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NEW AND OLD PROCESSES TO PRODUCE PURE BUTADIENE [1]

by

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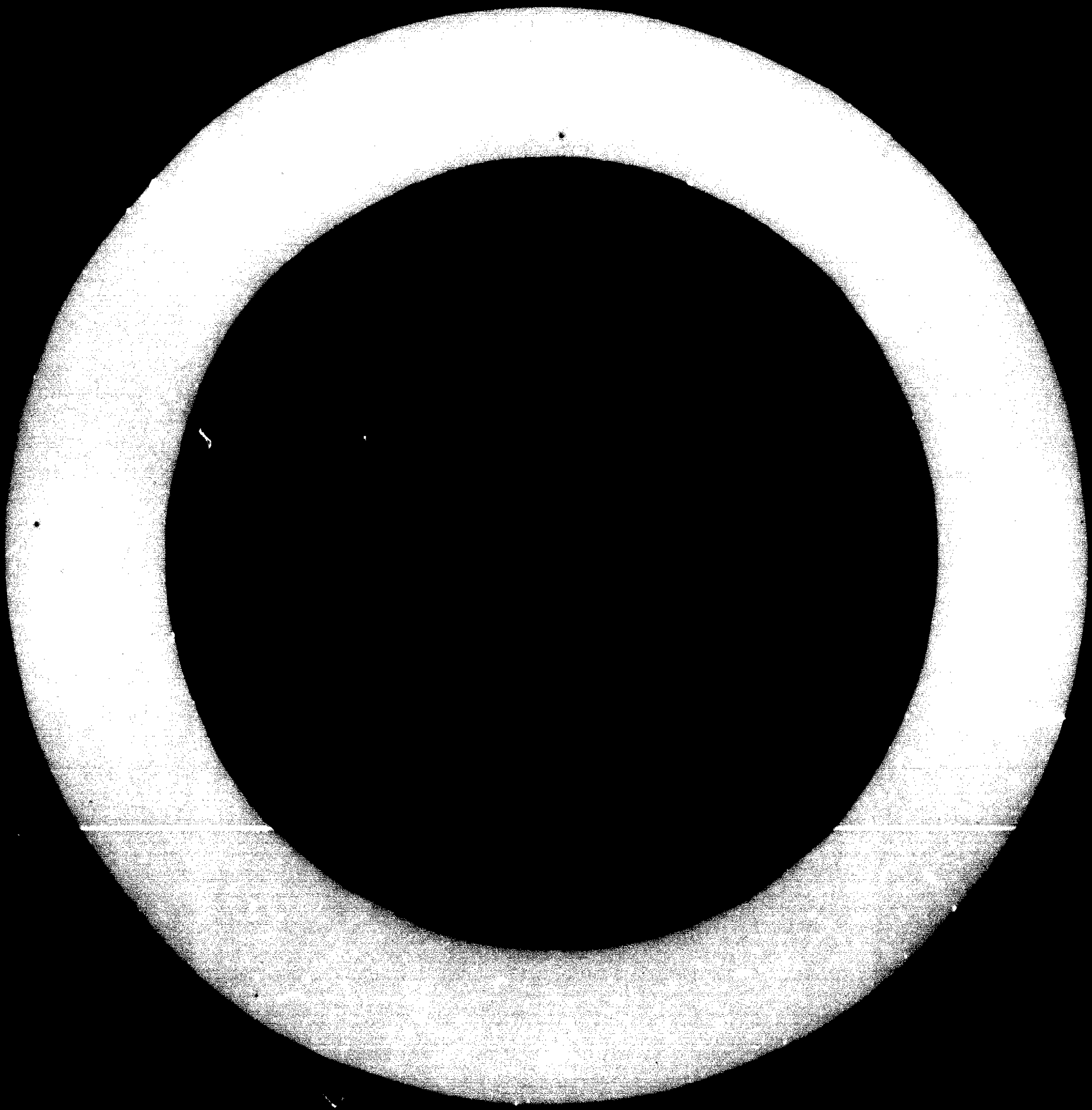

NEW AND OLD PROCESSES
TO PRODUCE PURE BUTADIENE

(English Edition)

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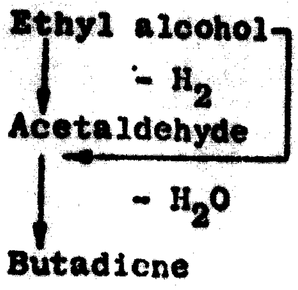
HISTORICAL REVIEW

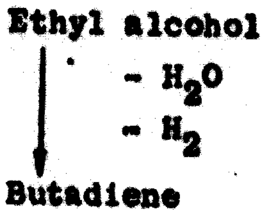
In the year 1860 G. Williams investigated the thermal degradation of natural rubber; from the vapors he recovered a liquid named isoprene, which became viscous in contact with air and formed a rubber-like mass at elevated temperature. Based on this discovery, research activities began to find methods for making artificial rubber with improved mechanical properties. Based on G. Williams' discovery isoprene and 2,3-dimethyl butadiene, which has a similar chemical structure, were used as raw materials at first. From the latter monomer the so-called methyl rubber was derived. In 1885 the chemical structure of butadiene-1,3 became known. In the year 1909 F. Hofmann discovered that an artificial rubber with improved properties can be produced by thermal polymerization of butadiene. From that time on, parallel to the development of rubber synthesis, research work was started to develop industrial processes for the production of butadiene. According to the different sources of raw materials, development went into different directions in Russia, North America and Germany.

In Russia ethyl alcohol was the basic raw material:-

Ostromislensky 1915



Lebedew 1928



Today large amounts of butadiene are still produced from ethyl alcohol in the Soviet Union although some plants based on petrochemical raw materials have been installed in the meantime. The total production is estimated at 400,000 tons per year.

In Germany where the industrial chemistry was developed mainly on the basis of coal, acetylene derived from calcium carbide was used as raw material:-

<u>I.G. Farben</u> 1928 (four-step process)

Acetylene
$\downarrow + H_2O$
Acetaldehyde
$\downarrow \times 2$
Aldole
$\downarrow + H_2$
Butandiole
$\downarrow - 2 H_2O$
Butadiene

<u>Reppe</u> about 1937

Acetylene + Formaldehyde
$\downarrow$
Butindiole
$\downarrow + 2H_2$
Butandiole
$\downarrow -2H_2O$
Butadiene

This development had a boom during the period from 1939 to 1945. It came to a sudden end in 1945 when the factories were destroyed and had to be dismantled.

In North America the development took a different course. After 1940 the supply from Malaysia, where natural rubber production is concentrated, was threatened by the military conflict in the Pacific Ocean area. Therefore the American government established the RUBBER RESERVE COMPANY already in 1940. This company had to organize a strategical stock-pile of natural rubber and also had the order to support the production of synthetic rubber to meet the increased demand. As a result of these activities the industrial production of butadiene in the U.S. on a petrochemical basis increased within four years from zero to 400,000 tons per year and has reached a level of about 1.7 million tons per year today. At first, the known process of Ostromislensky starting with ethanol was adopted (Fig. 1). Subsequently own methods were developed based on crude oil and natural gas which were abundantly available as domestic raw materials. The hydrocarbons, butane and butene, recovered from natural gas or refinery gas are well suitable for dehydrogenation to butadiene. The process problems were solved and in 1945 reliable processes were available. The government owned plants, built under the government program, were sold to the private industry in 1955.

The bulk of the butadiene in the U.S. is produced by catalytic dehydrogenation of n-butene using a process developed by Standard Oil Development Co. In the years 1942 to 1945 seven plants with a total capacity of approximately 300,000 tons per year were built. Another catalytic dehydrogenation process starting from n-butane was developed by Catalytic Development Co. (Houdry) and the first two plants using this process came on stream in 1945. A third similar process comes from the laboratories of Phillips Petroleum Co. Dow Chemical Co. developed a dehydrogenation catalyst for butene with exceptionally good yields. The installed capacity using the Dow process was 355,000 tons butadiene in 1959. R.J. Harbour reported some details on selectivity and yields of the Dow catalyst at the World Petroleum Congress in New York in 1959.(24)

Dehydrogenation of n-butene is done in one reaction step (Fig. 2). The necessary reaction heat is added by mixing the feed with superheated steam. The feed comes mainly from cracker gases from refineries.

