

# **C<sub>4</sub> Hydrocarbon Production and Distribution**

**Howard Kehde, *editor***

**Chemical Engineering Progress Symposium Series**

**Number 103**

**1970**

**Volume 66**

# C<sub>4</sub> Hydrocarbon Production and Distribution

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Chemical Engineering Progress Symposium Series

Number 103

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Volume 66

*Published by*

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS

345 East 47 Street

New York, New York 10017

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American Institute of Chemical Engineers  
345 East 47th Street, New York, New York 10017

Library of Congress Catalog Card Number 79-128193

Printed in the United States of America by  
Commercial Printers of Connecticut, Inc.

## FOREWORD

This collection of papers presents a comprehensive view of supply and demand for  $C_4$  hydrocarbons. This field is in a state of flux, and the major supplier of the near future may become steam cracking of heavy hydrocarbons. For this reason, this latter subject is given special emphasis in this volume. The original presentations were made at the 64th National Meeting of the American Institute of Chemical Engineers held at New Orleans, Louisiana, in March, 1969. Specifically, the particular sessions involved were organized by the Petroleum Refining and Petrochemical Division of the AIChE, which is also responsible for this publication.

Naturally occurring butanes, contained in natural gas and crude oil, are experiencing a declining growth rate in the United States, and there is a major decrease in the ratio of reserves to production, part of which might be reversed by readjustment of the controlled price of natural gas by the United States government. Culbertson et al. outline the situation and also point out that the newer fields being discovered are leaner in  $C_4$  hydrocarbons. This then requires more expensive recovery methods, and Wolfe describes field processing methods, showing that the emphasis (86% of capacity) is on absorption or refrigerated absorption. Refrigeration is necessary also to supply the now diminishing feedstocks for chemical plants that produce ethylene and propylene by steam cracking of LPG.

Ethylene units feeding LPG produce only a small amount of butadiene and butenes. Cracking of heavier feedstocks, such as naphthas or gas oil, cause a tremendous increase in the production of these  $C_4$  hydrocarbons, and by-product  $C_4$ 's from such plants can conceivably become the major supply in the future. This is already occurring in Europe and Japan.

Steam cracking of heavy hydrocarbons has long been practiced in the United States as outlined by Spielman, but only in a few plants. One major disadvantage, as pointed out by Walker in his description of one of these plants, is the very great increase in the quantity of by-products produced per pound of ethylene and the necessity that these must all be upgraded and marketed. Plant design has new problems as discussed in the papers of Marshall et al. and Demarest et al. The selection of feedstocks is also important, and data are given by Kitzen et al., Lambrix et al., and Woebecke et al. One interesting plan for integrating the interest of the chemical plant and the petroleum refinery is offered by Rowell.

One of the major markets for  $C_4$  hydrocarbons is the manufacture of butadiene. Ruebensaal states that in 1961 35% was made from butane, 45% from dehydrogenation of butylenes, and the remaining 20% by recovery of by-product butadiene from ethylene plants. However, with heavier feedstocks becoming probable for ethylene plants in the United States (unless their availability is also limited as suggested in Kay's paper), by-product butadiene should rapidly increase at the expense of that made from primary processes (from butane or butylenes). The butadiene market forecasts show no real decline in growth but some product variations. Projections for styrene-butadiene rubbers are given by Ruebensaal, polybutadiene rubber by Kay et al., S type of latices by Gmitter, ABS by Shafer, nitrile rubber by Ramsey, with specialty uses by Hayes.

Butylenes have been used for chemicals, rubber, and gasoline (by alkylation with iso-butane). Smith discusses the latter market which has been largely dependent on the butylenes made by catalytic cracking in the refineries. He adds that the use of new zeolite type of cracking catalysts is materially reducing this supply and may require replacement of butylenes by other olefins (such as ethylene and propylene) in the future. Hunter also discusses the refinery production of butylenes as well as commenting that pollution controls may decrease the market for butanes for volatility in gasoline. This, plus the increase in hydrocracking, may increase the supply of saturated  $C_4$ 's. Cracking of these is, of course, practiced in the chemical industry. The use of normal butylenes for chemicals is outlined by Tucker, isobutylenes for butyl rubber by Ernst, and nonrubber uses of isobutylene by Perry.

