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International Technical Conference on the
Development of the Petrochemical Industries in
Developing Countries

Moscow, USSR, 21 - 31 October 1969

PET. SYMP. 3/6

PROCESSES FOR THE PRODUCTION OF PETROCHEMICAL
BASIC BUILDING BLOCKS 1/

by

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PET. SYNP. B/6

Laku, USSR, 20 - 31 October 1969

SUMMARY

PROCESS FOR THE PRODUCTION OF PETROCHEMICAL BASIC BUILDING BLOCKS 1/

by

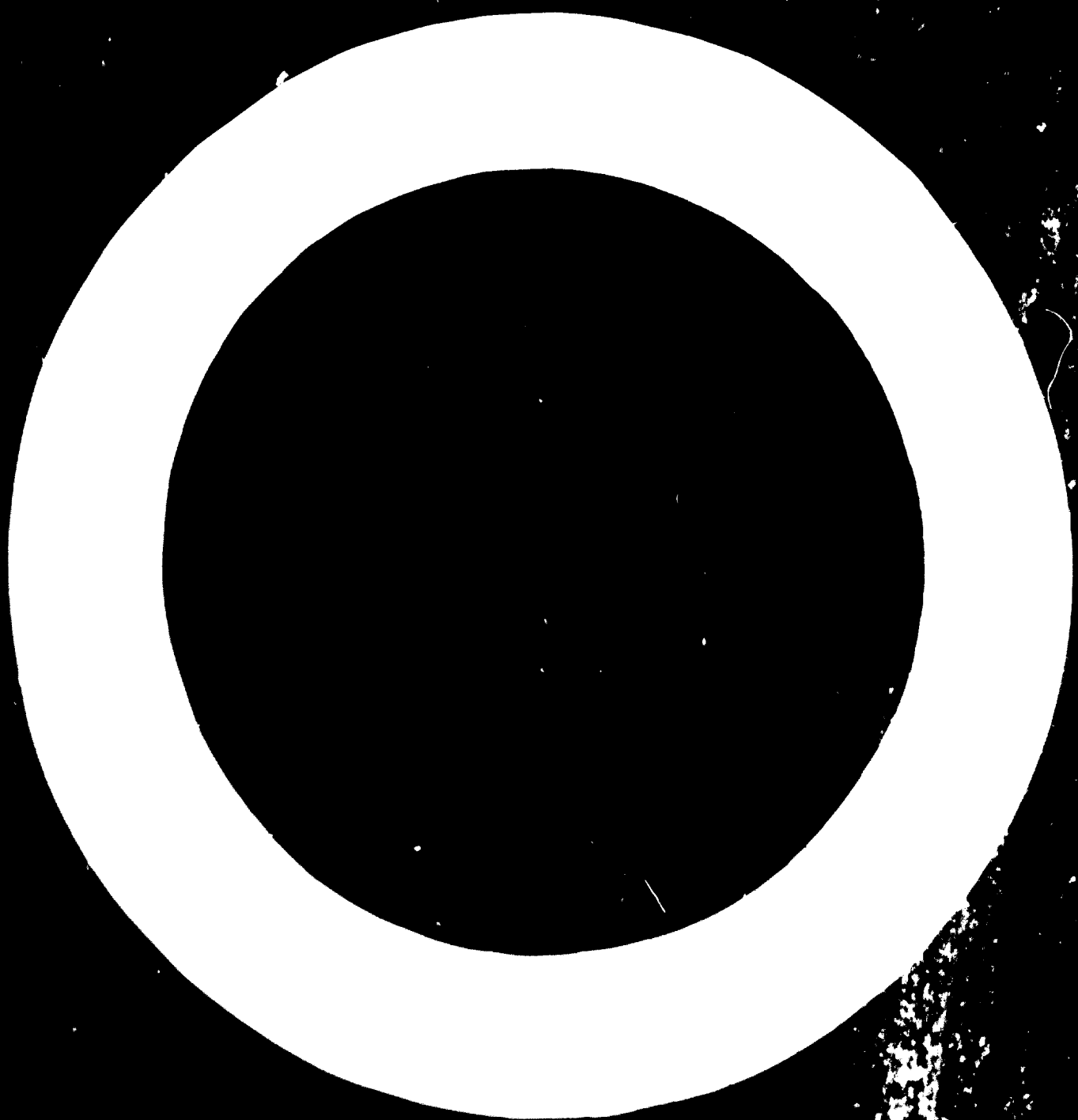
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In this paper the author discusses some of the processes now in operation or being developed which enable petrochemical building blocks to be made from raw materials other than naphtha. Recently developed methods for producing or isolating paper "building blocks" from non-petroleum materials are also described.

- (1) Production of ethylene from methanol via a fluidized flow process. Dehydrated methanol is injected into the fluidized bed of petroleum coke and cracked at 700°C over a catalyst. The advantage of the fluidized flow process over the other fluidized bed processes is that, for some of the reactions, the catalyst is of higher activity, and the process is more flexible.

The author is grateful to the Deutsche Forschungsgemeinschaft for the support of this work. The author is also grateful to the staff of the Institute for Petrochemical Research, Bad Soden, for their assistance in the preparation of this paper.



- C_4 stream (55% butadiene), and 0.45 tons of pyrolysis naphtha.
- (2) Production of acetylene and ethylene by the submerged flame process. In this process oxygen is, as it were, burnt underneath the surface of the oil, as a result of which cracking of the oil at a very high temperature in the neighbourhood of the flame takes place, the large volume of oil leading to rapid quenching of the products of cracking and hence retention of a considerable quantity of acetylene. The details of the process and its economics are described. 1 ton of acetylene and 1.18 tons of ethylene are obtained from 5.27 tons of crude oil and 5.1 tons of oxygen.
 - (3) Crude oil cracking by the Hochst HF process. This is at the development stage. The principle lies in the combustion of the tail gas with oxygen followed by the injection of secondary steam and the petroleum fraction to be cracked. The temperature is controlled by the quantity of petroleum injected which in itself determines the acetylene - ethylene ratio. The process is fully described including an economic assessment.
 - (4) The BILCO process for the manufacture of acetylene. The current process is described in which natural gas, liquid gas or naphtha is cracked by the heat developed from the incomplete combustion of the raw material with oxygen.
 - (5) The hydrogen electric arc process. This enables a much higher yield of acetylene from hydrocarbon raw material to be obtained. Hydrogen is used as a carrier gas. The techniques of avoiding soot and the burning of electrodes are described.
 - (6) Purification and conversion of olefin fractions by hydrogenation. The propylene fraction is fully hydrogenated to remove methylacetylene and propadiene for the production of polymer grade propylene. Various combinations of these operations are discussed and evaluated. If there is no demand for propylene it can be fully hydrogenated and returned to the cracking plant.
Butadiene is normally removed from the C_4 stream (see section 7).

The residual stream must be hydrogenated to free from the last traces of butadiene. Di- or triisobutene produced in the Bayer oligomerisation process can be hydrogenated by the Bayer cold hydrogenation process to very pure isoparaffin.

- (7) The BEP process of BSEP using N-methylpyrrolidone with 5 to 10% water to extract butadiene from the C₄ stream is described in full detail with costings.
- (8) Isobutene is sometimes required as a monomer, e.g. for the production of rubber polymers. The BEP process for its recovery via sulphuric acid treatment is described.
- (9) The BSEP isoprene extraction process using N-methylpyrrolidone is described. This is still at a development stage.
- (10) The cold hydrogenation refining of a pyrolysis naphtha to free the product from acetylene and diolefines to make it suitable as motor gasoline is described.
- (11) The BSEP-Schelven process for the gas phase hydrogenation of pyrolysis naphtha is described. This removes sulphur and olefins and makes it suitable for the extraction of aromatics.
- (12) The extraction of aromatics by N-methyl pyrrolidone from pyrolysis naphtha by the Lurgi-Brasovan process is described in considerable detail and fully evaluated.
- (13) Aromatics can be dealkylated e.g. toluene converted to benzene by the BSEP-Schelven process. Toluene and crude hydrogen e.g. from a catalytic reformer are converted catalytically to benzene and methane. Recirculation of unconverted toluene is carried out and about 1.5% diphenyl produced as a by-product.

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The raw materials which are suitably used for the production of the petrochemical basic building blocks such as ethylene, acetylene, propylene and the C₄-olefins, will always be adapted to the given local conditions. These interrelations were decisive for the fact that two large chemical companies in the Federal Republic of Germany, independently of one another, developed processes for the cracking of full range crude oils. Cracking was carried out in the middle-temperature region (below 900° C) for the production of the olefins ethylene, propylene and butylenes. These processes are known as the BASF fluidized bed process and the Hoechst moving pebbles process.

Compared with the USA, the pattern of consumption of petroleum products is completely different in Europe, and especially so in the Federal Republic of Germany. This also has a bearing on the selection of raw materials which are available for the manufacture of petrochemical basic building blocks. In the USA, 81% of the ethylene is made from ethane, 38% from propane and only 11% from naphthalene petroleum hydrocarbons (condensate, naphtha). In Europe, the ethylene requirement is obtained nearly exclusively from the thermal cracking of naphtha. In view of the large-scale production of ethylene as an aliphatic basic building block in the Federal Republic of Germany, a special position was developed for acetylene obtained from calcium carbide. This development must be understood in order to understand that there was a special interest in the development of a viable process for the manufacture of acetylene from petroleum hydrocarbons. The situation is similar for propylene production and the ethylene derivatives since the refineries in respect of raw material supply are not able to meet the interest in crude oil or gasin for producing petrochemical basic building blocks in the chemical industry during recent years.

The wide experience with electrothermal processes also triggered the development of hydrogenation cracking using the hydrogen-electric arc technique. Special attention was directed in the same way to the development of processes for the recovery of individual fractions of very high purity grade. Technological contributions made also came from our country with regard to separation of the aromatic fraction from the previously hydrogenated hydrolysis residues.

In the following, it will be reported on the processes being operated on a commercial scale already, as well as those which are still in developing stages.