Dehydrogenation of n-butane is more difficult and at first had to be done in two steps, in the first step from butane to butene and in the second step from butene to butadiene. Later on the process was improved by Houdry in such a way that both reaction steps could be realized in one reactor simultaneously (Fig. 3). In this process reaction heat is supplied by periodical heating of the catalyst during regeneration. The reactors are switched at short intervals in such a way that production and regeneration cycles alternate.

The conversion per reactor pass is relatively low in all dehydrogenation processes, although improvements have been reached recently by the addition of oxygen. In this so-called oxy-dehydrogenation the liberated hydrogen reacts with the oxygen immediately to form water, thus increasing yield and economics of the process. In all cases the problem of recovering the butadiene from mixtures with other C_4 hydrocarbons exists.

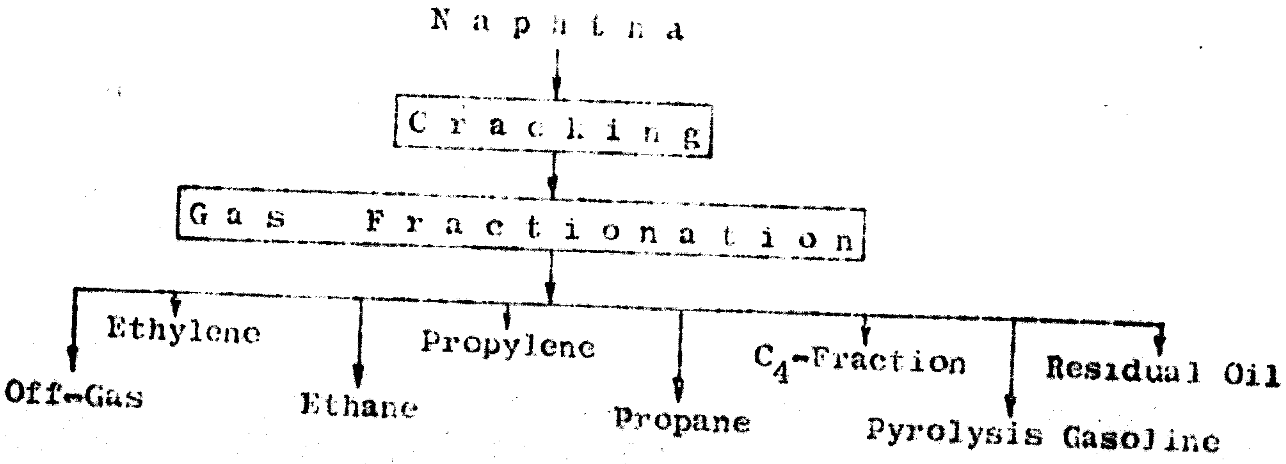
Owing to azeotrope formation and the narrow boiling points distillation cannot be considered so that other ways had to be found. Standard Oil Development Co. (ESSO) developed one of the first processes, the CAA process, which is illustrated in Fig. 3. Copper ammonium acetate solution and butadiene form a complex compound at low temperatures of around -10°C and separate again at elevated temperatures. This enables butadiene recovery by fractional extraction from C_4 fractions. This process was developed specifically for use in dehydrogenation plants and is particularly suitable for low butadiene concentrations in the feedstock.

Another way of butadiene separation is extractive distillation with a selective solvent. During the years after 1940 basic research into this technique was undertaken in the U.S. Some industrial plants used furfural with little water as additive as the solvent (see Fig. 2).

Other solvents, such as ammonia and acetone, were also tried out. SHELL CHEMICAL CORP., CALIFORNIA, achieved in 1956 a major improvement in the throughput of an existing plant by using acetonitrile instead of acetone.

While in the U.S. the butadiene demand is still covered mainly from dehydrogenation plants, the industrial development in Europe took a different course. The construction of a great number of cracking plants to produce ethylene from naphtha opened up a new source of butadiene. The processing of naphtha under the usual cracking conditions yields, apart from ethylene and other unsaturated hydrocarbons, also butadiene at economically attractive quantities.

As shown in the following diagram, an ethylene plant produces a variety of products from naphtha:



Depending on the severity of cracking the C_4-fraction has a butadiene concentration of 40-50%. The quantity of butadiene formed is influenced mainly by the type of feedstock (see Table 1) and only to a very little extent by the cracking severity. Fig. 4 presents a typical curve of the yield from the cracking of light naphtha in modern short-time crackers at varying cracking severity$^{1)}$. The chart clearly shows that the total yield of C_4-hydrocarbons decreases with increasing cracking severity while the quantity of butadiene remains constant.

The butadiene recoverable from ethylene production covers, since 1971, the total demand. The annual production rate in Western Europe is presently some 900,000 tons. The few dehydrogenation plants in Europe are losing importance because the butadiene from cracking plants is cheaper. A similar development took place in Japan where the present output is some 600,000 tons per annum.

The second part of this paper will deal with butadiene recovery from pyrolysis C_4-fractions.

TABLE I

BUTADIENE YIELD FROM TUBULAR CRACKERS IN DEPENDENCY OF FEEDSTOCK

Feedstock	**Butadiene Output related to Feed**
Ethane	-
Propane	-
Butane	approx. 2.5%
Light Naphtha	" 4.5%
Mid Naphtha	" 4.8%
Gas Oil	" 4.5%

BUTADIENE RECOVERY FROM PYROLYSIS C_4 FRACTIONS

The composition of the C_4-fraction from the fractionation of a gasoline pyrolysis plant lies within the limits given in Table II depending on feedstock, cracking conditions and design of fractionation unit. The individual hydrocarbons are listed according to their boiling point.

The C_4-fraction is recovered as debutaniser overhead in the gas fractionation unit and still contains all C_3-hydrocarbons and low boiling components not separated in the upstream depropaniser. Also a small amount of C_5-hydrocarbons, depending on the design of the debutaniser, passes into the overhead product and is thus present in the C_4-fraction.

As will be seen from Table II the boiling points of some C_4 hydrocarbons are so close to that of butadiene that distillative separation is not possible. Merely the separation of butene-2 has been carried out by distillation on a technical scale (see column 9 in Fig. 2), but the number of separating stages is so great that this column has to be divided into two separate columns in order not to exceed a technically feasible column length. Moreover, this distillation is possible only if, the same as with the dehydrogenation of butene, only traces of butyne-1 are present. The reason is that azeotropes exist between butyne-1 and trans-/cis-butene-2 whose boiling points are very close to that of butadiene-1,3.

As already mentioned, a selective solvent should preferably be used for butadiene separation. The ESSO-CAA process may be mentioned as an example of chemical extraction (see Fig. 3) the basic principles of which were described in detail by C.E. Morrel et al in 1954.2) This process uses an inorganic solvent which chemically binds the butadiene.

TABLE II

LIMITS OF COMPOSITION OF C_4-FRACTIONS IN Vol.% and Vol.ppm

	Boiling Point °C	Concentration
Ethylene	- 103.71	0 - 10 ppm
Ethane	- 88.63	0 - 10 ppm
Propylene	- 47.70	0.5 - 2.0%
Propane	- 42.07	0.1 - 0.5%
Propadiene	- 34.50	0.3 - 0.6%
Propine	- 23.22	0.5 - 1.0%
i-Butane	- 11.73	1.0 - 2.0%
i-Butene	- 6.90	25.0 - 35.0%
1-Butene	- 6.26	12.0 - 18.0%
Butadiene-1,3	- 4.41	40.0 - 50.0%
n-Butane	- 0.50	4.0 - 8.0%
Butene-2-trans	+ 0.88	4.0 - 6.0%
Butene-2-cis	+ 3.72	4.0 - 6.0%
Vinyl acetylene	+ 5.1	0.4 - 1.0%
Butyne-1	+ 8.07	0.1 - 0.3%
Diacetylene	+ 10.3	0 - 100 ppm
Butadiene-1,2	+ 10.85	0.1 - 0.2%
3-Methyl butene-1	+ 20.06	0 - 0.3%
Butyne-2	+ 26.99	0 - 100 ppm
i-Pentane	+ 27.85	0.1 - 1.0%
2-Methyl butene-1	+ 31.16	0 - 0.2%
n-Pentane	+ 36.07	0 - 0.2%
Pentene-2-trans	+ 36.35)	0 - 0.2%
Pentene-2-cis	+ 36.94)	0 - 0.2%
2-Methyl butene-2	+ 38.56	0 - 0.1%
Sulphur in the form of mercaptan		0 - 10 wt.pp
Water		200 - 1000 ppm
Peroxides (as H_2O_2)		0 - 100 ppm
Carbonyl compounds (as acetaldehyde)		0 - 100 ppm

Technical plants operating by the extractive distillation principle use organic polar substances as solvent, except for the ammonia. The ammonia process was published in 1946 by M. Poffenberger et al 3) and was operated by Dow Chemical, but it has not found a wide-spread use. K. Smeykal and H. Lütgert 4) investigated a plurality of organic solvents as to their suitability, but only furfural 5), 6), acetonitrile 7), 8), N-methylpyrrolidone 9), 10), 11), 12), 13), 14), dimethyl formamide 15), 16), 19) and dimethyl acetamide 17), 18), 20) have been applied on a commercial scale.