Western Europe has many steam cracking units on naphthas which provide appreciable by-product  $C_4$ 's as described by Ericsson. Therefore, only a small part of the butadiene demand in Europe must be met by primary processes. Possible oversupply of butadiene there and in Japan, which also is long on naphtha cracking, may add the factor of butadiene imports to the United States. Finally, Craig presents a detailed study of  $C_4$ 's in Mexico and Central and South America.

In the area of  $C_4$  hydrocarbon fundamentals, Myers discusses catalytic isomerization and hydrogenation of butenes. Cuprous chloride is used in butadiene recovery by complexing, and Long describes some of the chemistry involved. Gebhart et al. presents information on using gas hydrates to assist in separation of some of the hydrocarbon mixtures.

I wish to express my appreciation to the authors of the papers in this volume, all of which should be of broad interest to the industry. Thanks also to the chairmen of the sessions in New Orleans, R.W. Parsons, R.E. Babcock, S.M. Frank (for whom I was vice-chairman in the steam cracking area), W.A. McMinn, M.J. Auzine, G.H. Dale, and R.L. Robinson.

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# NATURALLY OCCURRING BUTANES

*LeRoy Culbertson, C. R. Ringham, and Bruce L. Bates*

The location of the major sources of naturally occurring butanes is discussed in this paper with major emphasis on butanes in natural gas and crude oil in the United States. An estimate on reserves and a forecast of future rates of production are included, and the effect of the major variables which influence rates of production is examined.

This paper will examine past production trends and estimate future production rates of naturally occurring butanes. It will be further limited to those butanes which are potentially available from crude oil and natural gas reserves in the contiguous forty-eight states of the United States. Those butanes are excluded that are produced in refineries other than those butanes contained in the crude at the inlet, which would exclude butanes produced by cracking or reforming operations. Thus, the subject matter will deal primarily with butanes that are recovered from natural gas processing facilities and from the fractionation of crude oil. No effort has been made to separately identify the iso and normal butanes that would be available from crude oil and natural gas, and we will deal in this paper with the amount of iso and normal butane collectively that has been recovered and that which is estimated to be recovered in the future.

## PREMISES

In connection with forecasting future rates of crude and natural gas production, it has been necessary to adopt several broad premises. First, it is assumed that there will be no significant changes between the relative values of the various sources of primary energy, and that there will be sufficient crude oil and natural gas produced to meet the logical markets for those two products. It is further assumed that there will be no revolutionary developments in the technology of natural gas liquids recovery or the refining of crude oil. In short, this paper attempts only to anticipate what would happen during the normal course of business between now and 1980, which we have selected as a reference year for forecasting purposes.

## ENERGY FORECAST

Various students of the United States energy market have forecast total energy demands for the year 1980 and have estimated what portion of those energy demands will be supplied by natural gas and crude oil. A study prepared by the Department of Interior in 1968 has been chosen as a reference base. It estimates that the total United States energy demand in 1980 will be 88.1 quadrillion B.t.u., which includes an estimated crude oil demand of 18.2 million barrels/day and a gas

