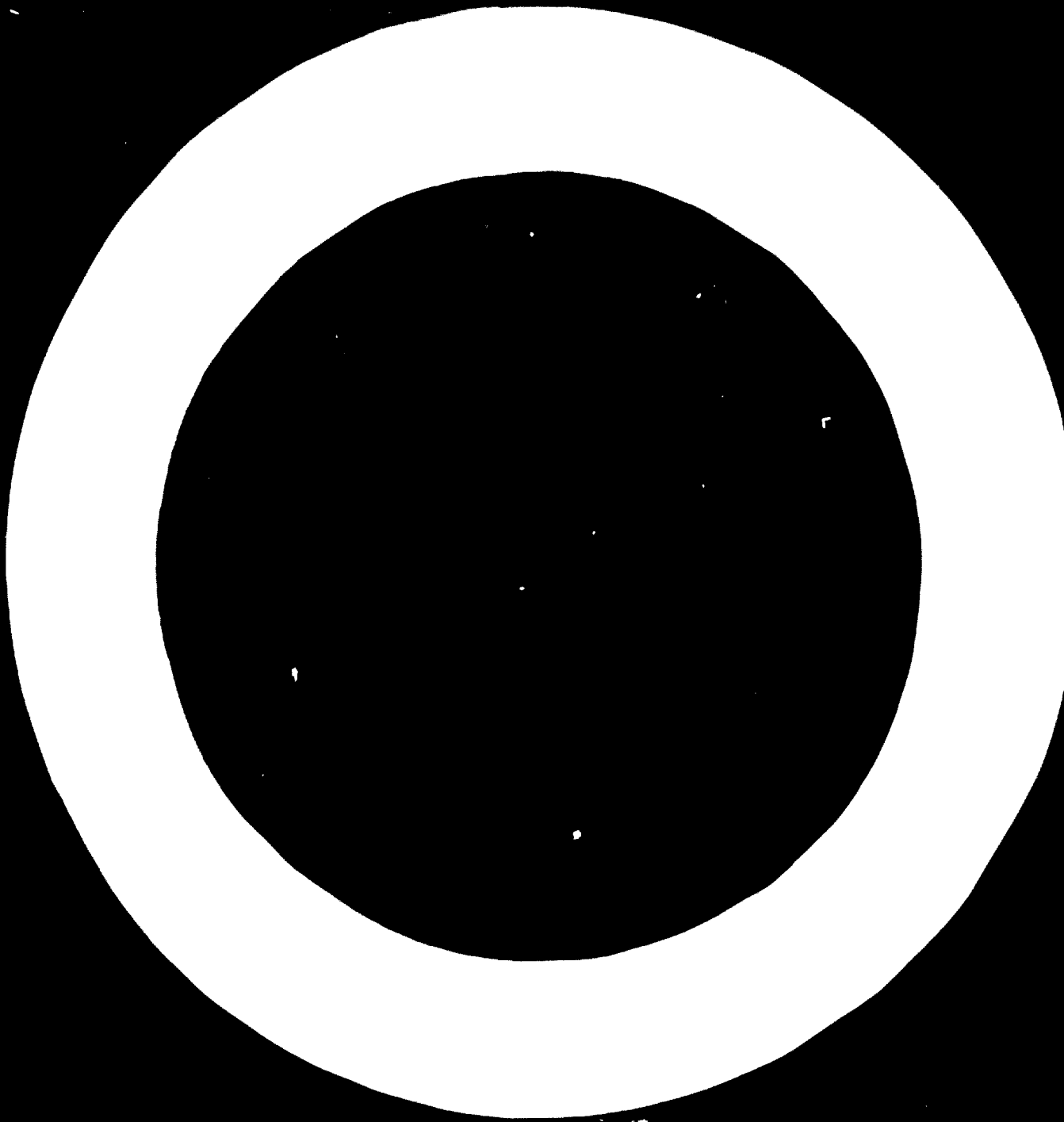
TYPICAL FLOW SHEET OF L.P. BENZENE HYDROGENATION PROCESS



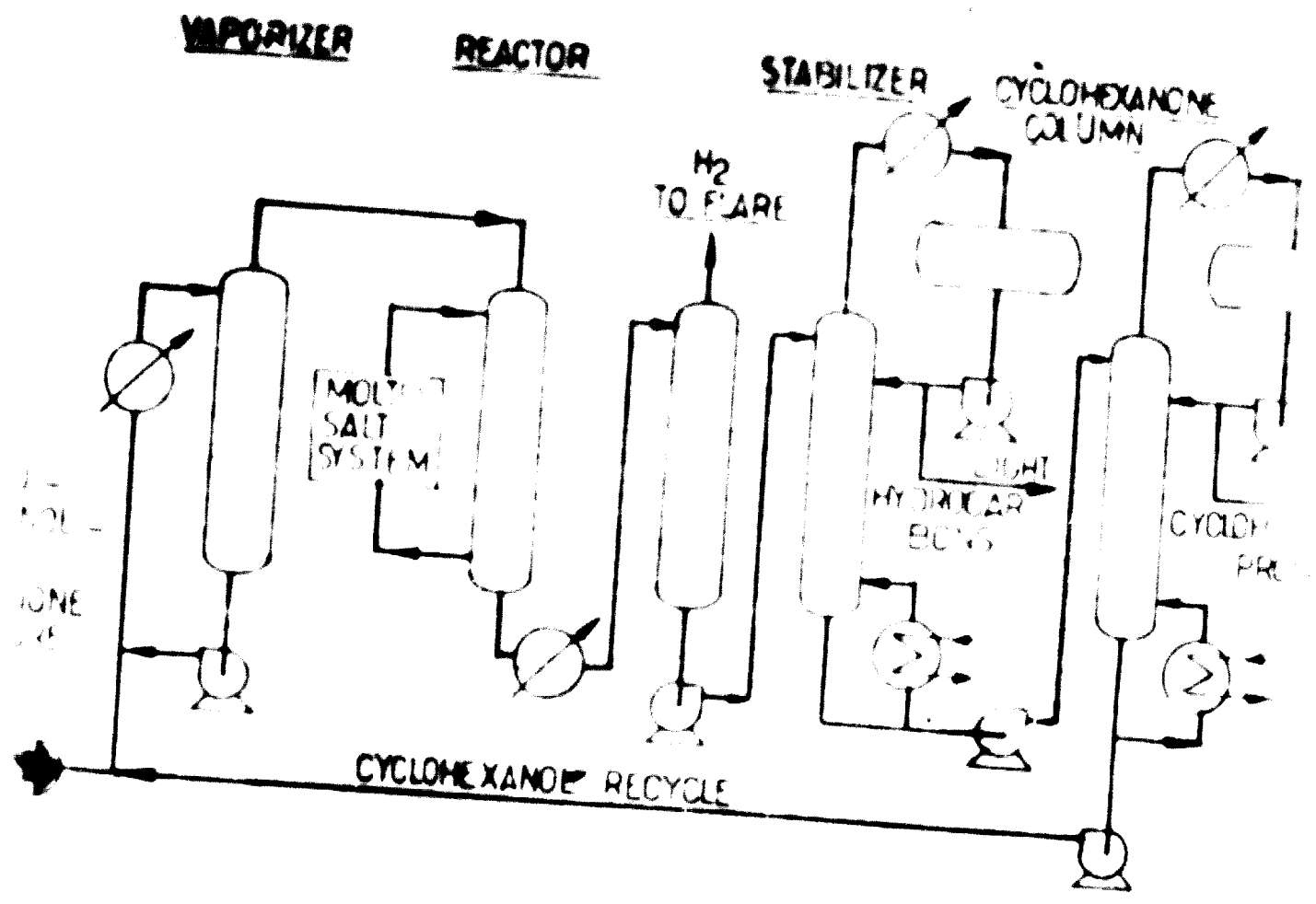