1. The BASF fluidized flow process for the production of styrene from crude oil

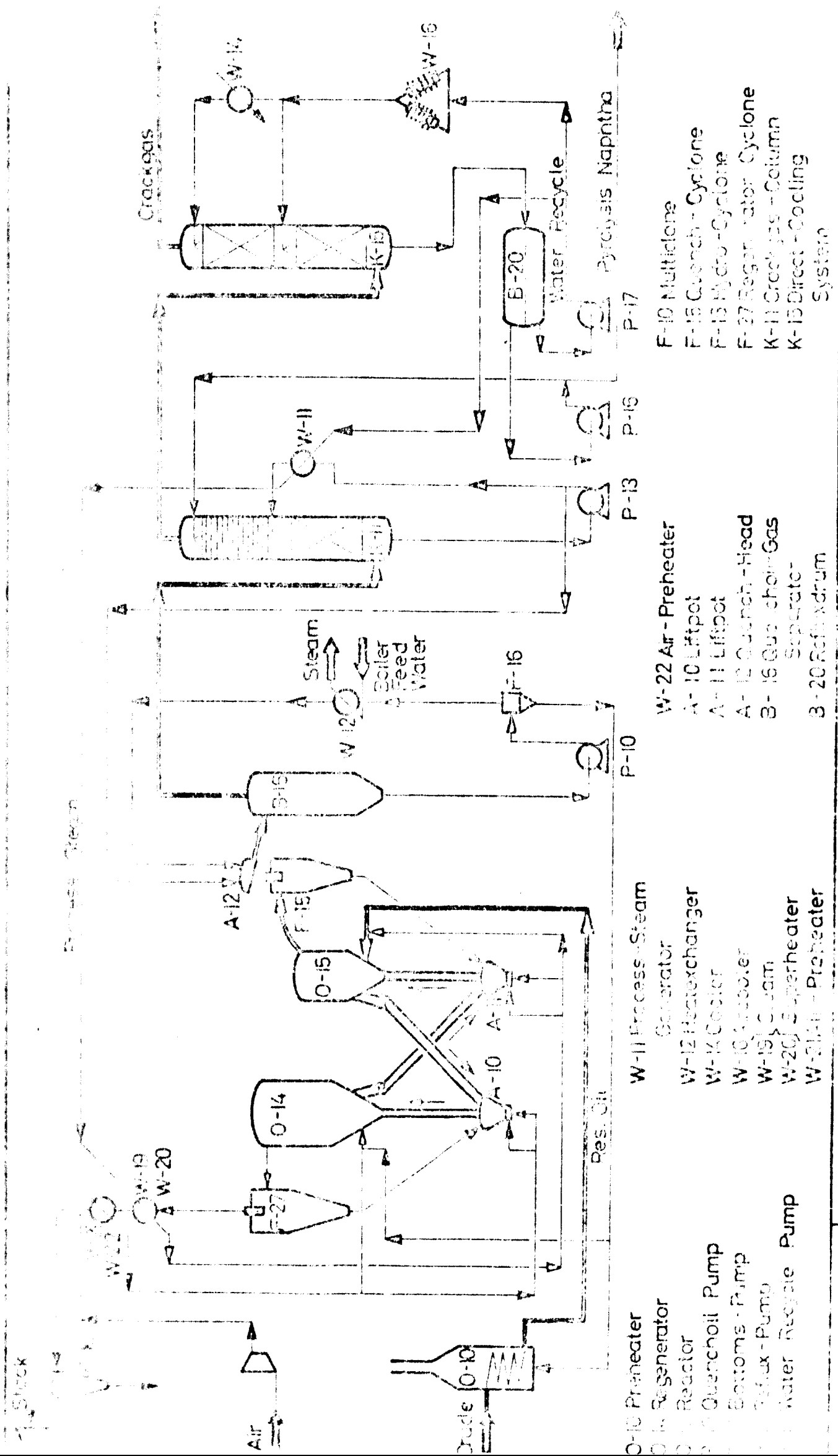
1.1 Justification of the process

The production of styrene from crude oil is of interest because it is a process which is independent of naphtha prices.

The fluidized-bed process requires oxygen for supplying the heat of reaction. The reaction takes place at about 720 °C in a fluidized bed of petroleum coke. Steam serves as the fluidizing medium to which oxygen is added. The heavy fractions of the reaction products are removed to the fluidized bed and are burnt there together with part of the petroleum coke.

Steam and gas is diluted with flue gas. This, as well as the need for oxygen, causes the spent are a disadvantage of the process.

The fluidized-bed process circumvents these drawbacks by carrying out



- O-10 Preheater
- O-14 Regenerator
- O-15 Reactor
- O-16 Quenchoil Pump
- O-17 Bottoms Pump
- O-18 Reflux Pump
- O-19 Water Recycle Pump

- W-11 Process Steam Generator
- W-12 Heatexchanger
- W-13 Cooler
- W-14 Cooler
- W-15 Steam
- W-20 Superheater
- W-22 Air Preheater

- A-10 Liftpot
- A-11 Liftpot
- A-12 Quench Head
- B-16 Quenchoil-Gas Separator
- B-20 Reflux Drum

- F-10 Multiclone
- F-15 Quench Cyclone
- F-18 Hydro-Cyclone
- F-27 Regenerator Cyclone
- K-11 Crackoils Column
- K-15 Direct-Cooling System

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Cracking - Primary Flow - Cracking (Air Feed - Process)

Fig 1

the generation of heat and the cracking reaction in separate parts of the cracking unit. In this way, air can be used as the combustion agent. The flue gas escapes into the atmosphere which means that crack-gas separation is not required. On the other hand it is necessary to circulate large amounts of heat carrier between the reactor and regenerator. This heat transfer constitutes the basic difference between this process and the fluidized bed process, and required many years of development work.

The inorganic material, as spherical as possible, is used as the heat carrier, whose diameter under operating conditions must be low. A mullite with a grain size between 0.5 and 2 mm has proved the most suitable material.

The main processing steps can be taken from Fig. 1. The heat carrier circulates between the reactor C-15 and the regenerator C-14, as the arrows indicate. The amount circulated is controlled by the slide gate G-15 and G-14 and the pneumatic conveying starts up through the conveying system. The conveying medium on the regenerator side is air, and on the reactor side, steam. The length of the sloping downpipes is so dimensioned that reactor and regenerator are barely separated on the ground level. For this reason, the two large apparatuses have to be placed at a height of about 20 m.

In the early trials, fluidized beds with grids were used both for the reactor and the regenerator. However, there were difficulties as regards fluidization and conveying of solids; this was best overcome by doing away with the grid and using a conical bed. The conical bed resulted in excellent operating conditions and did not entail any loss in yield

compared to the fluidized bed with grid. However, it cannot be described as an actual fluidized bed any more: it is a basket with powerful jolt mechanism, and the central heater is a vertical tubular electric furnace. The preheated crude oil is introduced into the reactor together with the catalyst, through lateral perforated pipes. About 0.7 tons of steam are used per ton of crude oil. Owing to the slight pressure drop in the subsequent operations, the reactor operates at slightly below atmospheric pressure. The cracking temperature range is between 700 and 720°C. The residence time in the reactor, as in the fluidized bed process, is 15-20 seconds.

In this process, the process is used as fuel for the generator; the combustion gas is used for combustion in the process which burns methane gas. The heat of the gas is transferred to the oil feed. It is noted that the heat of the gas is transferred to the heat of the process and used for preheating the feed.

In this process, the catalyst, a proportion of the feed are removed with the gas from the fluidized bed. A gas separator is provided in the reactor unit in order to separate the gas. The separation of the gas is achieved by centrifugal force by means of a gas separator. The volume of the gas fluidized bed in the reactor is controlled by the residence time. It is kept small in order to avoid secondary reactions. For this reason, about 5% of the circulated heat carrier are conveyed into the quenching cyclone. The gas is recycled from there to the catalyst circulation.

There is no risk of erosion here, since it is possible to use SiC-bricks

Section 1

The first part of the report deals with the general situation of the country and the progress of the work during the year.

The second part of the report deals with the results of the work done during the year and the progress of the various projects.

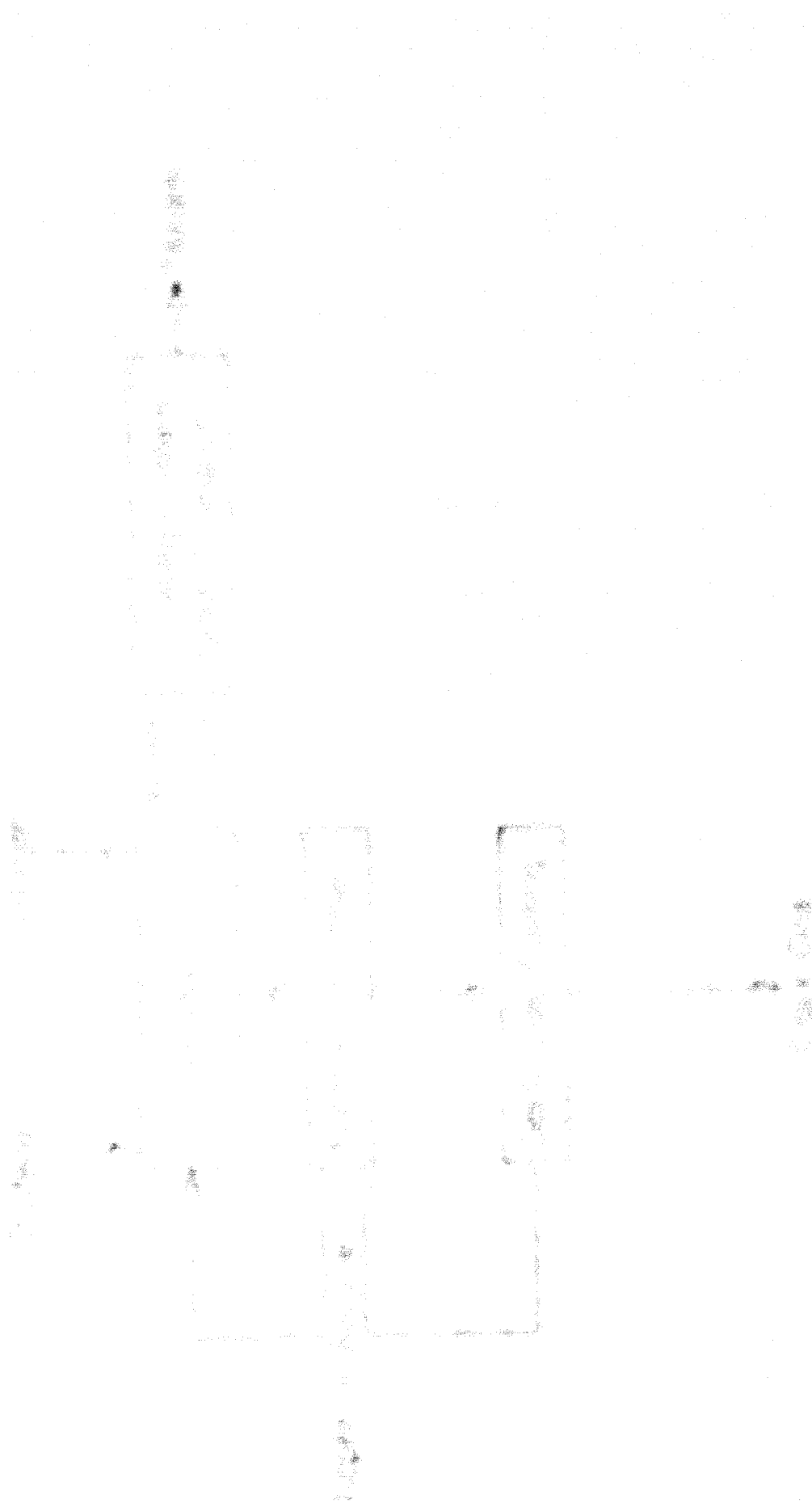
The third part of the report deals with the financial position of the organization and the results of the various projects.