demand of 24.6 trillion cu.ft./yr. This forecasting anticipates that the energy supplied by petroleum and natural gas will increase between 1967 and 1980, but that increase will not be as great as the increase in total energy demands. Thus, the percentage of energy now being supplied by petroleum and natural gas is 74% and by 1980 petroleum and natural gas will be supplying only 70% of the total energy demand. While this amounts to a reduction of approximately 4% in the percentage share of the total energy demands, it nonetheless represents a significant increase over 1967 production rates. Other estimates of energy demand for the United States vary considerably from the Department of Interior estimate. Some estimates of total energy demands run as high as 92 and others as low as 87.2 quadrillion B.t.u. Thus, it can be seen that the Department of Interior has perhaps been slightly less optimistic on future total energy demands, although the projections of crude oil demands are in very close agreement. Estimates of natural gas demands, however, vary from a high of 30.8 to a low of 23.6 trillion cu. ft. Variations in estimates of energy demands are cited at this point to emphasize that there is a significant difference in various experts' opinions as to what the total energy demands will be in 1980. As the basis for these estimates are developed, one should be able to assess the possible impact of variations in total energy demand on volumes of crude oil refined and natural gas produced. These volumes in turn will affect the problem of forecasting butane availability.

## FUTURE AVAILABILITY OF NATURAL GAS

Forecasts of energy demands are frequently subject to the qualifying statement that these demands are based on the assumption that adequate supplies of the primary forms of energy will be available. It is important to recognize that in the case of natural gas there are clear indications that unless current trends in the discovery of natural gas are reversed, by the year 1980 this assumption may not be valid. The American Petroleum Institute, American Gas Association, Inc., and the Canadian Petroleum Association have for several years published estimates of proven reserves of crude oil, natural gas liquids, and natural gas in the United States and Canada. The most recent of these publications is dated May, 1968, and reports proved reserves as of December 31, 1967, of 292.9

trillion cu. ft. of natural gas and 8.6 million barrels of natural gas liquids in the United States. Page 131 of the report tabulates estimated proven reserves of natural gas at year end and preliminary net production during the year by years for the period 1945 through 1967. Using this data, we have computed a reserves to production ratio by dividing the estimated proven reserves at year end by the preliminary net production during the same year. This gives a good indication of whether or not the industry is discovering replacement reserves in sufficient quantities to keep pace with the demand for natural gas on a historical basis. For the period from 1946 through 1967 the reserves to production ratio for natural gas has declined from a high of 32.5 yr. in 1946 to a low of 15.9 yr. in 1967. With this steady erosion in the reserves to production ratio, it can clearly be recognized that the demand for natural gas has historically outstripped the discovery of replacement reserves.

The Potential Gas Committee in its report titled "Potential Supply of Natural Gas in the United States as of December 31, 1966," states that the estimated potential supply of natural gas, not including proven reserves, is as follows:

Category	Trillions of Cubic Feet at 14.73 lb./sq. in. and 60° F.
Probable	300
Possible	210
Speculative	180
Total	690

The Potential Gas Committee describes the methods which were employed by a highly qualified team of reserves experts in arriving at potential gas reserves, but one key premise incorporated in their work has been the assumption of an adequate price for natural gas.

Natural gas sold in interstate commerce has the dubious distinction of being the only present major source of primary energy which the federal government has chosen to bring under price regulation at the point of production. It therefore appears incumbent on the authors to direct attention to the fact that unless adequate incentives are provided which will encourage the producers of natural gas to accelerate their exploration for this important source of primary energy, the assumption as to the adequacy of the supply of natural gas in 1980 and beyond is subject to serious question. The history of gas discoveries supports the contention that improvements in technology of gas exploration must be further supported by an upward revision in the federal government's attitude toward the value of gas at the wellhead. The Potential Gas Committee's analysis of future reserves which may be discovered under the assumption of adequate but reasonable prices indicates that the demands for 1980 could be met; however, under the present system of regulation it must be a combined effort of both government and industry if adequate supplies of this important primary source of energy are to be made available in the future. Considering the time lag between a revision of government policies relative to natural gas and the allocation of manpower

and money for the exploration, discovery, and development of natural gas producing capacity, it appears these changes in government policies should be made now. In forecasting the butanes available from natural gas, we have assumed that such will be the case.

While all are aware of current drilling activities on the North Slope of Alaska, it is not possible to evaluate this future impact until more information on the magnitude of the deposits is available.