Fig. 5 gives a comparison of 24 solvents. Selectivity, defined as the ratio of the Bunsen absorption coefficients, is plotted versus solubility expressed by the alpha value for butadiene. The best suitable solvents are those with high selectivity and high solubility located at the far right-hand top in Fig. 5. It is obvious that the four solvents located in the circle have the most favourable properties. These are dimethyl formamide, N-methylpyrrolidone, acetonitrile and dimethyl acetamide which have already been applied commercially. The presentation in Fig. 5 gives only a general survey. The Bunsen absorption coefficients are the result from equilibrium measurements between the single hydrocarbon and the solvent, while in technical extraction distillation the mass transfer is between a hydrocarbon mixture and the fat solvent with water addition. The measure for the separation effect is the relative volatility of the individual C_4-hydrocarbons versus butadiene in the presence of the fat solvent at distillation temperature. V.A. Gorškov et al. 21) carried out measurements with the usual solvents the results of which are given in Table III. Column 1 compares the relative volatility under ideal conditions without solvent. It will be seen that separation of butene-1 and isobutene is not possible by simple distillation but that extractive distillation with one of the solvents listed does not create any problems. The high relative volatility of methyl acetylene is, however, reduced so strongly by the solvent that proper separation by extractive distillation is impossible. A further exception is furfural solvent which reduces the relative volatility of cis-butene-2. The initial butadiene recovery plants (Phillips, Shell) therefore consisted of <u>one</u> extractive distillation and one or two normal distillation units. Butanes and butenes were separated in the extractive distillation column, methyl acetylene and other low-boilers were removed overhead from the first normal distillation column and C_4-acetylenes (including cis-butene-2 in the case of furfural) were recovered as bottoms product from the second normal distillation column (see Fig. 6).

In view of the more severe cracking conditions applied during recent years the vinyl acetylene content in the C_4-fraction from naphtha crackers has increased heavily. At the same time the requirements demanded from the purity of butadiene with regard to acetylene compounds have become more stringent. This has rendered distillative separation of acetylenes as illustrated in Fig. 6 difficult. At a relative volatility of 0.807 versus butadiene separation is rather costly. Moreover, vinyl acetylene tends to polymerisation and is, as all acetylenes, dangerous at high concentrations. The acetylene compounds are therefore first removed from the C_4-fraction by mild hydrogenation which requires extra investment cost and involves a butadiene loss of 3-5%. The new processes (BASF, Nippon Zeon, Union Carbide) eliminate hydrogenation and solve the problem by two-stage extractive distillation where butanes and butenes are separated in the first stage and acetylenes in the second stage (see Fig. 7).

T A B L E III

RELATIVE VOLATILITY OF DIFFERENT HYDROCARBONS VERSUS 1,3-BUTADIENE IN THE PRESENCE OF SOLVENTS

	Without Solvent (ideal)	Acetonitrile + H_2O *	D M F	N M P + H_2O	D M A + H_2O	Furfural + H_2O
n-Butane	0.877	2.63	2.44	2.29	2.21	1.93
Butene-1	1.07	1.78	1.82	1.80	1.71	1.63
Isobutene	1.08	no specification				1.42
t-Butene-2	0.861	1.49	1.48	1.42	1.38	1.21
c-Butene-2	0.789	1.30	1.30	1.30	1.24	1.07
Methyl acetylene	2.10	1.12	0.97	1.13	1.15	1.37
Butadiene-1,3	1.00	1.00	1.00	1.00	1.00	1.00
Butadiene-1,2	0.666	0.728	0.700	0.712	0.672	0.638
Ethyl acetylene	0.684	0.476	0.473	0.489	0.500	0.550
Vinyl acetylene	0.807	0.403	0.335	0.325	0.353	0.474

DMF = Dimethyl formamide

NMP = N-Methylpyrrolidone

DMA = Dimethyl acetamide

Solvent/C_4 mixture ratio: 2:1

Temperature: 50°C

BASF developed a process scheme where the two solvent cycles are combined so that one single stripper suffices (see Fig. 8).

In the design of butadiene plants special attention has to be paid to the polymerisation tendency of butadiene. R. F. Robey et al.[22)] proved that butadiene dimerises spontaneously to vinyl cyclohexene similar to the Diels-Alder reaction. The reaction velocity merely depends on the temperature. According to Robey et al. about 22 ppm dimers per hour occur in pure butadiene at 40°C. As an inhibitor to hold back dimerisation is not available, the butadiene has to be kept constantly at low temperature to prevent the vinyl cyclohexene content from reaching an unduly high level. In particular during extended storage the temperature should not exceed 20-25°C.

Apart from dimerisation, chain polymerisation also takes place which is initiated mainly by peroxides. These occur in little quantity when butadiene gets into contact with oxygen or air. Care must therefore be taken to see that oxygen does not enter butadiene recovery plants. The formation of peroxide compounds and the resulting catalytic polymerisation can be effectively prevented by inhibitors. Suitable inhibitors are pyrogallol, hydroquinone and similar compounds. Tertiary butyl catechol is mostly used in practice. It is added to the finished butadiene product in lots of 10 - 100 ppm depending on the means of transportation and the storage period.

Another rather unpleasant kind of uncontrolled polymerisation is the formation of so-called "popcorn" polymer which occurs in the gas phase and produces a porous mass which expands and which is even capable of bursting steel vessels. The reaction mechanism is not clarified yet and there exists no inhibitor which is effective in the gas phase. These problems can only be avoided by keeping oxygen away from the plant and by operating at low temperatures. The exclusion of oxygen is not a problem provided that the plant is suitably designed and operated carefully. In this connection it is of importance to avoid contact of the C_4-feed with oxygen before entering the plant, which could happen during filling into tank trucks and in transit. Operation at low temperatures is an economical problem which is the reason why most of the processes make a compromise.

Another reason for keeping operating temperatures low is the fact that most of the high boiling solvents are no longer sufficiently stable at their boiling point. To reduce the boiling temperature 5-10% water are added to the solvent in some cases. A high boiling point has, however, the advantage that the solvent can easily be removed from the product streams while in the case of acetonitrile having a relatively low boiling point additional water wash and redistillation of the acetonitrile containing water are required. Redistillation is aggravated by azeotrope formation.

In all processes a small partial stream of the solvent is regenerated to remove high boiling polymers and degradation products. Regeneration takes place in a simple vacuum distillation column, the bottoms product being discharged from the plant while the overhead solvent is returned to the cycle.

Finally a few words may be said about the purity of the butadiene. The specifications have become more stringent during recent years. The first generally accepted standards were established in the forties by the U.S. Government and were based on the manufacture of SBR rubber (styrene butadiene rubber). This synthetic rubber was produced by emulsion polymerisation using radicals as catalysts. Unconverted residual butadiene is recovered and returned, if possible, to the butadiene recovery plant for purification. Impurities in the butadiene reduce more or less the polymerisation velocity. To balance this disadvantage more catalyst has to be added which impairs the economics of polymerisation. Besides, some unsaturated compounds, such as vinyl acetylene, adversely affect the quality of the polymer in so far as they result in undesired branching or cross-linking of molecule chains. The influence the individual components have on polymerisation was investigated by R.L. Frank et al.[23)] and the results were used to establish a standard specification in 1947 which is given in the first column of Table IV.

This specification became more stringent with the continuing progress in the field of polymerisation over the years and the present specification for normal styrene butadiene rubber is shown in column 2 of Table IV. When in 1960 stereospecific 1,4 cis-polybutadiene was introduced as a new synthetic rubber type, the requirements regarding butadiene purity increased. This new product is obtained by polymerisation using sensitive organo-metallic catalyst. The presence of foreign matter in the butadiene causes irregularities in the molecule chains formed and thereby impairs the quality. Column 3 of Table IV gives a specification for stereospecific rubber.