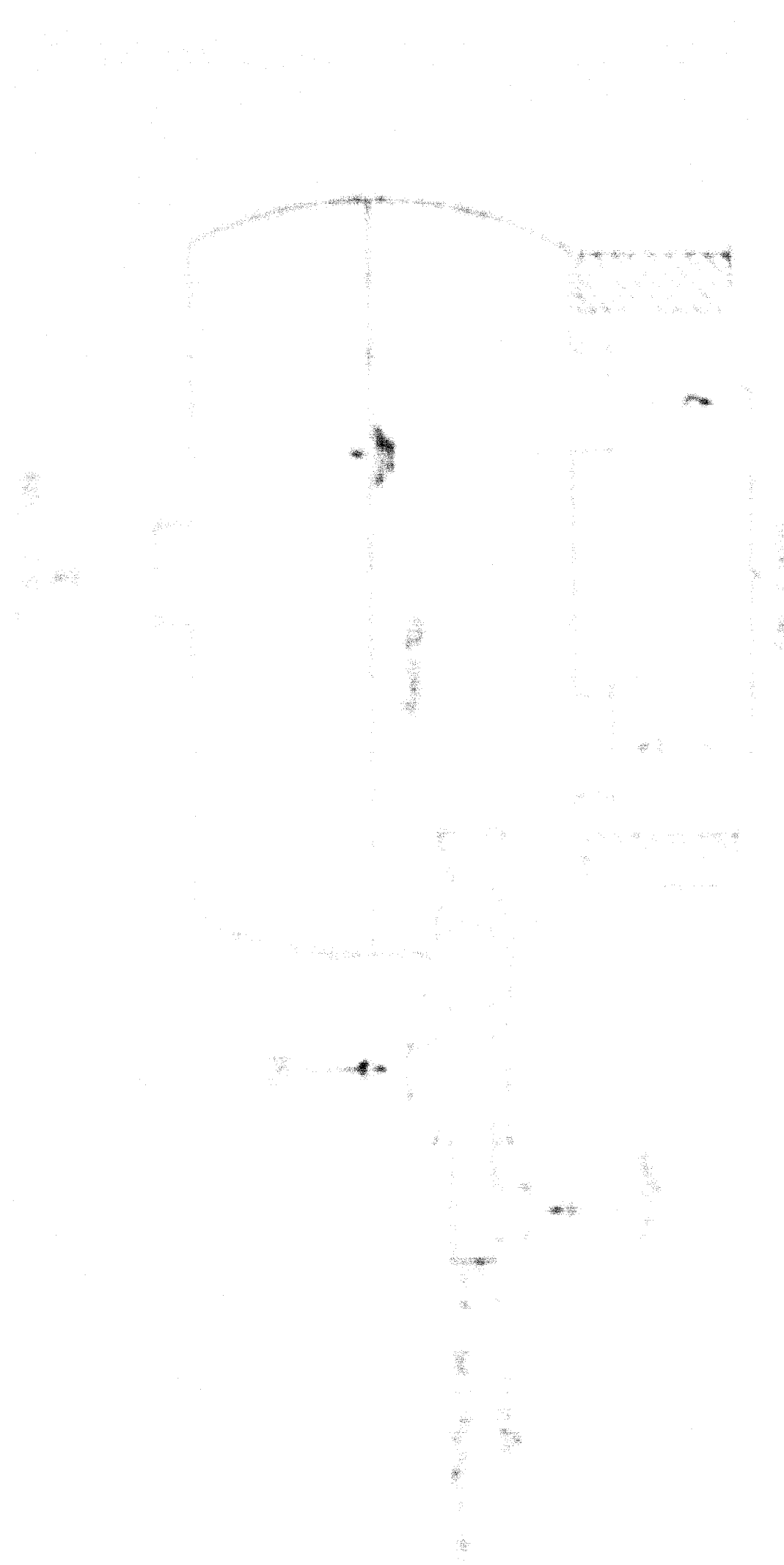
The fourth part of the report deals with the work done during the year and the progress of the various projects.

Section 2

The first part of the report deals with the general situation of the country and the progress of the work during the year.

If there is any more, I.6 m.t. of crude oil, we should get it.





of ethylene produced. The following yields of by-products are obtained:

C ₃ -cut (95 % propylene)	0.50 ton/ton C ₂ H ₄
C ₄ -cut (85 % butadiene)	0.25 " "
Pyrolysis naphtha	0.45 " "

The residual oil formed is burnt quantitatively in the process, whilst an excess of 0.7 ton/ton C₂H₄ of fuel gas (H₂ + CH₄) remains.

If

the C₃-cut is valued at DM 165/m.t. (4 DM = 1 US \$)

the C₄-cut at DM 105/m.t.

the pyrolysis naphtha at DM 90/m.t.

and the fuel gas at DM 80/m.t.

and if a current price of U.S. \$1.21/kg C₂H₄ (2.4 US Centa/lb) is arrived at, the investment costs of DM 170,000,000 (US \$17,800,000) will cover depreciation, taxes, interest and maintenance.

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Chem. Abstr. Fuel. Ref. 44 (1965) B, pp. 134-142

2. The Production of Acetylene and Ethylene by the BASF

2.1. Acetylene

The production of acetylene by the BASF is carried out in a series of steps. The process starts with the production of acetylene from calcium carbide. The carbide is produced by the reaction of calcium and carbon in an electric arc furnace. The acetylene is then purified and stored in a special container. It is then used in a variety of applications, such as the production of acetylene lamps and in the synthesis of other chemicals.

2.1.1. The reaction of calcium and carbon in the electric arc furnace

The reaction of calcium and carbon in the electric arc furnace is carried out at a temperature of approximately 3000°C.

The reaction is carried out in a special furnace.

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The reaction is carried out in a special furnace.

The reaction of calcium and carbon in the electric arc furnace (see Fig. 1) takes place in an oil bath. The reaction is carried out in a special furnace. The reaction is carried out in a special furnace. The reaction is carried out in a special furnace.

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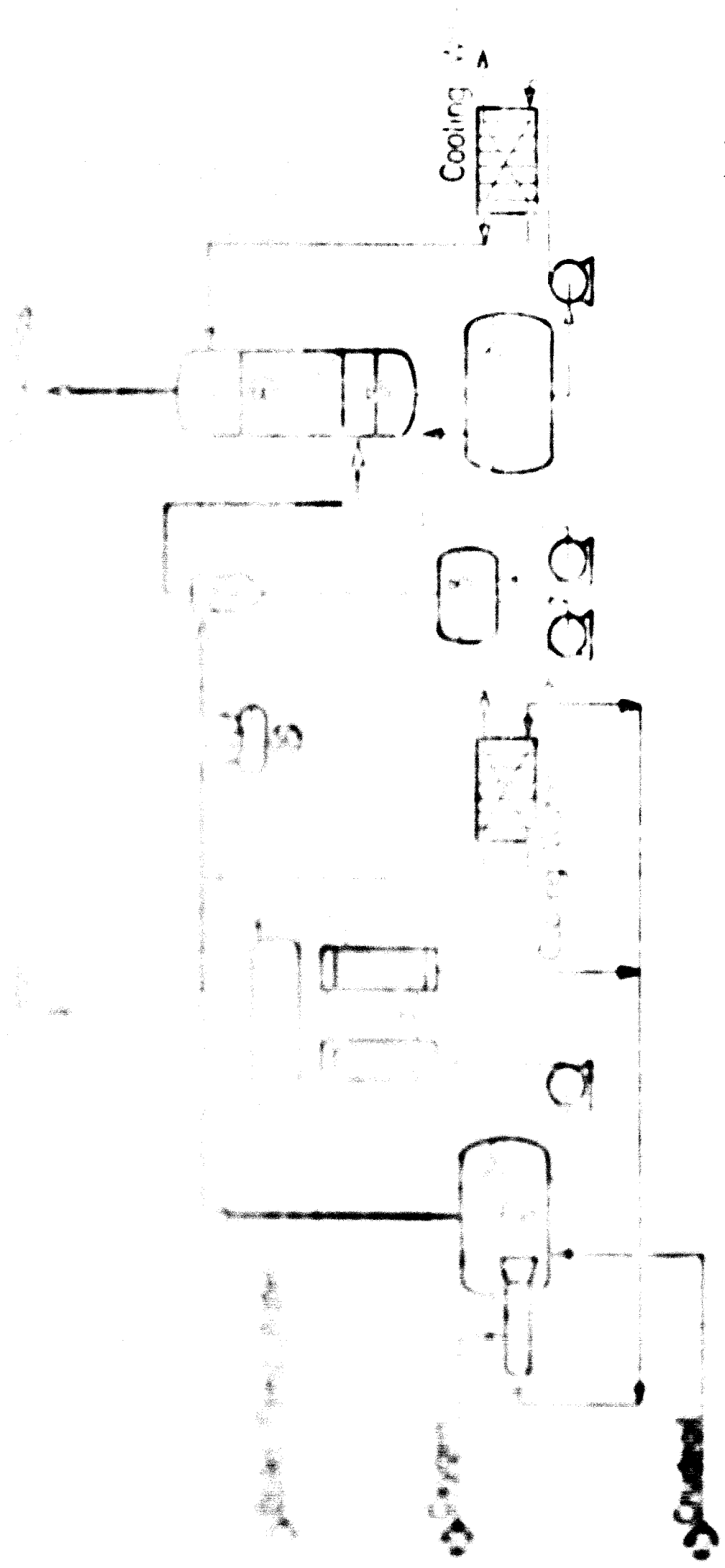
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Crackgas - Cooling

Naphtha Scrubber

Oil-Cooling System (Steam Generation)

Reactor



There are two kinds of gas separation processes for the production of acetylene which can be seen from the fig. 5. As regards investment and operating costs, there is very little difference between the two. The processes employ a scrubber immediately following the crack gas production unit. In this, the major part of the CO_2 and all the H_2S are removed.

In separation process 1, first the remaining CO_2 is removed with sodium hydroxide solution and the gas subsequently dried with ethanol. By

recovery of H_2O , CH_4 , C_2H_6 and higher hydrocarbons are condensed and separated from the gas. The gas consists of H_2 , N_2 and H_2 . The

acetylene is separated from the gas by distillation and the gas is dried with ethanol. The acetylene is separated from the C_2 -distillate by absorption in a counter-current column and separated from the gas.

In separation process 2, the gas scrubber is followed by an N-methyl-2-pyrrolidone scrubber in which the acetylene together with the C_3 - and C_4 -hydrocarbons are absorbed. However, acetylene is separated in a counter-current column which is operated at a low temperature. The gas consists of pure acetylene, C_3 - and C_4 -hydrocarbons and H_2 . The C_3 - and C_4 -hydrocarbons are separated from the gas by distillation following its concentration, and the acetylene is separated from the gas in the low gas in the scrubber. The acetylene is removed from it by partial condensation at a low temperature and recovered by distillation.

2.2 Some technical data

(Feedstock: crude oil)

a. Purity of the products

	Acetylene % by vol.	Ethylene % by vol.
Purity	99.8-99.9	99.9

b. Investment (based on conditions in the Federal Republic of Germany)

Total cost of a plant for 30,000 metric tons/yr. acetylene (turn key, but without site development and auxiliary plants such as air separation, power station, tank farm, etc.)