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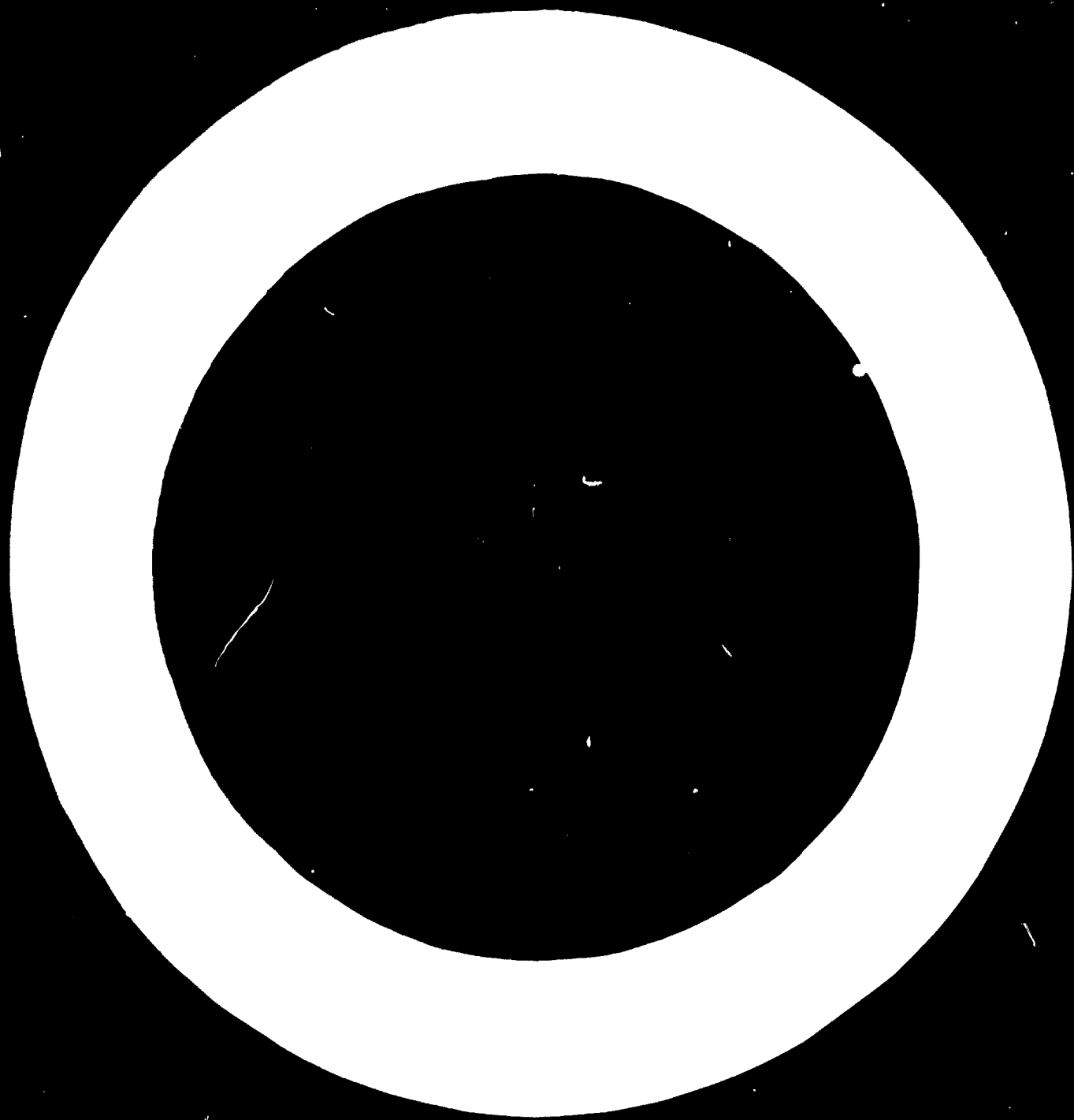
1.6 - TYPICAL FLOW SHEET FOR