The two-stage processes available nowadays enable the production of high purity butadiene. They are economic and have proved their merits in commercial operation. Besides, they can well cope with variations in the acetylene content of the feedstock.

TABLE IV

VARIOUS BUTADIENE SPECIFICATIONS

		SBR-Standard 1947	Styrene-Butadiene-Rubber Grade	1,4-cis-Polybutadiene Grade
Butadiene-1,3	min.	98.0 wt.%+)	99.0 Vol.%+)	99.5 Vol.%+)
Butadiene-1,2	max.	no specification	no specification	100 ppm
Acetylenes	max.	1000 ppm	500 ppm	100 ppm
Sulphur as H_2S	max.	100 ppm	100 ppm	5 ppm
Carbonyl compounds as acetyldehyde	max.	100 ppm	100 ppm	50 ppm
Peroxides as H_2O_2	max.	10 ppm	10 ppm	5 ppm
Vinyl cyclohexene	max.	2000 ppm	1000 ppm	500 ppm
Residue from evaporation	max.	1000 ppm	100 ppm	50 ppm
C_5-hydrocarbons	max.	0.2 Vol.%	0.2 Vol.%	0.1 Vol.%

+) The balance mainly consists of butene.

LITERATURE

1) K. Naumburg,
"Ethylene Production by short-time and intensive Cracking of Petroleum Fractions",
Paper to the 12th regular Conference of the Processing of Petroleum held at Bratislava (Czechoslovakia) 13th to 15th September, 1967.

2) C.E. Morrell, W.J. Paltz, J.W. Packie, W.C. Asbury and C.L. Brown
Trans. Amer. Inst. Chem. Engrs. 42 (1946) 473 to 494

3) N. Poffenberger, L.H. Horsley, H.S. Nutting and E.C. Britton
Trans. Amer. Inst. Chem. Engrs. 42 (1946) 815 to 826

4) K. Smeykal and H. Lütgert
Chem. Techn. 14 (1962) 4, 202 to 207

5) J. Happel, P.W. Cornell, D.B. Eastman, M.J. Fowle, C.A. Porter and A.H. Schutte
Trans. Amer. Inst. Chem. Engrs. 42 (1946) 189 to 214

6) W.D. Peters, R.S. Rogers
Hydroc. Proc. 47 (1968) 11, 131 to 134

7) J.D. van Dalen and J.C. Zomerdijk,
Europ. Chem. News 30th Sept., 1966, 52 f.

8) H.D. Evans and D.H. Sarno
Paper 5, P.D. 21, 7th World Petroleum Congress, Mexico April 1967

9) H.M. Weitz, U. Wagner and O.H. Schmidt
Chem. Ing. Techn. 32 (1960) 12, 796 to 801

10) H. Kröper, H.M. Weitz and U. Wagner
Hydroc. Proc. 41 (1962) 11, 191 to 196

11) H.M. Weitz and U. Wagner
Erdöl u. Kohle 16 (1963) 6, 562 to 570

12) H. Kröper and H.M. Weitz
Oil and Gas Journal (1967) 9th Jan. 98 to 104

13) H. Klein and H.M. Weitz
Hydroc. Proc. 47 (1968) 11, 135 to 138

14) B. Hausdörfer, U. Wagner, H.M. Weitz
Chem. Ing. Techn. 40 (1968) 23, 1147 to 1152

15) S. Takao
Hydroc. Proc. 45 (1966) 11, 151 to 154

16) T. Yoshimura
Chem. Engng, (1966) 9th May 134 to 136

17) W.W. Coogler, Jr.
Oil and Gas Journal (1967) 22nd May 99 to 101

18) W.W. Coogler, Jr.
Chem. Engng, (1967) 31st July 70 to 72

19) M. Hebel, M. Kaspereit
Chem. Techn. 23 (1971) 7, 419 to 423

20) R.R. Bannister, E. Buck
Chem. Eng. Progr. 65, (1969) 9, 65 to 68

21) V.A. Gorskov, S. Ju. Pavlov, A.B. Kilnos, A.N. Busin
and T.E. Petrova
Chim. prom. (1971) 11, 807 to 812

22) R.F. Robey, H.K. Wiese, C.E. Morrell
Ind. Eng. Chem. 36 (1944) 1, 3, to 7

23) R.L. Frank, J.R. Blegen, G.E. Inskeep, P.V. Smitz
Ind. Eng. Chem. 39 (1947) 983 to 895

24) R.J. Harbour
Brennstoff-Chemie 40 (1959) 12, 389 to 392

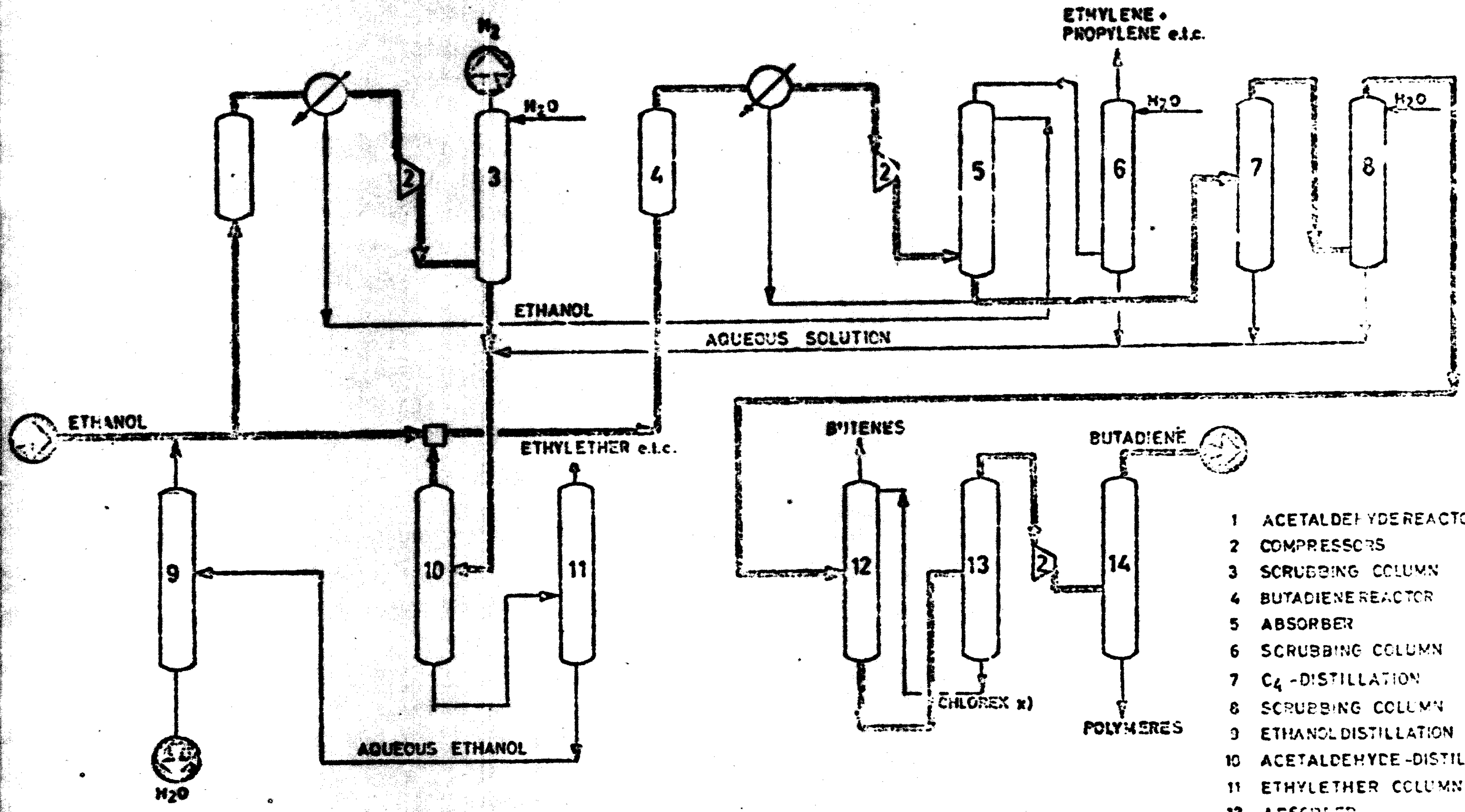
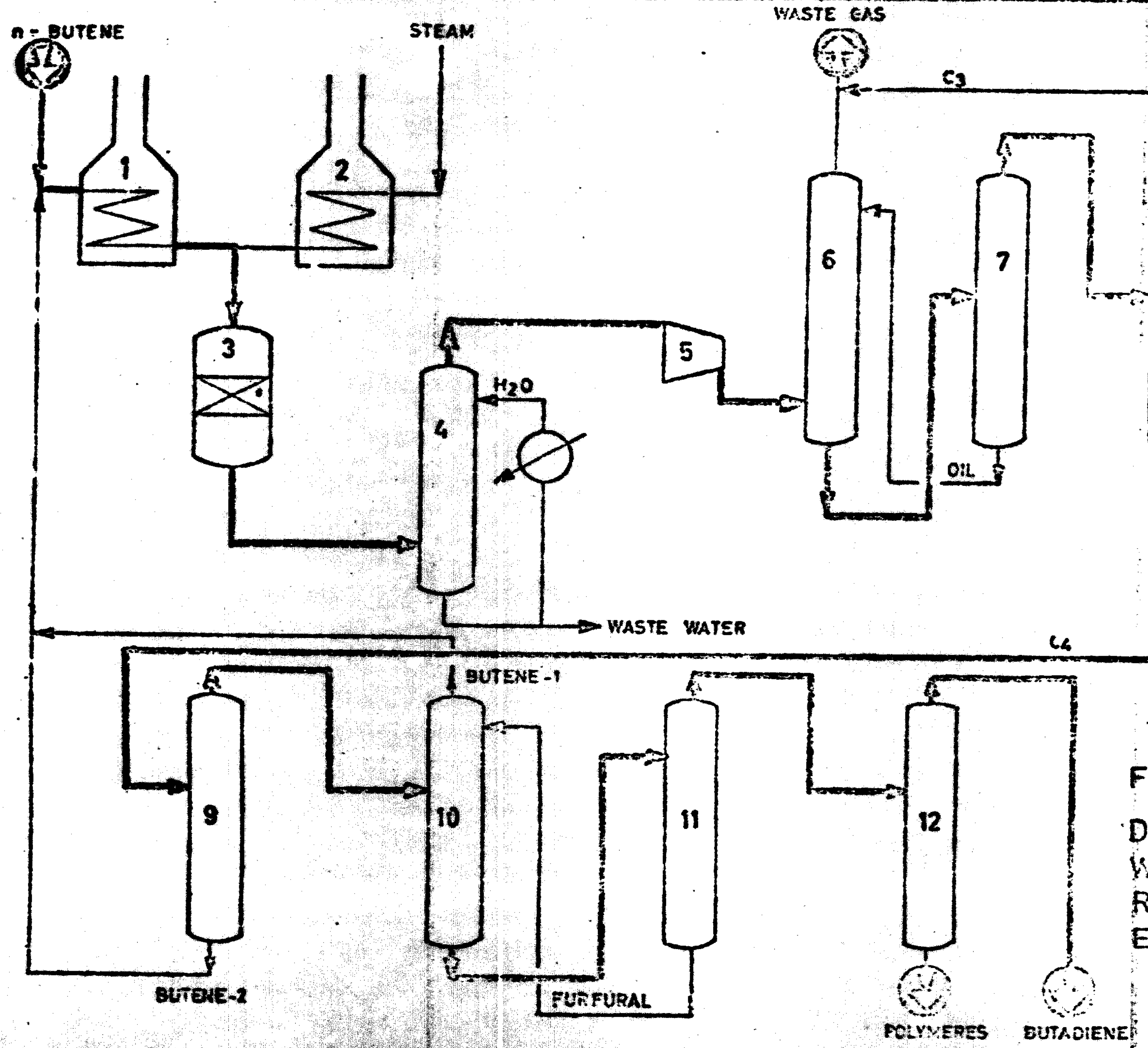