DM 40,500,000.-- (US \$ 10,125,000)

c. Consumption of utilities per 100 kg acetylene

Separation process		I	II
Electricity	kWh	286	277
cooling water (25° C/12° C)	m ³	29.5	30.5
Boiler fuel per metric ton		0.97	0.96

d. Consumption of materials per 100 kg acetylene

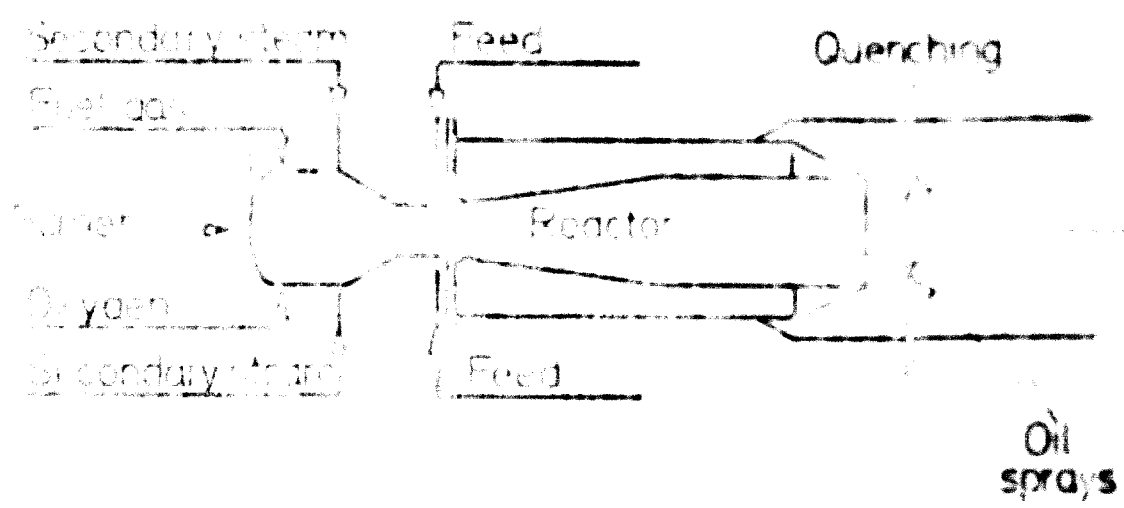
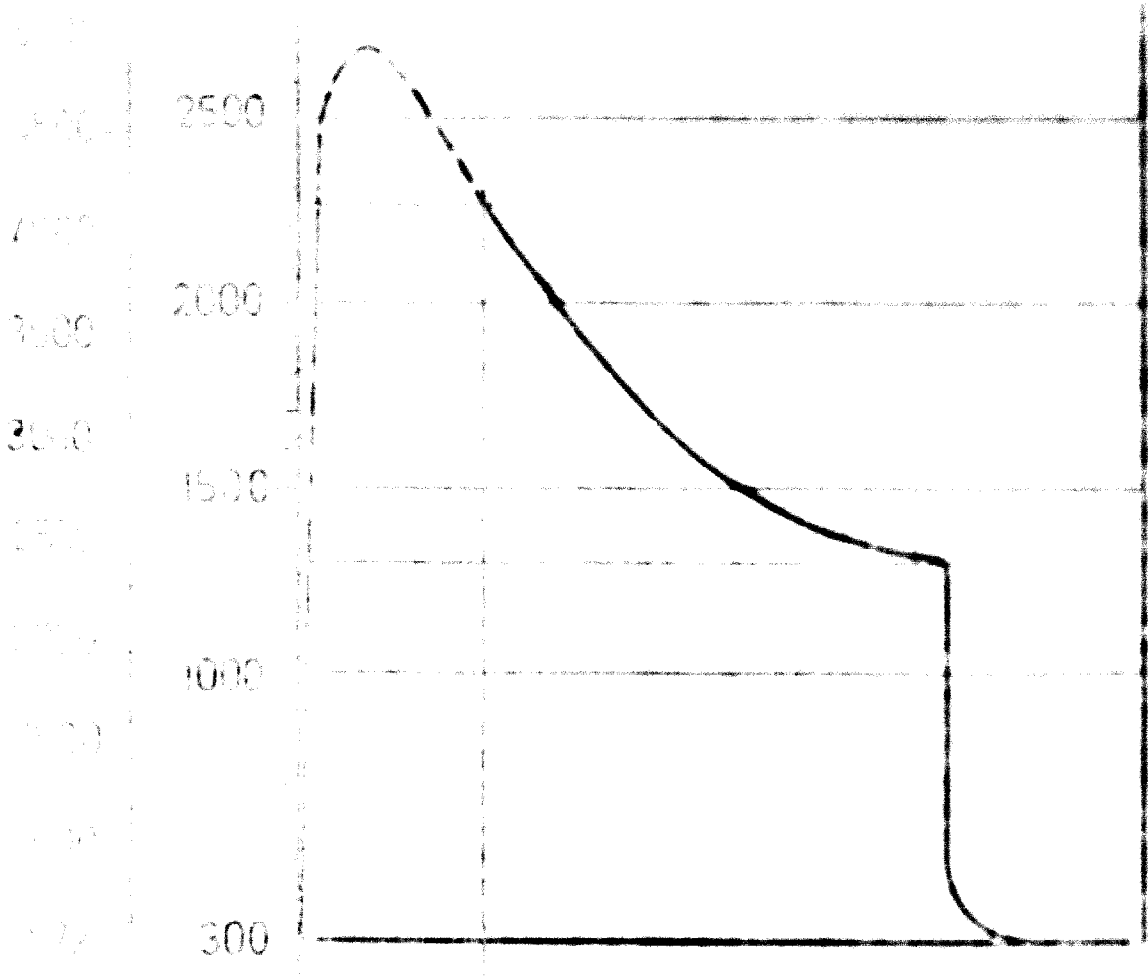
Consumption per 100 kg acetylene		I	II
Iron nail	kg	827	827
Oil	m ³	510	510
Sealing agent for CO ₂ cylinder	kg	0.4	0.4
Welding torch calculated as 100%	kg	4	4
Acetylene	kg	0.3	0.3
Acetylene	kg	0.15	-
Spool	kg	-	0.5-1
Sealing agent for C ₃ , C ₂ cylinders	kg	-	0.35
Compressed air	m ³	25	25
Nitrogen	m ³	50	50

e. Expenditure per 100 kg acetylene

Expenditure per 100 kg acetylene		I	II
Gas cylinder (10 atm. gauge)	metric ton	0.85	0.5
Ethylene	kg	118	118
Iron nail (W. of 100 value 200 kg)	m ³	1135	1135
(CO, H ₂ , C ₂ H ₄ , <0.3 ppm S)			
C ₂ and C ₃ hydrocarbons	kg	92	92

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Temperature profile of the MIP-Reactor System (injected)

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essentially the same reaction conditions being equal, the more the
equilibrium is shifted in favour of acetylene. A final cracking
temperature of 1100°C corresponds approximately to a weight
ratio of 1.5 parts of acetylene to 2.5 parts of ethylene.

When the reaction temperature the cracking equilibrium is
shifted in favour of ethylene and the cracked gas
contains 70% ethylene (500°C). A cracking catalyst
is used in the reaction tube. The amount of the tail gas
is small and the reaction is clearly
exothermic. The reaction is virtually
complete. The reaction is precisely
controlled. These condi-
tions are obtained in a reactor which operates
at 1100°C and 1000 psi.

The reaction is carried out using a number of crude-
oil fractions of various distillates, shown in the reaction represented
above. The reaction is carried out with naphtha,
gasoline, kerosene, diesel oil, and the atmospheric
distillate. The reaction is carried out from which
the reaction is carried out, which is carried out (arabco). The
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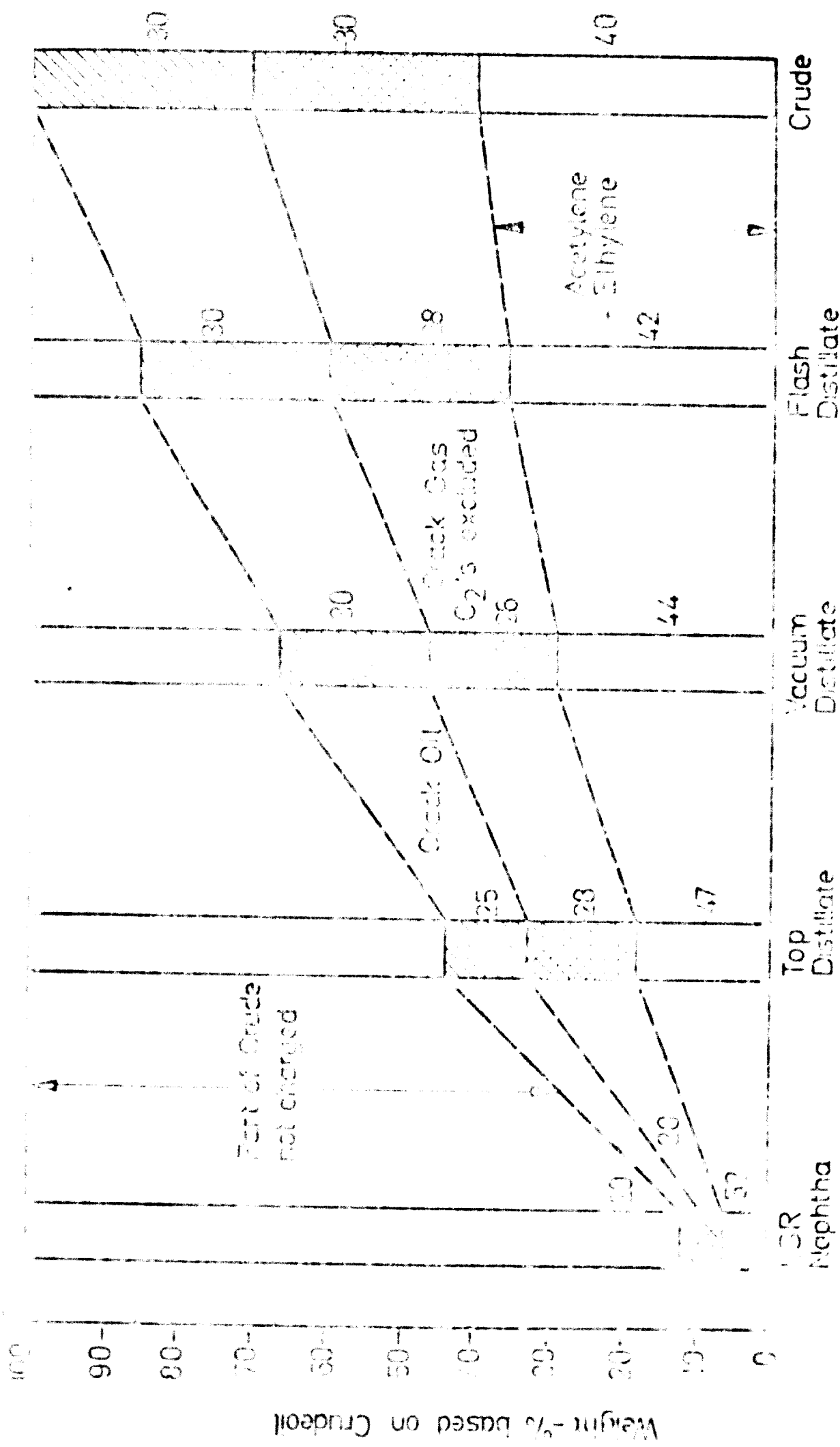


Fig 7

Pattern of Products obtained by the Cracking of Crudeoil and its Fractions (Hoechst-HIP - Process)



System Configuration

Process Flow

Control System

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7. The seventh part of the document is a list of names and their corresponding addresses. The names are listed in the left column, and the addresses are listed in the right column. The names are: [illegible], [illegible], [illegible], [illegible], [illegible]. The addresses are: [illegible], [illegible], [illegible], [illegible], [illegible].

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Financial Statement for the Year Ending 1954

Assets	Liabilities
Current Assets	Current Liabilities
Fixed Assets	Long-Term Liabilities
Total Assets	Total Liabilities
Equity	

Additional text at the bottom of the page, possibly a signature or footer.