T.E.P. AND OTHER MANUFACTURING PROCESSES



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1.7 TYPICAL FLOW SHEET OF I.F.P. CYCLOHEXANONE PROCESS



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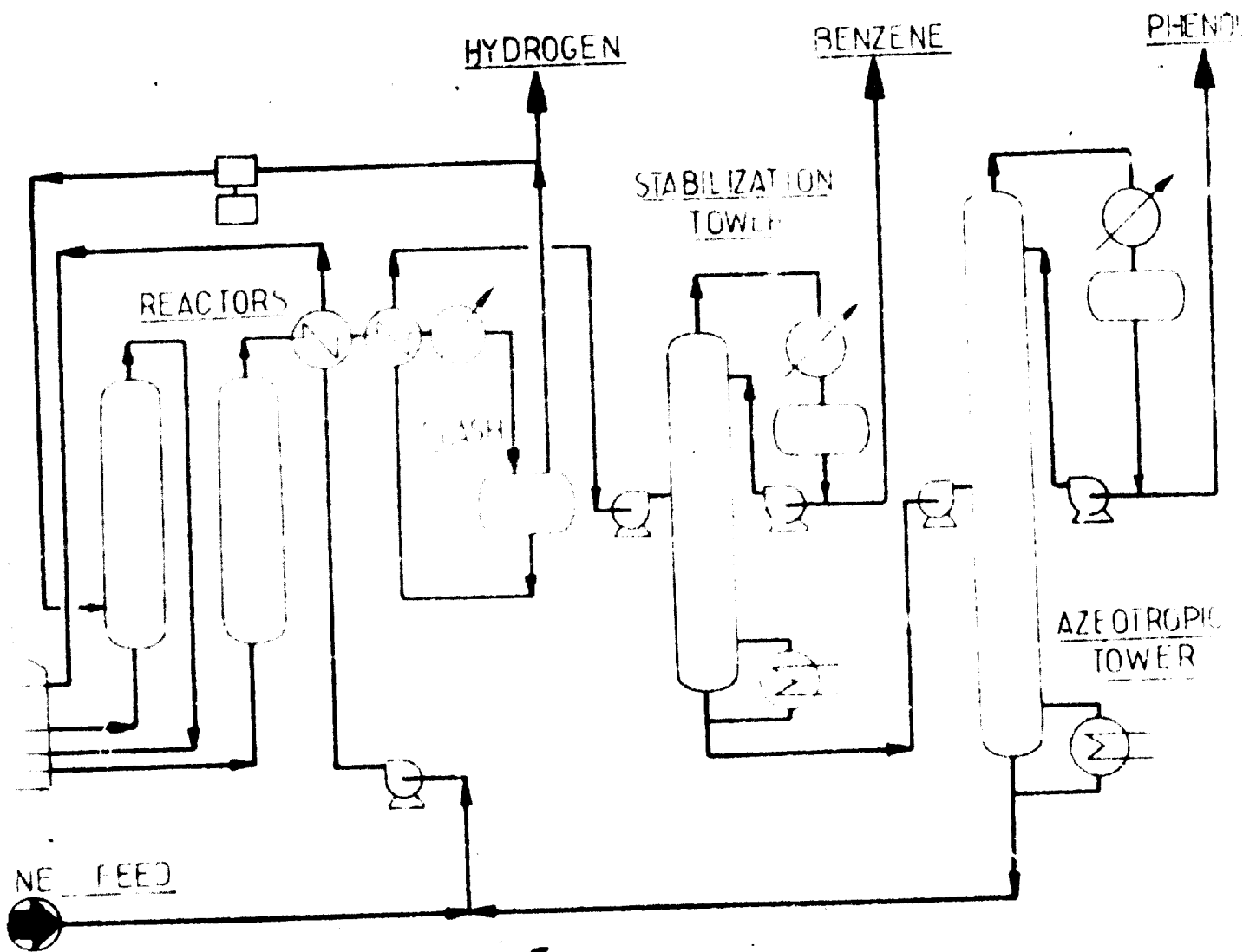