FIG 1 BUTADIENE PRODUCTION FROM ETHANOL CARBIDE & CARBON-PROCESS

(BY OSTROMISLENSKI)

1	ACETALDEHYDE REACTOR
2	COMPRESSORS
3	SCRUBBING COLUMN
4	BUTADIENE REACTOR
5	ABSORBER
6	SCRUBBING COLUMN
7	C_4 -DISTILLATION
8	SCRUBBING COLUMN
9	ETHANOL DISTILLATION
10	ACETALDEHYDE -DISTILLATION
11	ETHYLETHER COLUMN
12	ABSORBER
13	STRIPPER
14	BUTADIENE COLUMN

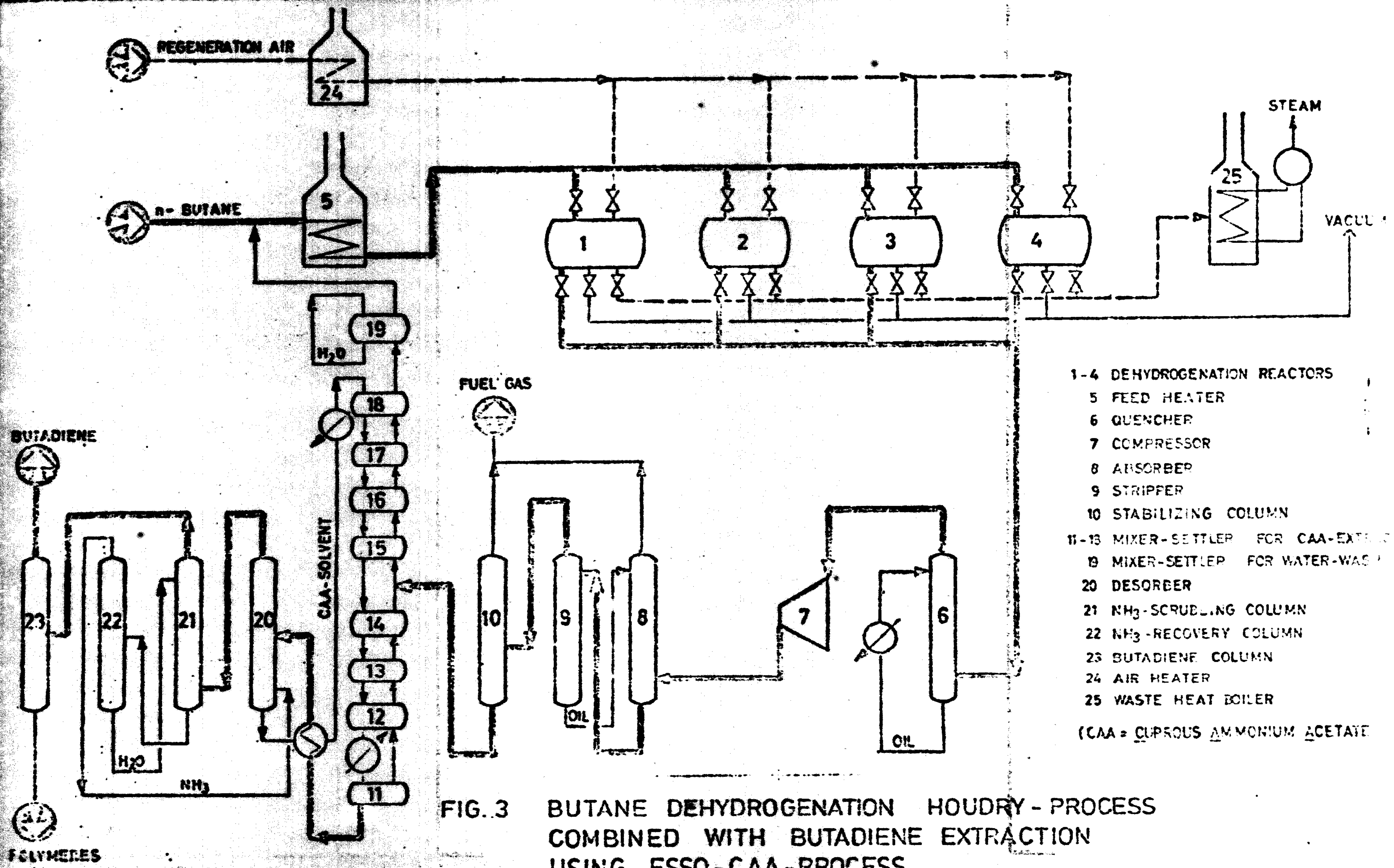
x) „CHLOREX" = ββ' -DICHLORETHYLET



1 BUTENE SUPERHEATER
2 STEAM SUPERHEATER
3 REACTOR
4 QUENCH TOWER
5 COMPRESSOR
6 ABSORBER
7 STRIPPER
8 STABILIZING COLUMN
9 BUTENE-2 COLUMN
10 FURFURAL-EXTRACTIVE-DISTILLATION
11 FURFURAL-STRIPPER
12 BUTADIENE-COLUMN