...	4	8	0	
...	7	7	9	Dynamic force
...	20	31	40	10/100 mm
...	4	30	40	10/100 mm
...	7	7	7	10/100 mm

...	17.00	17.35	17.35
...	0.41	0.61	0.61
...	3.73	4.70	6.27
...	0.10	0.10	0.10
...	0.76	0.96	1.36
...	15.61	11.21	18.91
...	17.19	39.75	1.31

...	1.04	- 1.64	- 1.64
...	36.51	38.12	39.59

At a daily production of 30/100 kg the following prices thus result for

...	45.37	50.30	54.22
...	5.3	5.7	6.2

Literature references:

- F.V. Krammer 6th World Petroleum Congress, Sect. IV - Paper 12-PD 8. 1963
H.F. Leabner Chemical Engineering
W.R. H. Lass Feb. 25, 1966
H.W. Schlarzen
E. Schneck Symposium Acetylene-Ethylene DECHEMA-Frankfurt, March 1968

4. The BASF Process for the manufacture of acetylene by partial oxidation of hydrocarbons

4. Principle of the process

Gasoline or other easily vaporizable hydrocarbons (natural gas, liquified gas or light oil) are preheated and mixed in the gaseous state with oxygen and steam. The mixture is then heated to the temperature of the hydrocarbon. The mixture is then fed into a reactor where it is partially oxidized. The reaction is exothermic and the heat released is used to preheat the feed. The reaction products are cooled and the acetylene is separated from the other products. The acetylene is then purified by scrubbing with N-ethylpyrrolidone and by fractionated desorption from the solvent.

The main by-product formed is a gas consisting essentially of carbon monoxide and hydrogen which, for example, can be used for ammonia synthesis.

The ammonia produced has a purity in excess of 99.5% which, if required, can be increased to 99.9% by washing with sulphuric acid.

4.2 Manufacture of ammonia

At present, about 50% of the ammonia produced from natural gas is used in the fertilizer process, and 10% in the synthesis of urea and other nitrogenous compounds.

The ammonia produced in the synthesis of urea is about 99.5% pure and is used in the fertilizer process.

Component	Weight %	Molar %
Ammonia	99.5	99.5
Water	0.5	0.5
Carbon dioxide	0.0	0.0
Hydrogen	0.0	0.0
Carbon monoxide	0.0	0.0
Nitrogen	0.0	0.0
Oxygen	0.0	0.0
Argon	0.0	0.0
Other gases	0.0	0.0

Production rate per shift 8 men per shift

Weight of material 1000 kg

Time taken per shift 1000 kg/1000

Weight of material per shift 1000 kg

Weight of material per shift 1000 kg

It is found that the material is not uniform in size. In order to obtain the

desired size of material, the material is crushed in a crusher. The

crusher is of the type of a jaw crusher. The material is crushed in a

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Table 11
Summary of Results

Case No.	Initial Value	Final Value
1	1.00	1.00
2	1.00	1.00
3	1.00	1.00
4	1.00	1.00
5	1.00	1.00
6	1.00	1.00
7	1.00	1.00
8	1.00	1.00
9	1.00	1.00
10	1.00	1.00
11	1.00	1.00
12	1.00	1.00
13	1.00	1.00
14	1.00	1.00
15	1.00	1.00
16	1.00	1.00
17	1.00	1.00
18	1.00	1.00
19	1.00	1.00
20	1.00	1.00
21	1.00	1.00
22	1.00	1.00
23	1.00	1.00
24	1.00	1.00
25	1.00	1.00
26	1.00	1.00
27	1.00	1.00
28	1.00	1.00
29	1.00	1.00
30	1.00	1.00
31	1.00	1.00
32	1.00	1.00
33	1.00	1.00
34	1.00	1.00
35	1.00	1.00
36	1.00	1.00
37	1.00	1.00
38	1.00	1.00
39	1.00	1.00
40	1.00	1.00
41	1.00	1.00
42	1.00	1.00
43	1.00	1.00
44	1.00	1.00
45	1.00	1.00
46	1.00	1.00
47	1.00	1.00
48	1.00	1.00
49	1.00	1.00
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89	1.00	1.00
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91	1.00	1.00
92	1.00	1.00
93	1.00	1.00
94	1.00	1.00
95	1.00	1.00
96	1.00	1.00
97	1.00	1.00
98	1.00	1.00
99	1.00	1.00
100	1.00	1.00

MEMORANDUM FOR THE RECORD

On 10/10/54, the following information was received from the [redacted] regarding the [redacted] of the [redacted] in the [redacted] area. The [redacted] was [redacted] by [redacted] and [redacted] on [redacted] at [redacted]. The [redacted] was [redacted] and [redacted] on [redacted] at [redacted]. The [redacted] was [redacted] and [redacted] on [redacted] at [redacted]. The [redacted] was [redacted] and [redacted] on [redacted] at [redacted]. The [redacted] was [redacted] and [redacted] on [redacted] at [redacted]. The [redacted] was [redacted] and [redacted] on [redacted] at [redacted].

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Parameter	Unit	2	1
Flow rate	l/h	3,100	2,500
Flow rate	l/h	250	150
Refine ratio		10.9	10.0
Effluent concentration	mg/l	300	30
Effluent concentration	mg/l	610	150
Investment	(\$)	1,000,000	50,000
Investment	(\$)	1,300,000	10,000
Effluent concentration	mg/l	10	0.01

2) Parameters of the model of the plant - treatment

The model of the plant - treatment is based on the following assumptions:

1. The plant is a continuous flow system with a hydraulic retention time of 10 hours.

2. The influent concentration is 1000 mg/l.

3. The effluent concentration is 10 mg/l.

4. The flow rate is 3100 l/h.

5. The plant is operated at a constant temperature of 20°C.

6. The plant is operated at a constant pH of 7.0.

7. The plant is operated at a constant dissolved oxygen concentration of 2.0 mg/l.

8. The plant is operated at a constant sludge concentration of 3000 mg/l.

9. The plant is operated at a constant sludge age of 10 days.

10. The plant is operated at a constant sludge yield coefficient of 0.5.

11. The plant is operated at a constant sludge decay coefficient of 0.1.

12. The plant is operated at a constant sludge settling velocity of 0.3 m/h.

13. The plant is operated at a constant sludge density of 1.05 g/cm³.

14. The plant is operated at a constant sludge moisture content of 95%.

15. The plant is operated at a constant sludge ash content of 10%.

16. The plant is operated at a constant sludge nitrogen content of 5%.

17. The plant is operated at a constant sludge phosphorus content of 2%.

18. The plant is operated at a constant sludge sulfur content of 1%.

19. The plant is operated at a constant sludge potassium content of 1%.

20. The plant is operated at a constant sludge calcium content of 1%.

21. The plant is operated at a constant sludge magnesium content of 1%.

22. The plant is operated at a constant sludge sodium content of 1%.

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97. The plant is operated at a constant sludge fluorine content of 1%.

98. The plant is operated at a constant sludge boron content of 1%.

99. The plant is operated at a constant sludge aluminum content of 1%.

100. The plant is operated at a constant sludge silicon content of 1%.

Data on analysis of fresh feed and product, on hydrogenation conditions, on utilization consumption and investment are given in table 2.

Table 2

Full hydrogenation of acrylonitrile C₃-out

Reaction temperature	°C	30 ——— 60
Pressure	atm. gauge	35
Fresh feed space velocity	m ³ /m ³ catalyst.hr	7
Recycle: fresh feed		2 : 1

Analysis of feed and after hydrogenation

Component	Feed	mol %	Product
C ₂	0.14		0.14
methylacetylene + propylene (C ₃ H ₄)	4.31		< 20 ppm
propylene	91.79		0.62
propane	4.17		98.94
C ₄	0.19		0.30
	100.00		100.00

Fresh Feed	metric tons/yr	100,000
Utilities: H ₂ (60 Vol %)	m ³ /hr	9,300
: Refrigeration energy for the removal of heat of reaction	10 ⁶ kcal/hr	8
: cooling water	m ³ /hr	60
: electricity	kWh/hr	50
Investment	US \$	205,000
Catalyst charge	kg	1.8

6.2 Hydrogenation of minor amounts of Butadiene remaining in C₂-raffinate

The product C₂-out is rich in butadiene so that in general pure butadiene is separated therefrom. The remaining C₂-out (raffinate) still contains a small amount, about 0.5-1.0%. Also C₂-out contains a small amount of the butadiene remaining after contain butadiene in the feed range. For the further chemical treatment through the plant, it is recommended that it is recommended to remove the butadiene. The amount of butadiene hydrogenation has proved to be small. The mode of operation is the usual one for the cold hydrogenation, but especially adjusted to the fact that it is filled here. The results of the hydrogenation for this case will be seen that the butadiene in the feed is nearly completely hydrogenated, but that practically all of the butadiene is hydrogenated to butane.

By a suitable design, it is also possible to combine the hydrogenation with nearly complete isomerization of

n-butene-1 into n-butene-2. In performing the process in this way a distillative separation between n-butene-1 and n-butene-2 becomes possible; in distillation the n-butene-1 and n-butene-2 together with the non-isoprenic diene and gas which are not at the pressure together with n-butene are taken as bottoms. Thus a large part of the butene in the original feed is received as butene-2 for further chemical processing.

Table 3

Selectivity of the Hydrogenation

Reaction temperature	°C	25 — 60
Pressure	atm. gauge	12.6
Fresh feed space velocity	m.l./g ³ catalyst/hr	20
Recycle: fresh feed		0 : 1

Analysis of the Gas after Hydrogenation

Component	parts by weight	
	inlet	outlet
Butanen	9.2	9.7
Isobutene	45.5	45.5
n-butene-1	27.6)	25.3)
n-butene-2	17.3)	19.5)
	44.9	44.8
Butadiene	0.4	200 ppm
	100.0	100.0

might be able to improve the sensitivity by distilling the water
 before use. The hydroperoxide is now 10% can be used as water
 present in the feed. The way of the water is 10/100.

Table 1

Table 1. Reaction conditions

Reaction temperature	°C	150 — 220
Pressure	atm. gauge	40
Flow rate of gas velocity	m ³ /m ³ catalyst.hr	2
Reaction time	hr	1 : 1

Table 2. Analysis before and after 10% O₂ addition

Specification	Units	D I B feed	C 8) hydro- genated product	T I B (C 12) feed	hydro- genated product
bromine number	g/100g	50	0.005	100	0.01
content of aromatics	%	0	0	0	0
initial boiling point	°C	98	98.5	174	169
50 Vol% up to final boiling point	°C	100.5	99.5	174	175
	°C	101	100.5	181.5	179
Octane number RON, unleaded		99.8	99.1	99.8	100.6
+1.5 cc TEL/ US-gal		100.4	101.2	100.3	102.2
MON, unleaded		89.2	97.0	89.0	98.0
+1.5 cc TEL/ US-gal		91.1	101.0	89.8	102.4

From Feed Type	1977	1978
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...

The average ... of ... nitrogen ... in operation, ... 1,135,000 ... tons/yr.

... ..

... ..

- 1.
- 2.
- 3.
- 4.

... .. for the recovery of butadiene from

Substantially all the ... products formed during the production of ... are cracked ... for the manufacture of ... of the following "poly-cis" quality: ... total acetylene under 50 ppm ... total diene ... from acetylene and ... containing pyrolytic ...