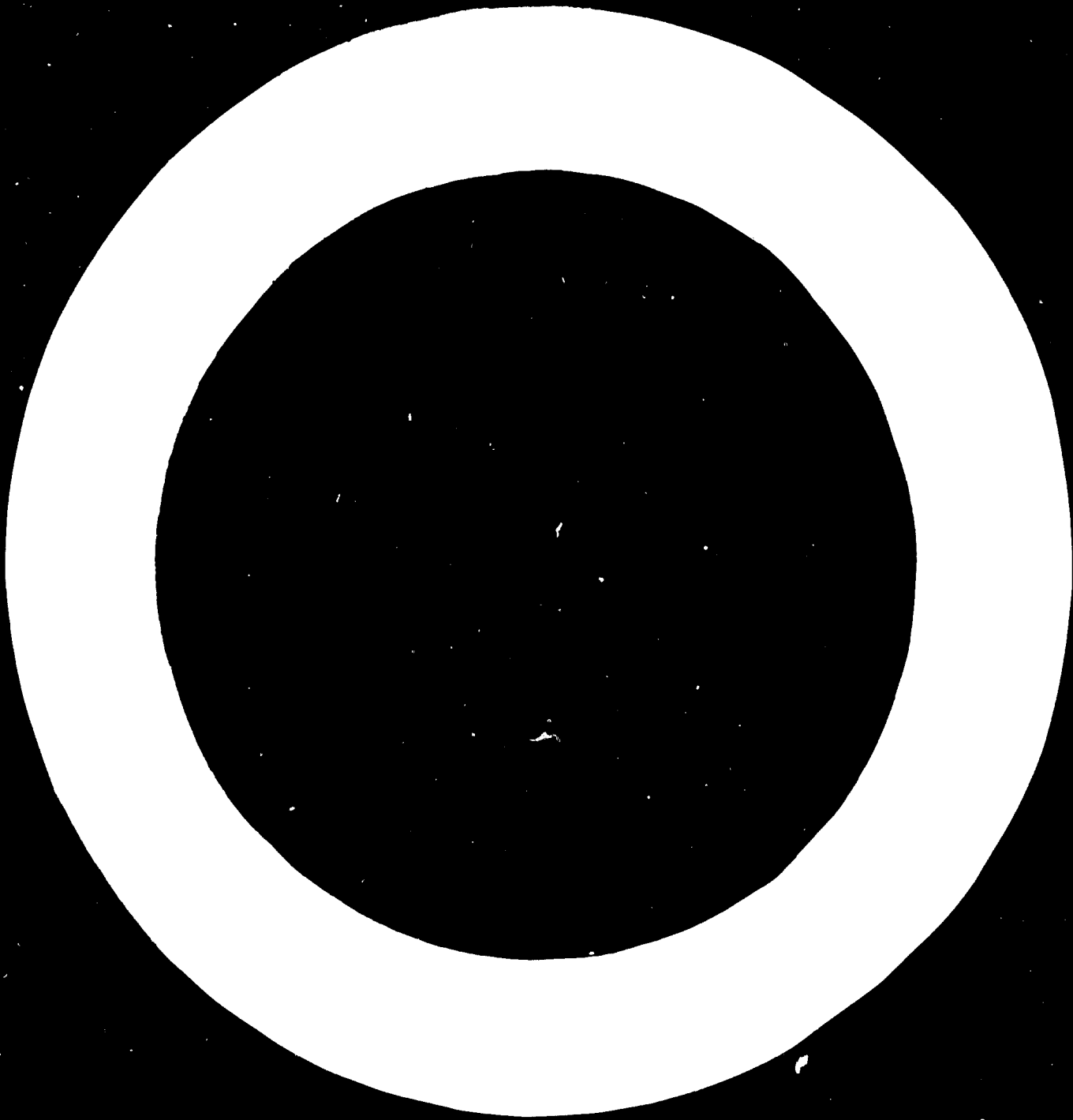
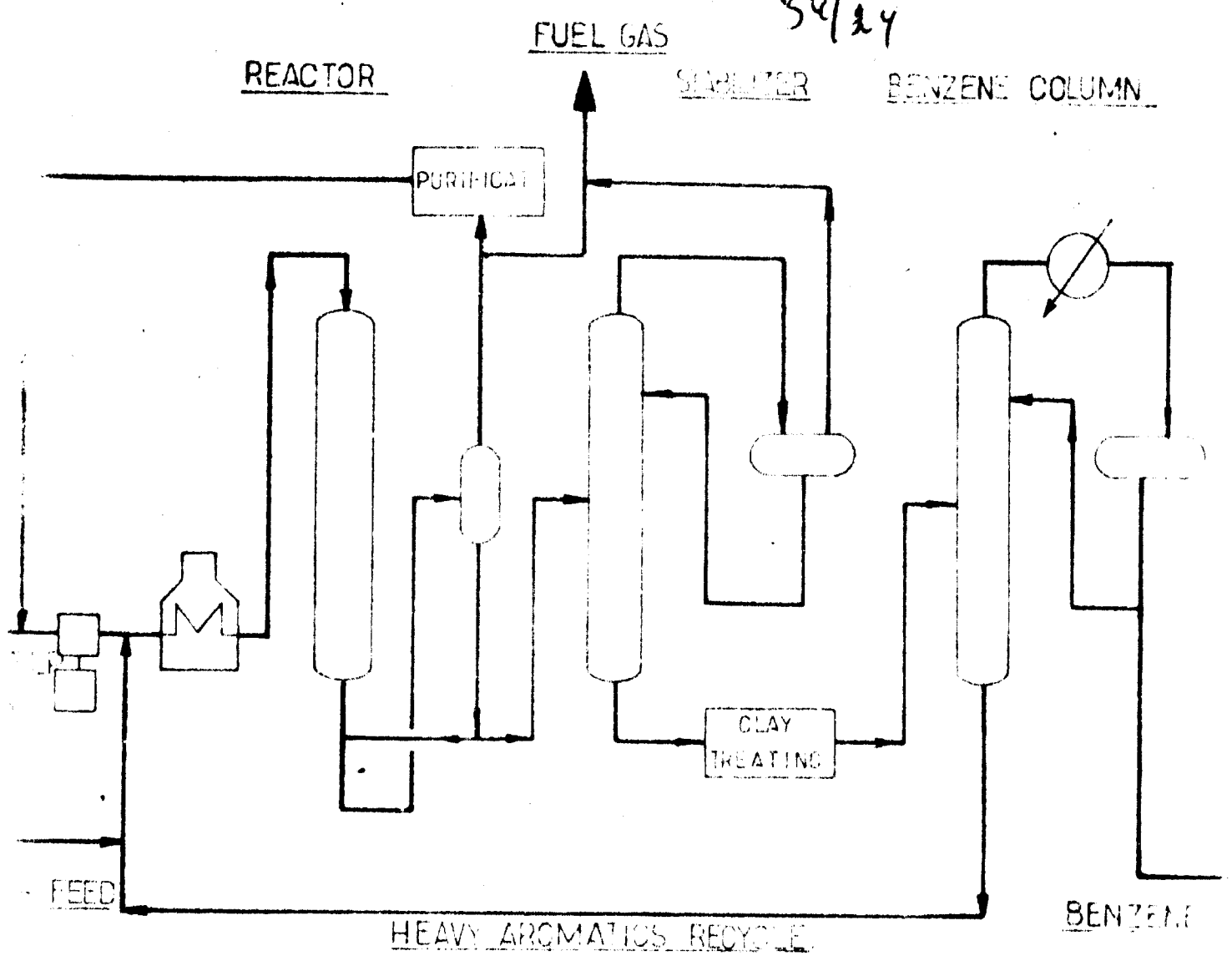


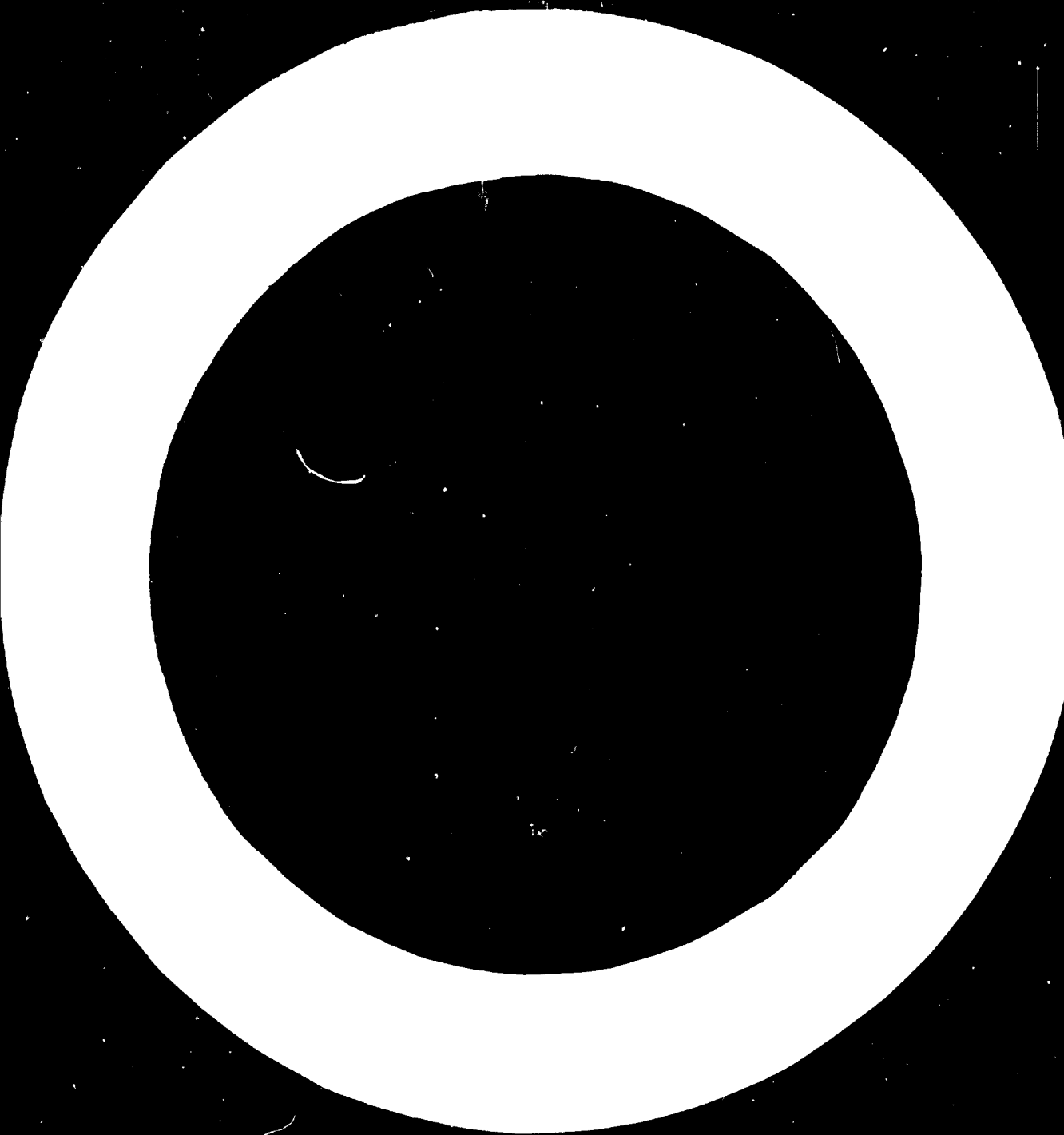
Fig 8 — TYPICAL FLOW SHEET