FIG. 2

DEHYDROGENATION OF n-BUTENE
WITH SUBSEQUENT BUTADIENE
RECOVERY BY FURFURAL
EXTRACTIVE DISTILLATION

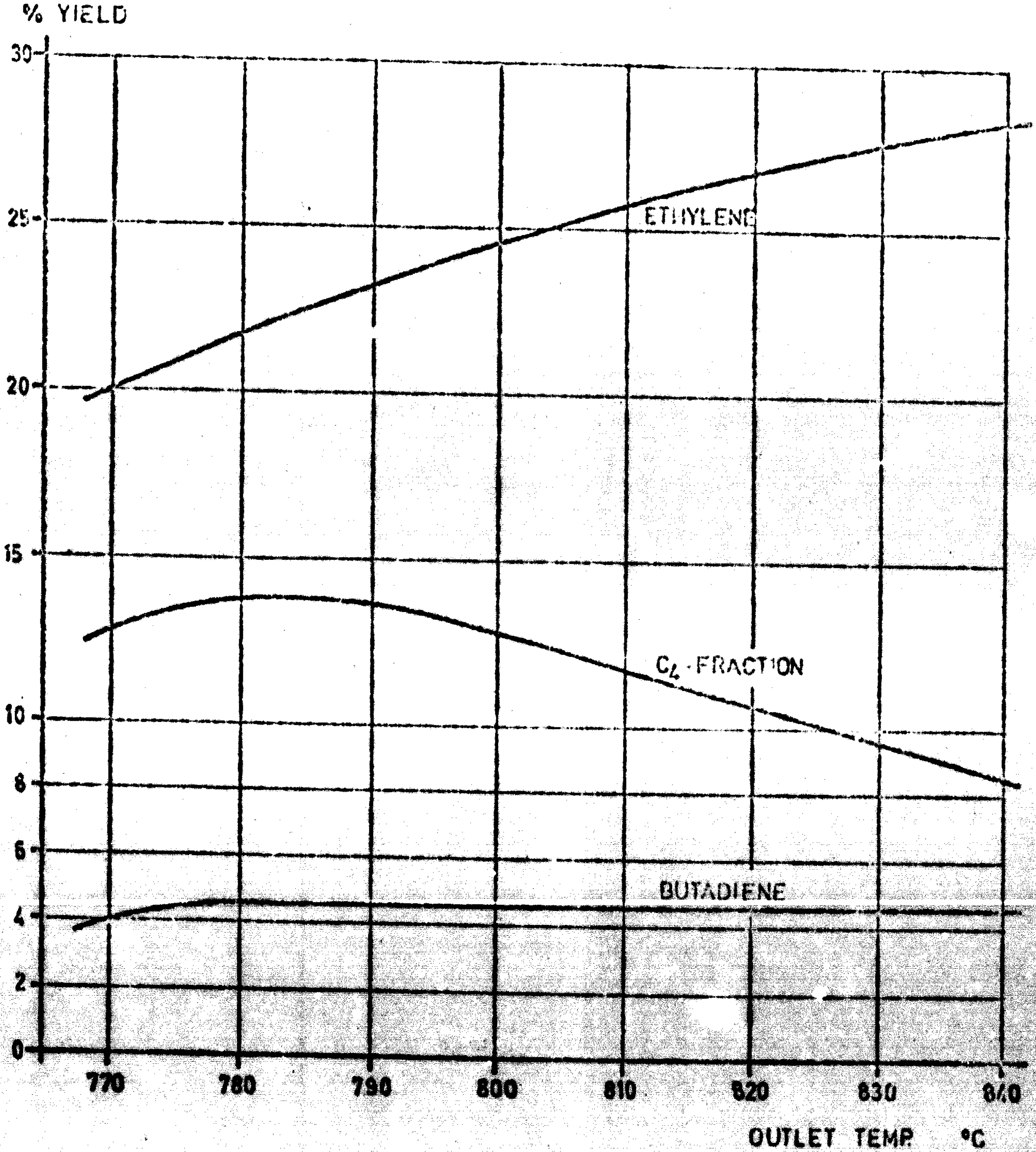


1-4 DEHYDROGENATION REACTORS
5 FEED HEATER
6 QUENCHER
7 COMPRESSOR
8 ABSORBER
9 STRIPPER
10 STABILIZING COLUMN
11-18 MIXER-SETTLER FOR CAA-EXT
19 MIXER-SETTLER FOR WATER-WAS
20 DESORBER
21 NH_3-SCRUBBING COLUMN
22 NH_3-RECOVERY COLUMN
23 BUTADIENE COLUMN
24 AIR HEATER
25 WASTE HEAT BOILER