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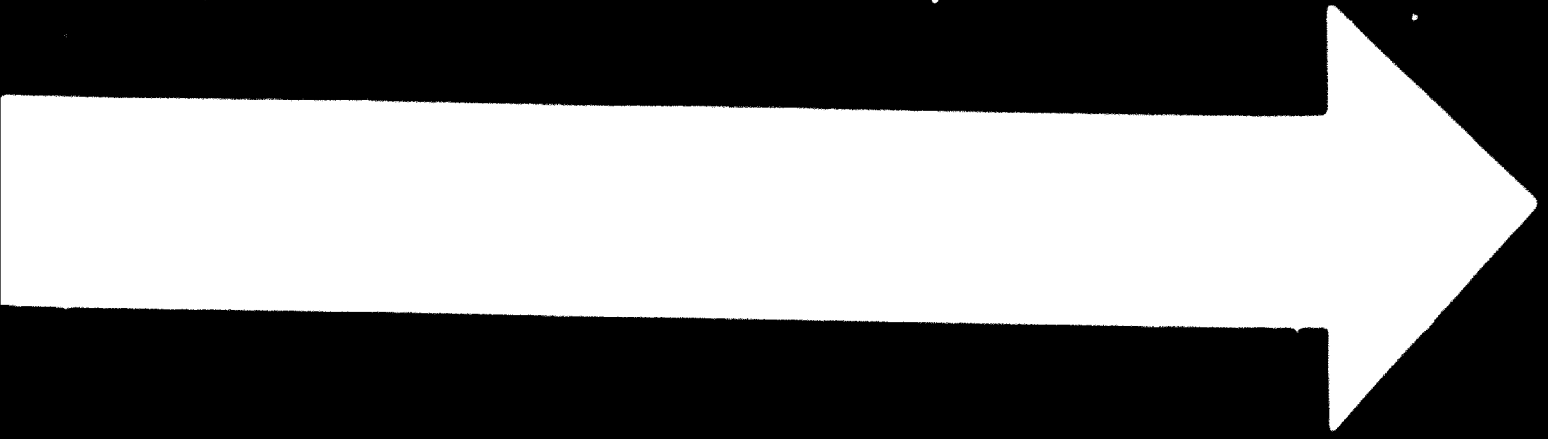
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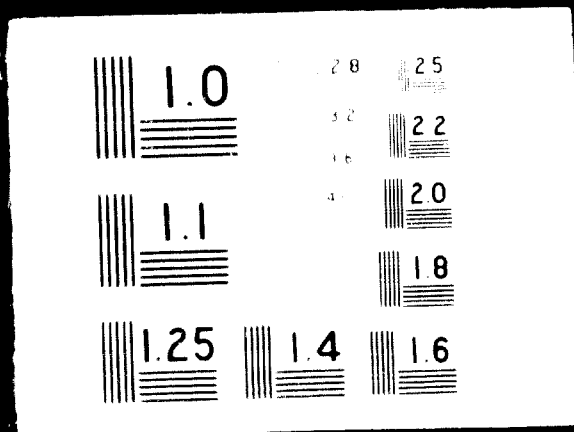


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We regret that some of the pages in the microfiche copy of this report may not be up to the proper legibility standards, even though the best possible copy was used for preparing the master fiche.

of the 1954 Berlin Botanical Congress 1953,

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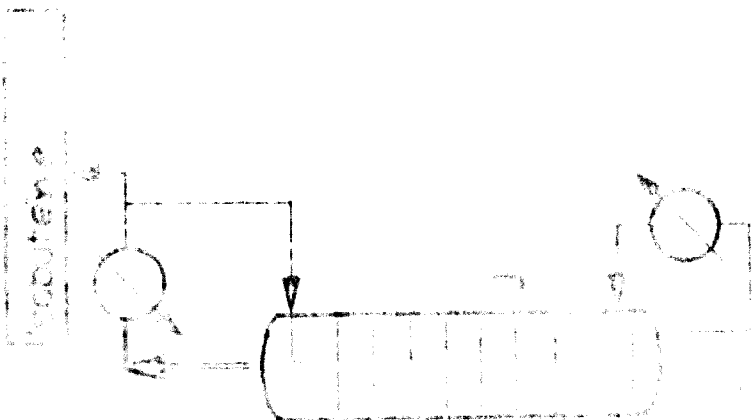
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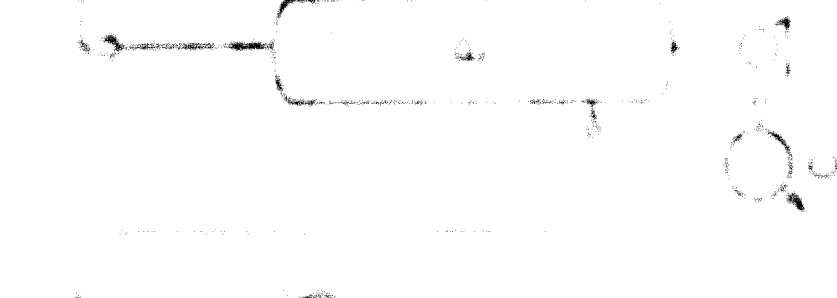
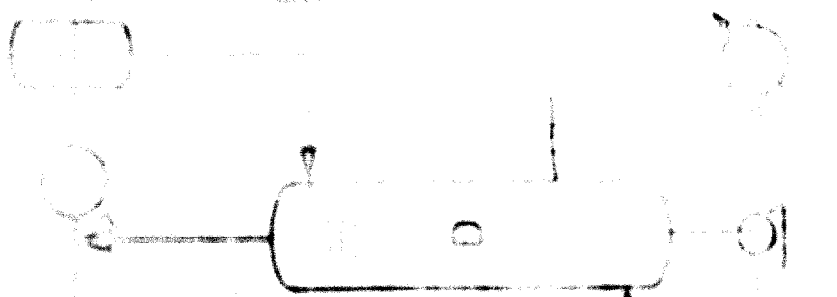
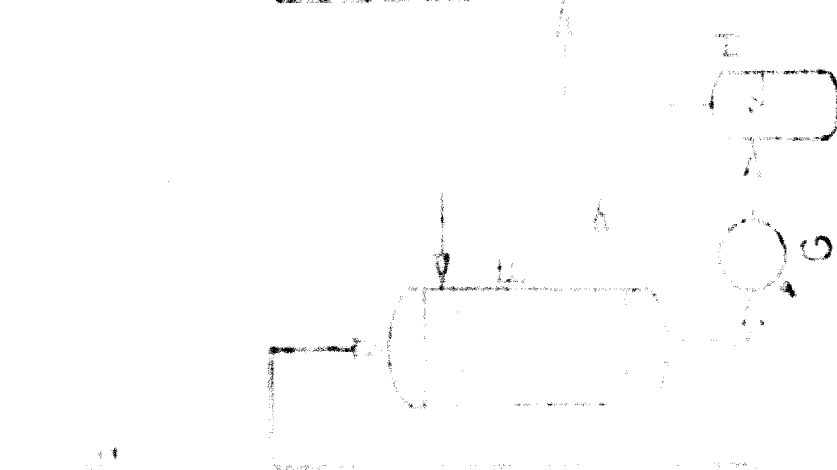
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A TO A



02H2

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Table 1 - continued

Butadiene-1,3	43.7	- 4.41°C
Acron	1.1	-

The process is followed by a distillation for the recovery of acrylonitrile. This makes it possible to use all residues - containing pyrolysis gas - as a feedstock as well as to produce an insoluble material that contains the highest known activity from a monomer of 1,3-butadiene. The yield is 90 - 95 % of dry liquid products is formed (less than 1 % calculated on the monomer).

The isolation of isobutene from butane-butene-methane mixtures such as the Kerosene cracking effluent pyrolysis, is not possible by normal distillation because of the position of the boiling points (see Table 1).

Some special distillation solvents for the economical separation of isobutene from such mixtures are known. There is, however, possibility of recovering isobutene by distillation by the great chemical reactivity of isobutene with some reagents.

The most suitable chemical reaction for the isolation of isobutene is the addition of water to tertiary carbon-carbon double bonds with proton.

Isobutene recovery process

The recovery of isobutene from recovery of isobutene (fig. 10) can be divided into several steps: adsorption, isolation and if necessary,

distillative purification of the tert.-butanol, dehydration and rectification of the isobutene. The isobutene is selectively absorbed from the gaseous liquid mixture at about 30°C in a bubble column A with the aid of the sulphuric acid-containing absorption solution. Tert.-butanol is being formed. The absorption solution flowing from the absorber passes into a distillation column B in which the tert.-butanol formed is distilled at reduced pressure as an azeotrope (with water). The absorption solution is recycled to the absorber after cooling in C.

The absorption solution flowing into the distillation column contains a small amount of physically dissolved n-butenes. The overhead vapors of the absorber therefore contain, besides the tert.-butanol-water-azeotrope small amounts of n-butenes which are separated by distillation in a second, smaller column. These n-butenes as well as small amounts of isobutylene formed in the bottoms of column B by dehydration of the tert.-butanol, are separated from the tert.-butanol-azeotrope in B and recycled to A. The tert.-butanol-azeotrope is drawn off from the bottoms of B and introduced into a heated dehydrating furnace D; dehydration takes place in the presence of activated aluminium oxide at 250°C. The reaction mixture condensed in condenser E is separated in separator H into the two reaction products isobutene and water. The isobutylene is then freed from traces of higher boiling contaminants (diisobutene, tert.-butanol) by fractionating in column J.

3.2 Investment, consumption figures and manufacturing costs

Investment (Indiabattery Limits)

US \$ 500,000 (DM 1,125,000)

(Price in Federal Republic of Germany, without taxes, engineering fee)

Feedstock:

Butene mixture (50 wt % isobutene) 13,370 metric tons/yr

Operating hours per year: 8 000

Product:

Isobutylene 6 000 m.t./yr

Isobutylene: 92.5 %

n-butylene: 7.0 %

Loss: ethanol + diisobutene: 0.01 %

Utilities:

Consumption figures (per ton isobutene)

Steel (4 mm. gauge) 2.5 m.t.

Electricity: 500 kWh

Natural gas: 140 m³

Cooling water: (25°C) 400 m³

Operating costs calculation

DM per m.t.

Steam (DM 6/m.t.)	15.00
Electricity (DM 4/100 kWh)	20.00
Natural gas (DM 6.5/100 m ³)	9.10
Cooling water (DM 2/100 m ³)	8.00
Chemicals:	<u>2.00</u>
Operating costs	DM 54.10/m.t. isobutene US \$ 13.525)

Capital costs (4 year capital return)

DM 1,125,000/yr

i.e. DM 187.50/m.t. isobutene

Maintenance (4 % of investment costs/yr):

DM 180,000/yr

i.e. DM 30 / m.t. isobutene

Personnel (2 men per shift)

DM 10 /hr

DM 13.35 /m.t. isobutene

Feedstock (isobutene in the butene mixture):

DM 100 /m.t.

Manufacturing costs

DM 385 /m.t. isobutene

(US \$ 96.25)

Isoprene Extraction, MAF - IWI Process

Following the work on the recovery of butadiene from pyrolysis C₄-cuts it was investigated whether the IWI-process is also suitable for the recovery of isoprene from pyrolysis C₄-cuts. It was found that isoprene

of high purity and in a good yield can be recovered from C₅-cuts (table 1). It was found to be advisable to place an HEP liquid-liquid extraction step before the H₂O counter-current gas scrubbing step.