OF IFP PHENOL PROCESS



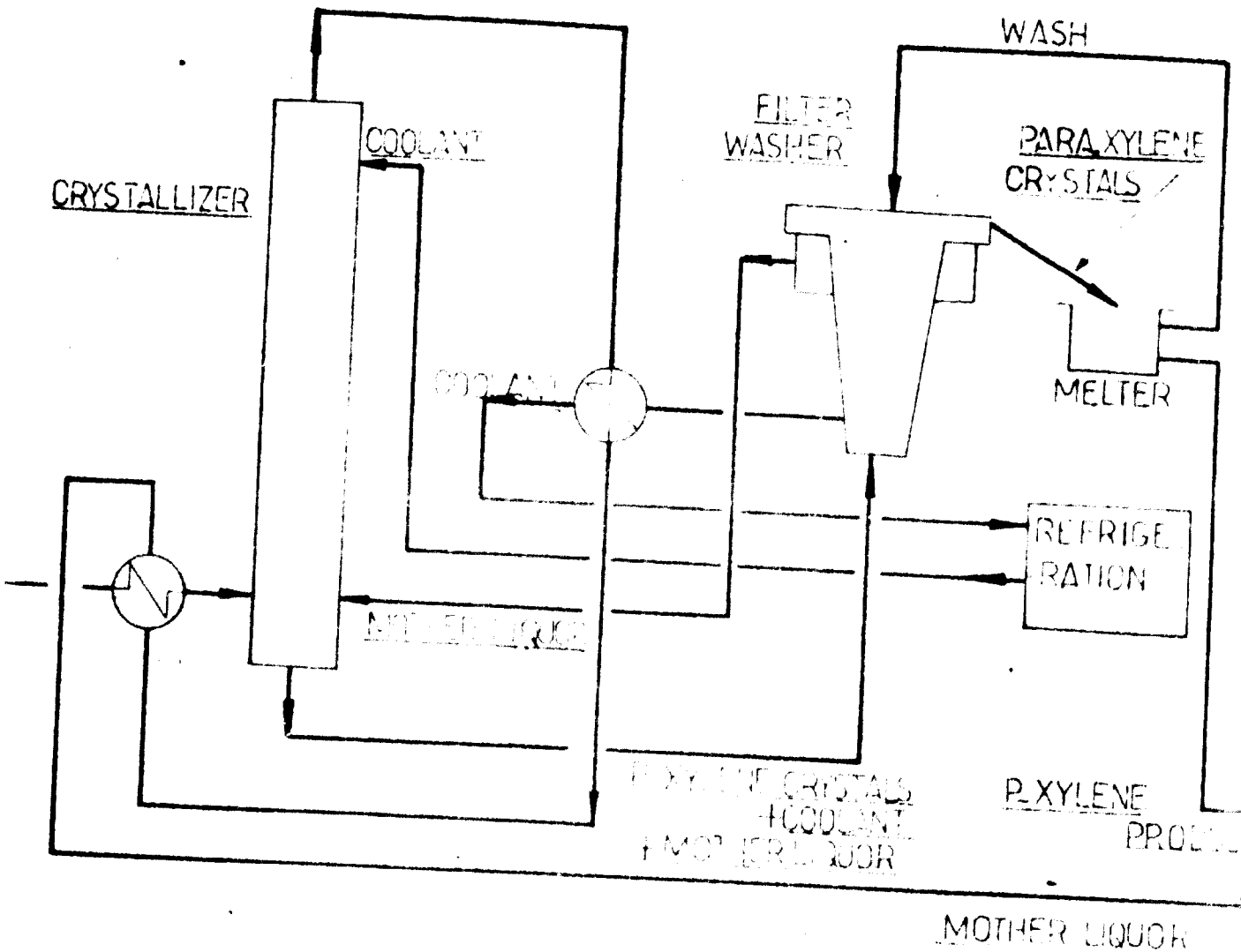
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10 - TYPICAL