(CAA = CUPROUS AMMONIUM ACETATE

FIG. 3 BUTANE DEHYDROGENATION HOUDRY - PROCESS COMBINED WITH BUTADIENE EXTRACTION USING ESSO-CAA-PROCESS

FIG. 4 CRACKING YIELDS FROM LIGHT NAPHTHA



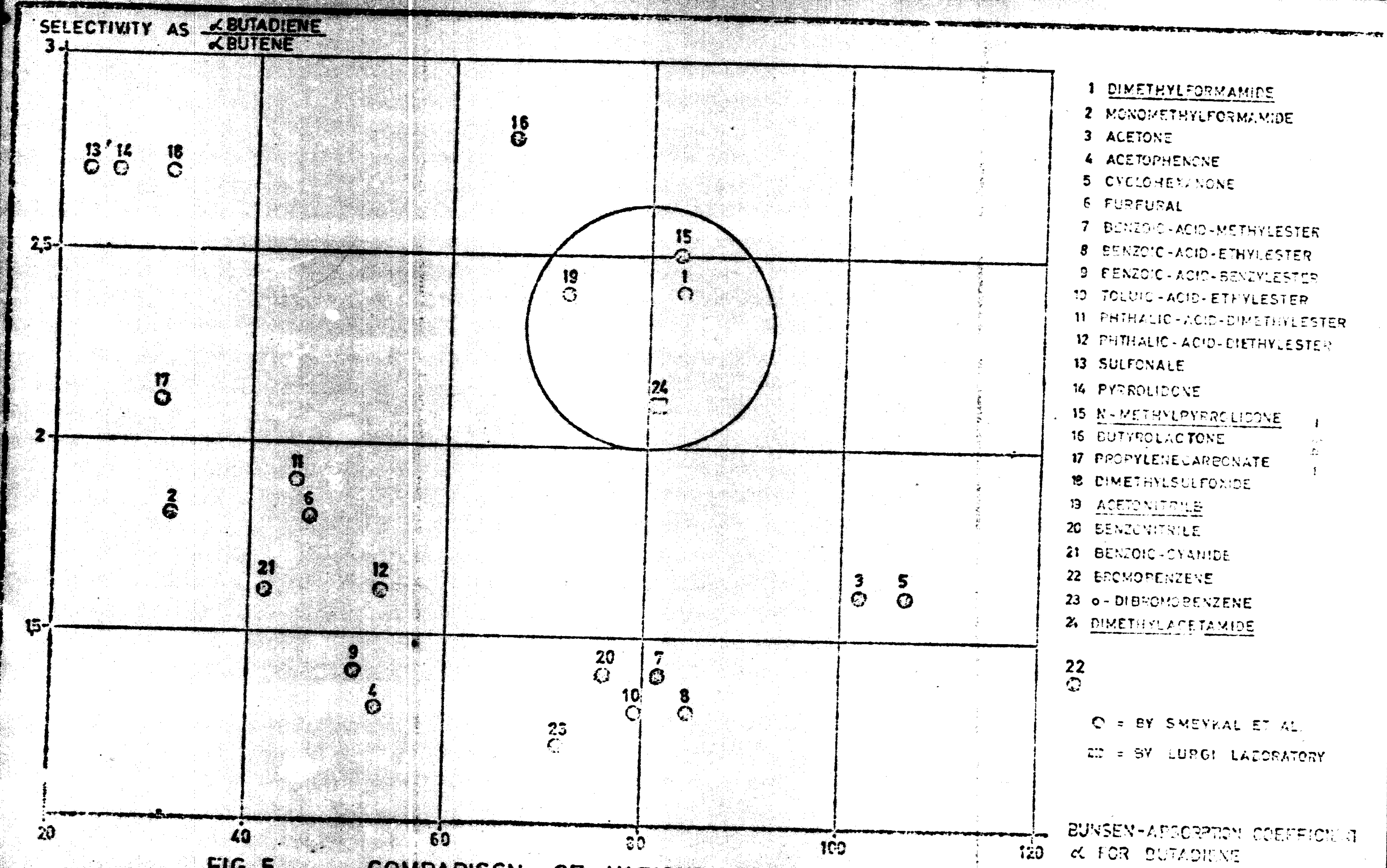


FIG 5 COMPARISON OF VARIOUS SOLVENTS

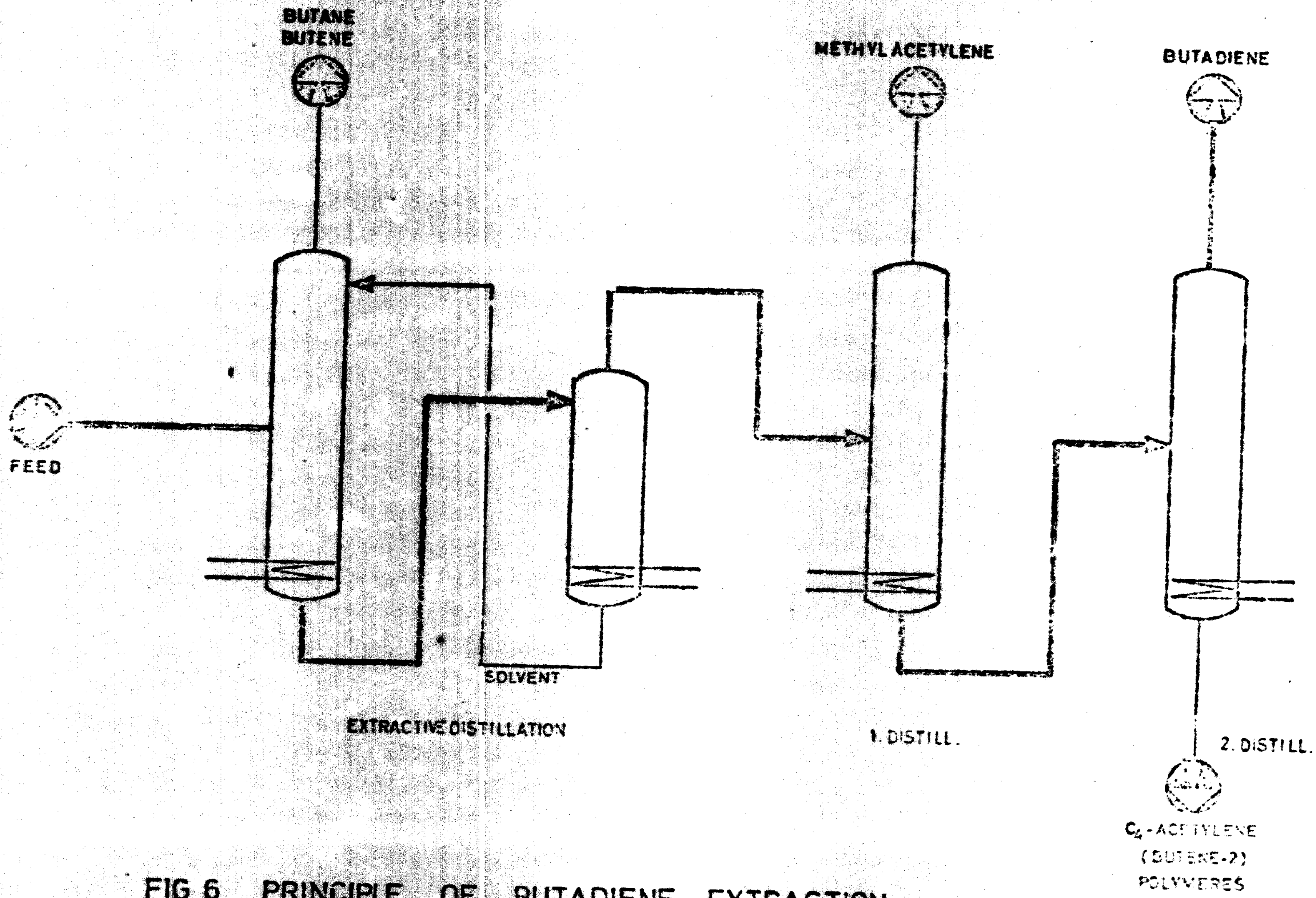


FIG 6 PRINCIPLE OF BUTADIENE EXTRACTION WITH ONE EXTRACTIVE DISTILLATION AND TWO NORMAL DISTILLATIONS (SHELL, PHILLIPS)

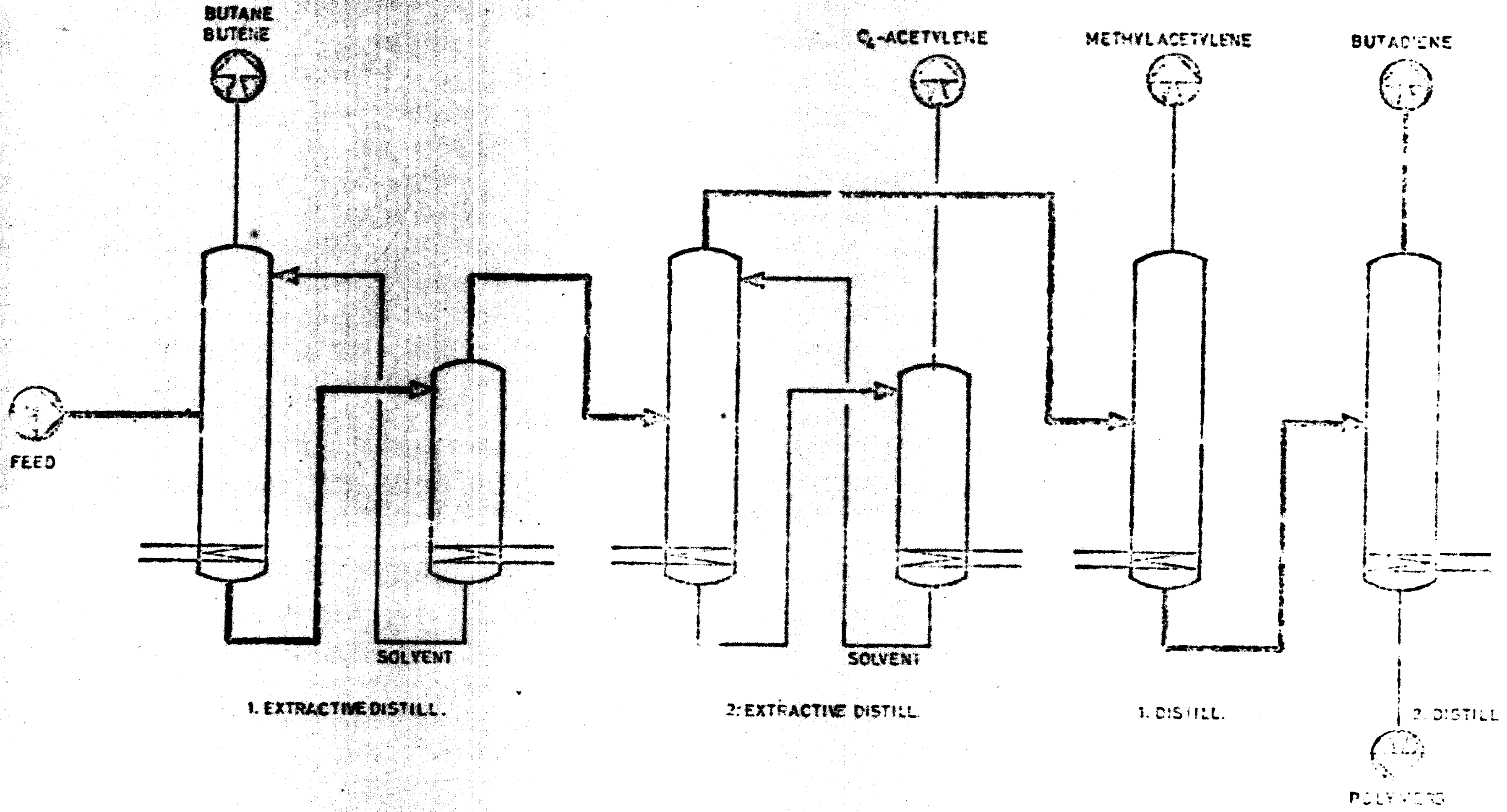


FIG. 7 PRINCIPLE OF BUTADIENE EXTRACTION WITH TWO EXTRACTIVE DISTILLATIONS AND TWO NORMAL DISTILLATIONS (NIPPON ZEON UNION CARBIDE)