Table 1

Elemental analysis of a cyclohexadiene-containing pyrolysis C₅-cut

	wt %
Alkenes	0.9
Diene	26.1
Diene	24.1
Diene	4.2
Diene	11.8
Diene	13.7
Diene	1.6
Diene	0.1
Diene	8.8
Diene	7.5
Diene	5.2

RECOVERY OF DIENE

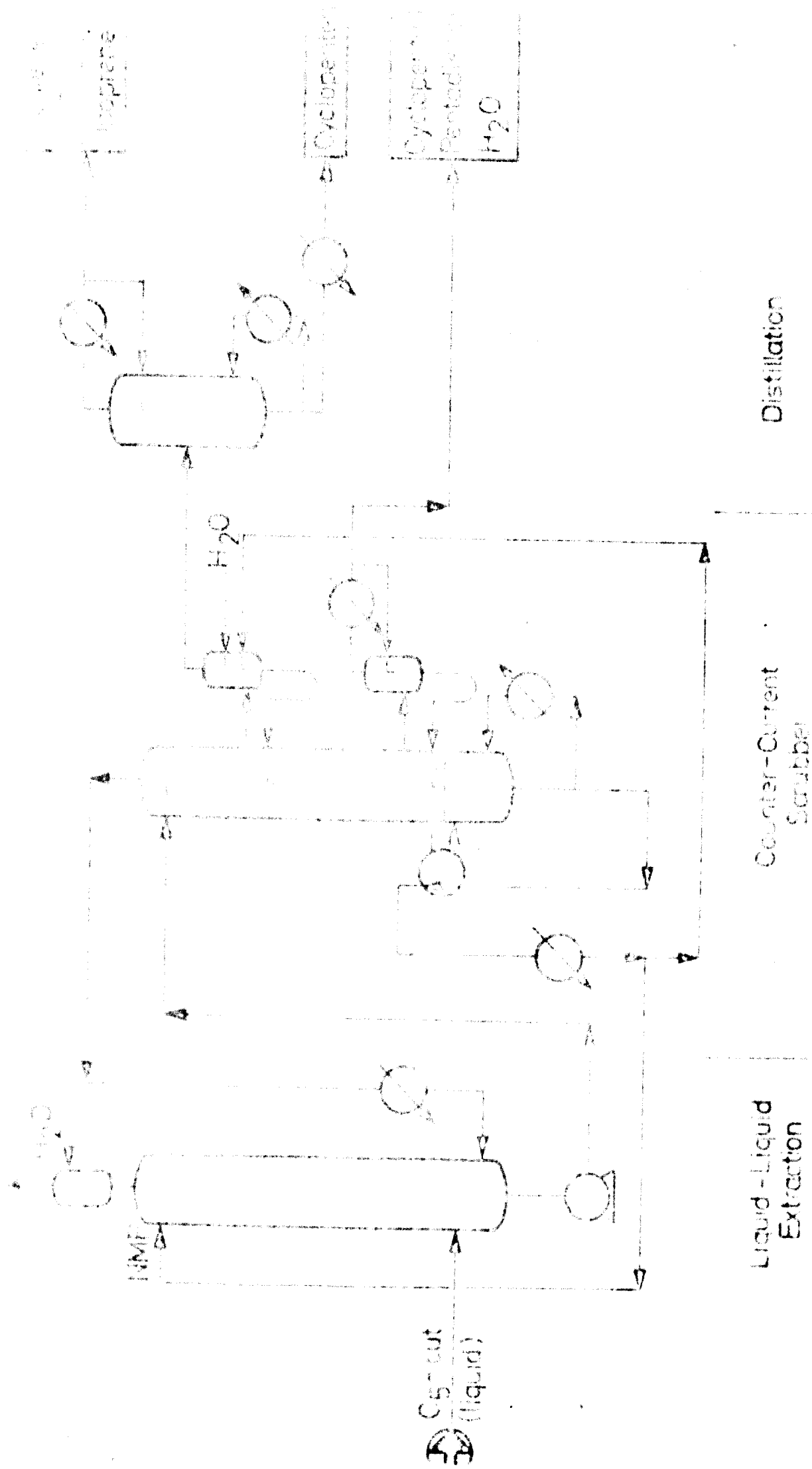
The diene content of the pyrolysis C₅-cut is 10 to 14% on average - which can be recovered economically from the gas stream.

The diene was purified by means of a H₂O counter-current gas scrubler - which is a very simple and cheap method - the required amount of

circulated solvent, corresponding to the isoprene concentration, is dependent on the amount of C_4 -cuts to be used as feedstock. In the case of isoprene recovery, therefore, a relatively large plant would be necessary in relation to the moderate isoprene amount. In addition, the entire C_5 -cut would have to be vaporized which in turn would require a large amount of steam for heating. In comparison, however, to separate the pentanes which are contained in amounts between 40 and 50 % in the C_5 -cut, a considerably small amount of solvent would be needed for a liquid-liquid extraction by the use of water-containing N-methylpyrrolidone. This makes it possible economically to absorb the total isoprene including the other C_5 -diolefins in N-methyl-pyrrolidone by means of such a liquid-liquid extraction. A proportion of the pentenes is dissolved in the N-methylpyrrolidone at the same time.

The N-methylpyrrolidone which contains the isoprene, the other C_5 -diolefins and part of the pentanes, as shown in the flow sheet (fig. 11), is freed from the dissolved hydrocarbons by introducing it into the head of a distillation column. On heating and boiling in the usual way in the bottom of this column. Thus in this column, under the conditions of counter-current scrubbing, the isoprene is separated from the other accompanying components. This separation process, in contrast to separation of the pentanes, requires a relatively large number of trays, but this is quite feasible in a distillation column.

The amount of solvent was considerably reduced by removal of the pentanes in the preceding liquid-liquid extraction. The mixture of pentenes and a small amount of isoprene collected as overhead of the column is condensed



and recycled at a suitable level into the liquid-liquid extraction column. Corresponding to their solubility, the C_5 -hydrocarbons accumulate at various levels in the column from which they are drawn in the usual way as side streams.

The isoprene is removed as the uppermost side stream. If the isoprene contains excessive amounts of pentadienes, cyclopentadiene or C_5 -diolefins (i. e. compounds with higher solubility), these are removed from the isoprene in an addition scrubber, as has already been shown analogously for the removal of acetylene in the butadiene recovery.

Distillation is not sufficiently selective for separation of the isoprene and cyclopentene. Since the boiling point difference of these hydrocarbons is, however, 10°C, i. e. the relative volatility is 1.4, a separation of the accompanying component from the diolefin is possible with some difficulty, like in the system butadiene-ethylenacetylene.

The studies aiming at employing this process on an industrial scale have not yet been completed. However the results obtained so far indicated that the basis for the recovery of isoprene of high purity from cracked gasolines with the aid of SO_2 are very favorable.

10. Recovery of Pyrolysis Gasoline-Liquid-Phase "Cold Hydrogenation"

As regards the pyrolysis of naphtha as a severe thermal reforming, the pyrolysis naphtha is a thermal reformat which has to be refined to meet the required specifications. Thus indeed the use of the pyrolysis naphtha as motor gasoline blending component is a common one.

The apparatus used for the synthesis of the compound was as follows:

The reaction mixture was prepared by combining the following reagents: 10 g of sodium metal, 50 ml of anhydrous ether, and 100 ml of a 10% solution of sodium hydroxide in ethanol. The mixture was stirred for 24 hours at room temperature. The resulting solution was then added to a solution of 10 g of the starting material in 100 ml of ether. The mixture was stirred for 48 hours at room temperature. The reaction was then quenched with 100 ml of water and the mixture was extracted with ether. The ether extracts were combined and the solvent was removed by distillation. The residue was purified by distillation to give the final product.

The yield of the product was 85%. The boiling point of the product was 100°C at 10 mm Hg. The refractive index was 1.45. The density was 0.85 g/ml. The molecular weight was 100. The infrared spectrum showed a strong absorption at 1700 cm⁻¹. The NMR spectrum showed a singlet at 7.2 ppm and a doublet at 4.5 ppm.

References

1. J. Smith, J. Org. Chem., 1950, 15, 123.

1. J. Smith, J. Org. Chem., 1950, 15, 123.	2.	3. J. Doe, J. Org. Chem., 1955, 20, 456.
4. A. Brown, J. Org. Chem., 1960, 25, 789.	5. G. White, J. Org. Chem., 1965, 30, 1012.	6. H. Black, J. Org. Chem., 1970, 35, 1345.
7. I. Green, J. Org. Chem., 1975, 40, 1678.	8. K. Blue, J. Org. Chem., 1980, 45, 2011.	9. L. Red, J. Org. Chem., 1985, 50, 2344.
10. M. Purple, J. Org. Chem., 1990, 55, 2677.	11. N. Yellow, J. Org. Chem., 1995, 60, 3010.	12. O. Grey, J. Org. Chem., 2000, 65, 3343.

Table 1. Summary of the results of the regression analysis.

Variable	Parameter	Estimate	Standard Error	t-statistic	Probability > t
Constant	Intercept	1.234	0.123	10.03	0.0001
	Age	0.056	0.012	4.67	0.0001
	Gender	0.123	0.034	3.62	0.0004
	Education	0.089	0.018	4.94	0.0001
	Income	0.012	0.003	4.00	0.0001
	Health	0.034	0.008	4.25	0.0001
	Marital Status	0.067	0.015	4.47	0.0001
	Religion	0.045	0.011	4.05	0.0001
	Occupation	0.023	0.006	3.83	0.0002
	Region	0.018	0.004	4.50	0.0001
Error	Mean	0.000	0.000	0.00	1.0000
	Standard Deviation	0.123	0.000	0.00	0.0000
	Minimum	-0.234	0.000	0.00	0.0000
	Maximum	0.345	0.000	0.00	0.0000
	Skewness	0.123	0.000	0.00	0.0000
	Kurtosis	0.456	0.000	0.00	0.0000
	Jarque-Bera	1.234	0.000	0.00	0.0000
	Probability > Chi-Square	0.543	0.000	0.00	0.0000
	Sample Size	100	0.000	0.00	0.0000
	Adjusted R-Square	0.876	0.000	0.00	0.0000

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c) Consumption of utilities and materials:

Per one metric ton of pyrolysis naphtha employing combined air and water cooling

Electricity	20 kWh
Steam	0.1 m.t.
Cooling water	6 m ³
H ₂ -consumption	40 - 80 m ³
Catalyst consumption	0.02 kg

11.3 Economy

The calculation is based on a plant for an annual throughput of 100,000 tons of pyrolysis naphtha which is connected to a selective hydrogenation unit operating by the BAYER process (Federal Republic of Germany conditions)

Investment for the key-turn plant	DM	2,600,000
	US \$	650,000
Interest and amortization	15 %	48.75
Maintenance	3 %	9.75
Personnel (1 man per shift) and supervision		7.50
Hydrogen (less calorific value credit for waste gas)		44.00
Utilities and other operating materials		32.00
Total manufacturing costs	DM/hr	142.00
	DM/m.t.	11.35
	US \$/m.t.	2.34

Literature references:

0. Reitz, "Treating Aromatic By-Product Light Oils from Pyrolytic conversions by the R.S.-Scholzen-Process for Light Oil Refining",
Proceed. 5th World Petrol. Congress, Vol. III, Paper 11 (1959).

12. Pure Aromatics Extraction-Liquid Solvent Process

The pyrolysis products of naphtha, compared with coal-tar light oil rich in aromatics, contain a much larger proportion of nonaromatics whose sharp separation from the aromatics by simple distillation would be uneconomical and impossible.

For this purpose Bergel's developed a solvent process by means of which, with the aid of NMP (N-methylpyrrolidone) as the solvent aromatics of the highest purity are obtained in optimal yields and requiring the lowest power consumption.