FLOW SHEET OF I.F.P. TOLUENE DESALKYLATION PROCESS

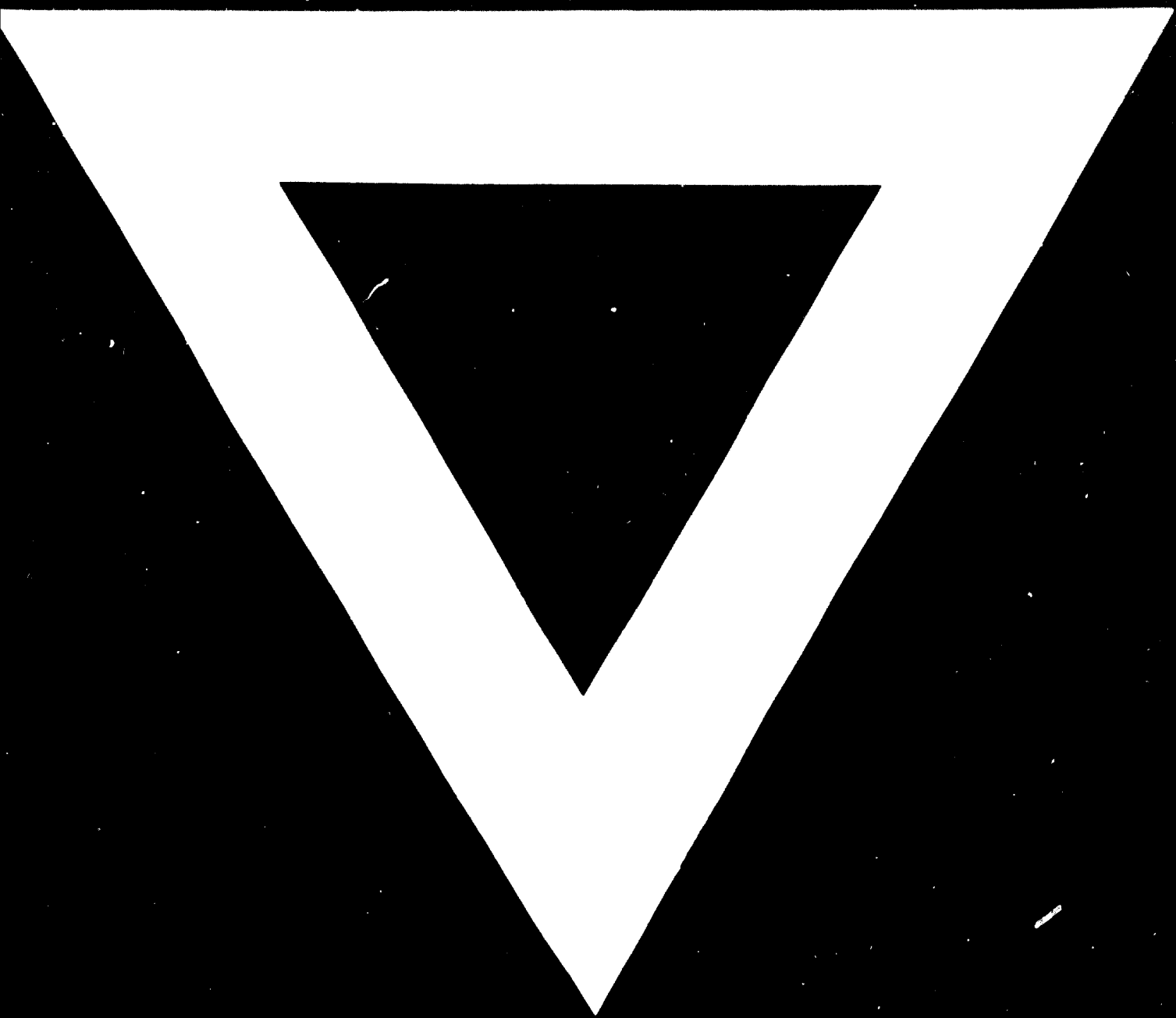


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D - TYPICAL FLOW SHEET OF P-XYLENE CRYSTALLIZATION PROCESS





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