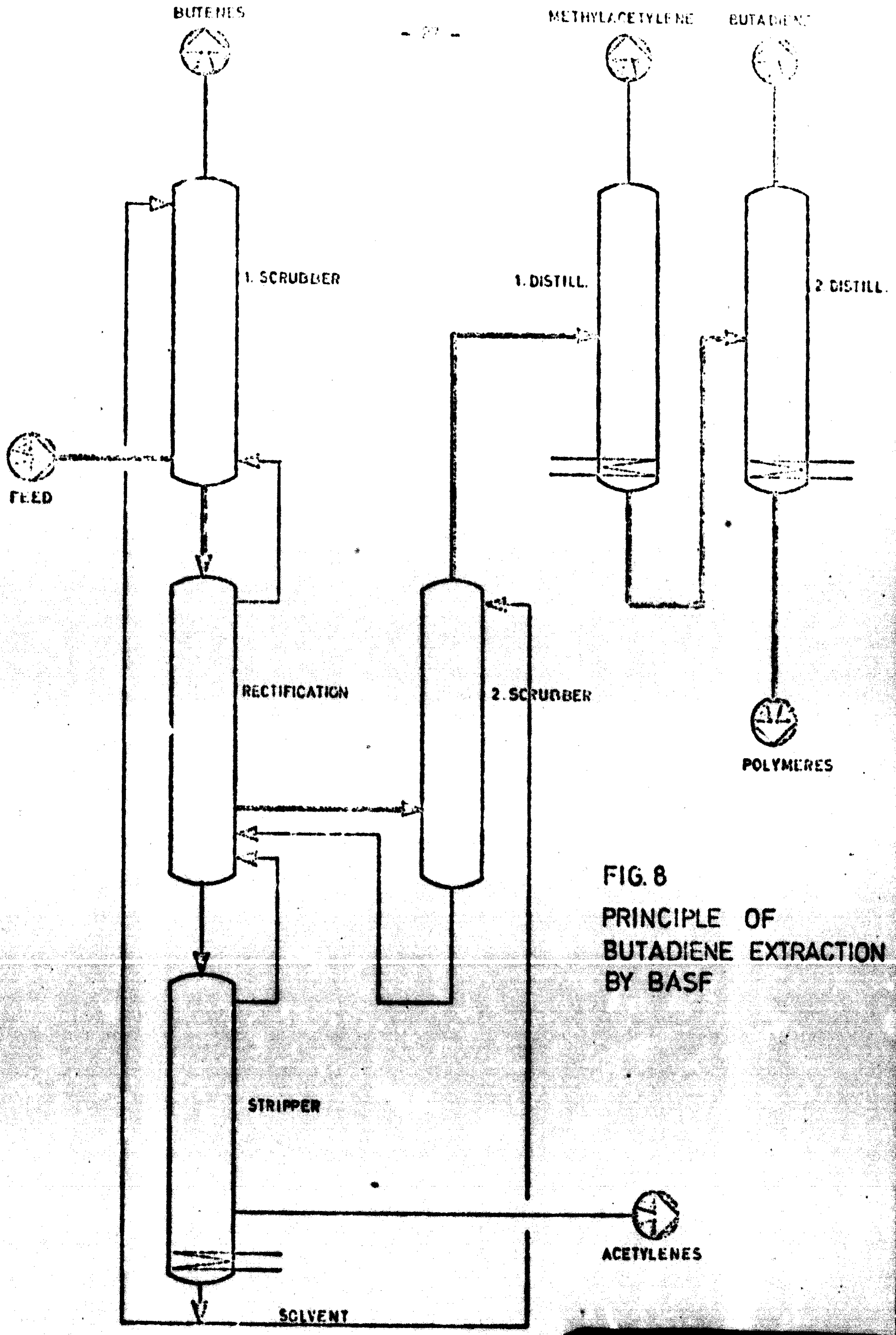
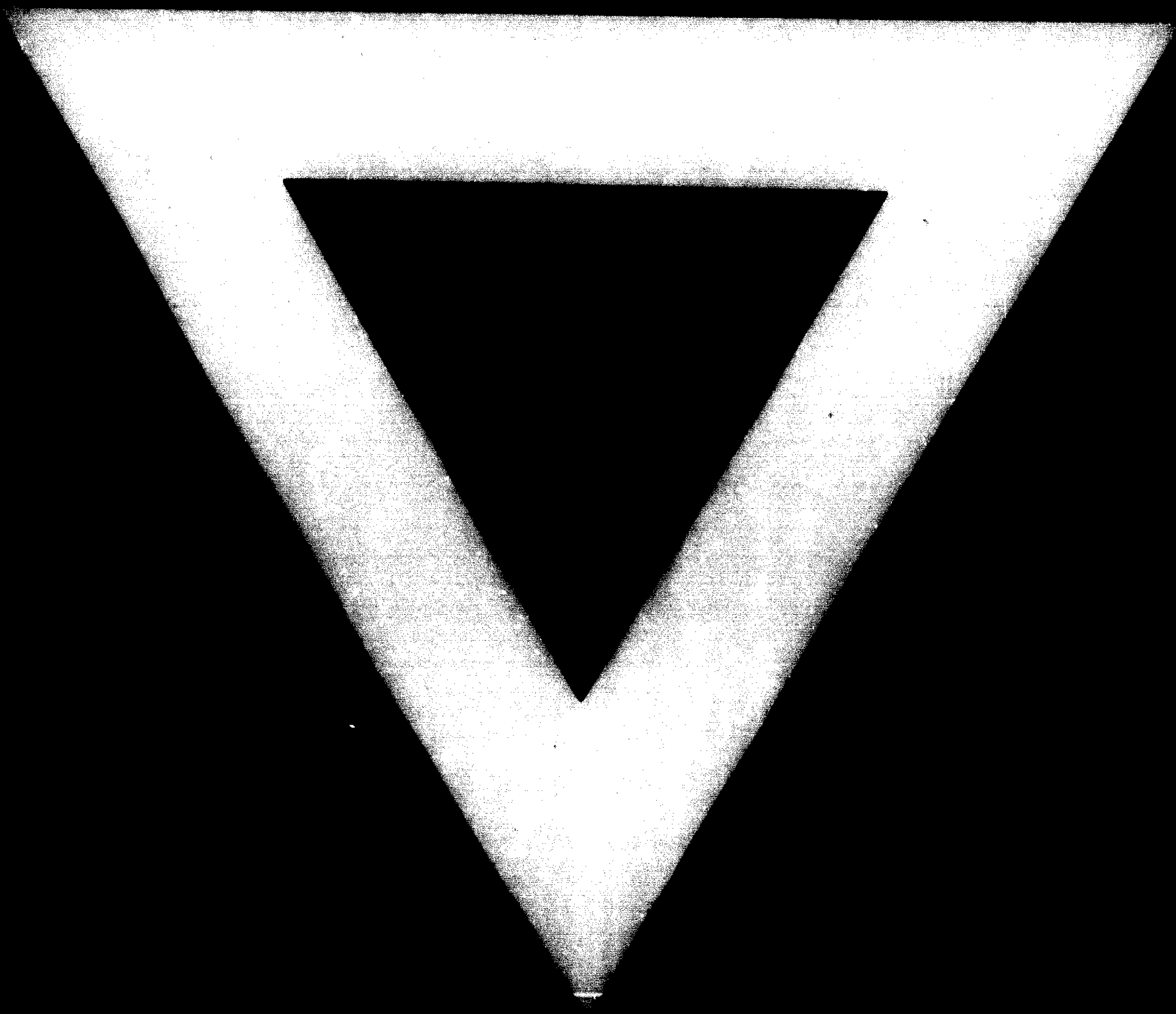


FIG. 8

PRINCIPLE OF BUTADIENE EXTRACTION BY BASF

[redacted]



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