The solvent process was developed for the extraction of aromatics with NMP/water as the solvent mixture. Improvement of the selectivity of the solvent by the addition of water as the mixing component made it possible to produce aromatics in a high degree of purity. However, it was found that distillative separation of the solvent/aromatic mixture by water distilling over the azeotrope with the aromatics cause a relatively high steam consumption.

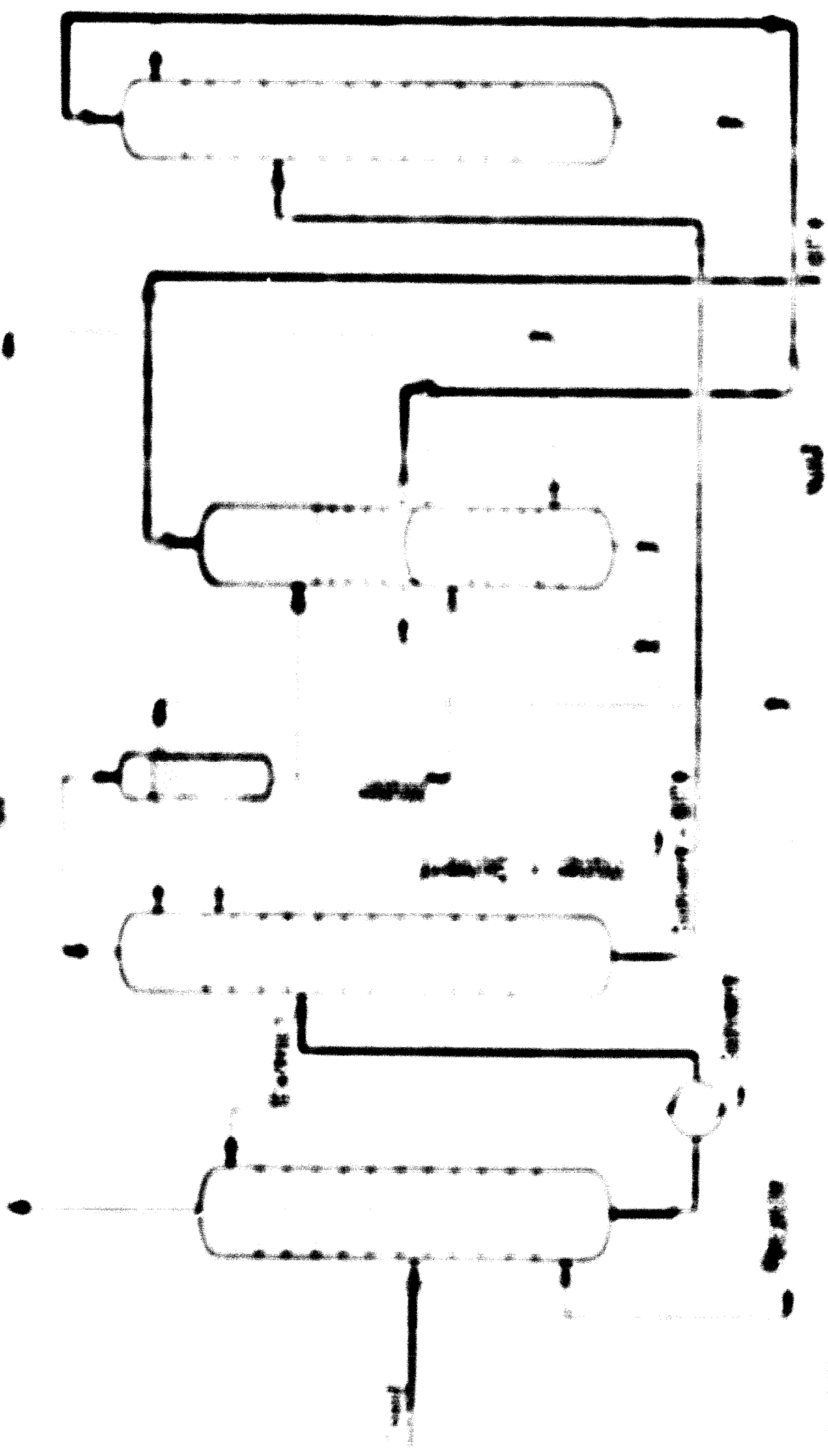
Further development of the process resulted in using glycol as the mixing component. The choice of the solvent mixture NMP/glycol not only reduced

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The first part of the report deals with the general situation of the country, the population, the economy, and the political system. It also mentions the main problems facing the country and the measures taken to solve them.

2. THE ECONOMIC SITUATION

The economy of the country is based on agriculture, which is the main source of income for the population. The main crops are wheat, cotton, and sugar.

The industrial sector is also developing, with the main industries being textiles, food processing, and mining. The government is investing in infrastructure and education to improve the economy.

The country has a high unemployment rate, which is a major problem. The government is trying to create more jobs by investing in infrastructure and education.

The country is also facing a balance of payments problem, which is caused by the high cost of imported goods and the low price of exported goods.

The government is trying to solve this problem by increasing the price of exports and decreasing the price of imports.

The country is also facing a foreign exchange shortage, which is caused by the high demand for foreign currency to buy imported goods.

The government is trying to solve this problem by increasing the price of exports and decreasing the price of imports.

The country is also facing a problem of inflation, which is caused by the increase in the price of goods and services.

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The government is trying to solve this problem by increasing the price of exports and decreasing the price of imports.

When further treatment being necessary, the pure aromatics can be separated from the individual components by distillation. The nonaromatics which are not removed at the top of the extractor column. They are removed from the bottom of the scrubbing column with some solvent, are drawn off as a separate stream, and transferred to the 1st stripper column. The solvent is separated in a separator into water and hydrocarbons. The hydrocarbons flow into the scrubbers, the hydrocarbons flow

Distillation Data

Component	Weight %	Boiling Point	Refractive Index
Gasoline	100	120-180	1.40-1.45
Gasoline	100	120-180	1.40-1.45
Gasoline	100	120-180	1.40-1.45
Gasoline	100	120-180	1.40-1.45
Gasoline	100	120-180	1.40-1.45
Gasoline	100	120-180	1.40-1.45
Gasoline	100	120-180	1.40-1.45
Gasoline	100	120-180	1.40-1.45
Gasoline	100	120-180	1.40-1.45
Gasoline	100	120-180	1.40-1.45

The above data are for the gas phase and are not applicable to the liquid phase.

based on a typical reformate or pyrolysis naphtha:

Steam (10-16 atm. gauge): 0.3 m.t.

an equivalent amount of heat in the form of fuel oil or fuel gas.

Cooling water: 20 m³

Electricity: 15 kWh

Sulfur: 0.1 kg

The steam consumption for the fractionating of 1 m.t. of pure aromatics in a following simple distillation plant depends on the ratio in which the hydrocarbons contained are present in the feedstock; it is known from experience to be between 0.5 and 0.6 metric tons.

14.3.2.2. Example

As an example of the foregoing, a calculation is given for a plant with an annual capacity of 100,000 metric tons. The amount of aromatics recovered is 10,000 metric tons/year (100 operating hours).

Investment (in millions of dollars) Dfl. 9,000,000
(US \$2,250,000)

Operating cost (in millions of dollars/year) 15

Operating cost (in millions of dollars/year)

Operating cost = 11.25 \$/yr

... ..
... ..
... ..

- = 402,00 t/hr
- = 42,00 t/hr
- = 23,25 t/hr
- = 13,00 t/hr
- = 222,1 t/hr

... .. $\frac{1-0,4}{0,4} = 1,5$

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Technical data:

Recovery of benzene from coal-tar light oils with 1-5% nonaromatics:

Yield:	95 - 99%
Crystallization points:	5.45 - 5.5° C
Utilities per one metric ton of pure benzene:	
Steam:	0.8 m.t.
Cooling water:	40 m ³
Electricity:	7.6 kWh
Solvents:	0.1 kg

Literature references:

1. "Production of pure aromatics by means of exothermic distillation and extraction"

Proceed. 11th Intern. Chem. Congress, Vol. 4, 29/43 (1953)

2. "The use of modified aromatics extraction with solvent combination"

Proceed. 11th Intern. Chem. Congress, Vol. 4, 13/20 (1953)

13. Hydrodealkylation-Toluene-Solvent process

Dealkylation in the presence of hydrogen has as its objective the splitting off of side chains and even saturated rings, from aromatic hydrocarbons in order to obtain from substituted compounds of which there is an excess, the required lower substituted compounds or preferably the unsubstituted basic compounds. Of the greatest importance today is the production of benzene from toluene and naphthalene from mono and dimethyl naphthalenes.

Work was already started by BLSF in the early nineteen-forties on the catalytic dealkylation of benzene homologues (DBP 861.238, 1943). These studies which originally were directed especially toward the production of toluene (besides benzene) from xylenes, were taken up again when a surplus of toluene was created through the petrochemical manufacture of benzene.

An industrial process was evolved which, in a first plant with an annual throughput of 120,000 metric tons toluene is to go on stream at Scholven-Chemie AG in the middle of 1969. The process can also be employed for the dealkylation of naphthalene homologues; it is briefly described in the following, by the example of the production of benzene from toluene.

13.1 Description of the Process

Excess gas from the gas reforming can be used to advantage as fresh gas for dealkylation instead of pure hydrogen. The fresh toluene together with the separated toluene and circulation gas is heated by heat exchangers and a pre-heater, and passed to the reaction zone which consists of two in-line reactors with regenerable catalyst. To limit a rise in temperature as a result of the high heat of reaction, quenchoil is added.

To remove the methane formed during dealkylation, part of the circulation gas, and in the case of reformer gas being used, the fresh gas itself, is conveyed to a hydrogen concentrating unit.

First the liquid reaction products are freed in a stabilizing column

at elevated pressures from the constituents that boil at a lower temperature than benzene. In a subsequent column at normal pressure the pure benzene is separated from non-aromatic toluene. The recycle toluene contains small amounts of non-aromatic products, especially diphenyl, which are removed in the recycling. If the diphenyl fraction can be used, for example, as a carrier oil, it can be recovered in an additional column. The valuation of this procedure is possibly higher than for the present one; by taking in-out, plant, and operating costs of distillation into lowered account.

13.2 Technical data

a) Yield:

(in the case of 1 toluene with 2% weight
o-*o*-aromatics and 3% by weight nonaromatics):

81.5% by weight pure benzene

1.5% by weight diphenyl fraction

b) Purity of product

Crystallization point	+	5.5° C
Bromine concentration	under	0.01 g/100 g
Total sulfur	under	1 ppm
Toluene content	under	100 ppm

c) Utilities and consumption of materials (for the dealkylation of 1 metric ton toluene with combined air and water cooling including distillation):

1. Introduction

2.1

2. Methodology

2.2

3. Results and Discussion

3.1

4. Conclusion

4.2

5. Acknowledgements

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6. References

6.2

7. Appendix

7.1

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11. Detailed description of the study

12. Discussion of the results and their implications

13. Conclusions and recommendations

14. Acknowledgements and funding sources

15. References and further reading

16. Appendix A: Data tables and figures

17. Appendix B: Questionnaire and interview schedule

18. Appendix C: Glossary of terms

19. Appendix D: List of abbreviations

20. Appendix E: Author's biography

21. Appendix F: Declaration of interest

22. Appendix G: Ethics approval

23. Appendix H: Contact information

24. Appendix I: Declaration of authorship

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