TABLE 1. GAS PRODUCED AND GAS PROCESSED IN  
THE UNITED STATES — TRILLION CUBIC FEET  
(Bureau of Mines data)

Year	TCF produced		Total	Tcf Gas processed
	Gas well gas	Oil well gas		
1958	9.2	4.0	13.2	8.5
1959	10.1	4.1	14.2	9.2
1960	10.9	4.2	15.1	9.8
1961	11.2	4.3	15.5	10.3
1962	11.7	4.3	16.0	11.1
1963	12.6	4.4	17.0	12.4
1964	13.0	4.4	17.4	13.2
1965	13.5	4.4	17.9	13.8
1966	13.9	5.1	19.0	14.9
1967	15.3	4.9	20.2	15.6

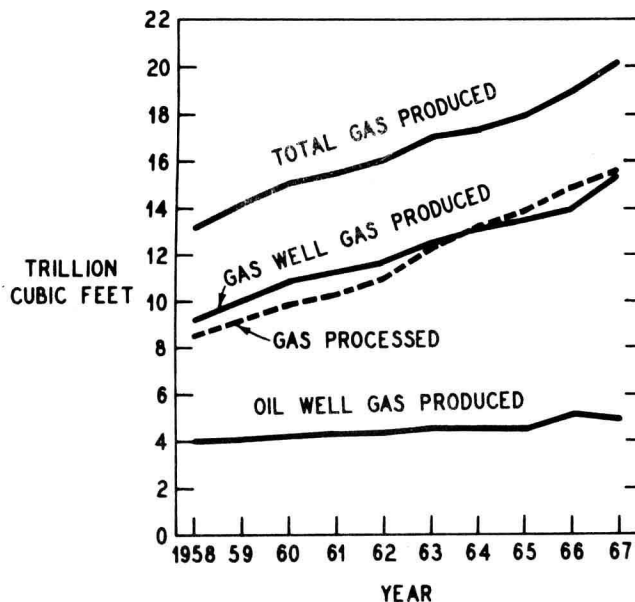


Fig. 1. Gas produced and gas processed in the United States, trillion cubic feet (Bureau of Mines data).

## BUTANES FROM NATURAL GAS

Table 1 shows the gas production and the gas processed in the United States expressed in trillions of cubic feet for the period 1958 through 1967 based on Bureau of Mines data. It will be noted from an examination of this table that annual gas production has increased from 13.4 trillion cu. ft. in 1958 to 20.2 trillion in 1967 and that gas processed has increased from 8.5 trillion cu. ft. in 1958 to 15.6 trillion in 1967 (see Figure 1). Table 2 relates the oil well gas production to the total gas produced, depicts the percentage of total gas production that has been processed for the extraction of natural gas liquids, and shows the butanes that have been recovered from natural gas during the same period. This table shows three significant trends. First, it shows that the percentage of total gas produced that is oil well gas has declined from 30.3 to 24.3%. Fewer sizable oil fields are being discovered as compared with the more prolific gas and distillate field developments. Next, this table shows that the percentage of gas processed compared with total gas production has increased from 64.4 to 77.2%. More extraction plants have been built, and many existing gas processing facilities have been expanded to accommodate increased gas de-

TABLE 2. OIL WELL GAS — GAS PROCESSED — BUTANES PRODUCED — UNITED STATES  
(Bureau of Mines data — modified butanes data)

Year	Oil well gas as percentage of total gas produced	Gas processed as percentage of total gas produced	Gallons butanes produced per thousand cu. ft. processed
1958	30.3	64.4	0.390
1959	28.9	64.8	0.397
1960	27.8	64.9	0.381
1961	27.7	66.5	0.379
1962	26.9	69.4	0.359
1963	25.9	72.9	0.342
1964	25.3	75.9	0.334
1965	24.6	77.1	0.335
1966	26.8	78.4	0.341
1967	24.3	77.2	0.355

livery rates. This trend most certainly will continue. Finally, this table shows that the gallons of butanes recovered per thousand cubic feet of gas processed have declined from a value of 0.390 in 1958 to 0.355 in 1967. This is to be expected, because the new gas discoveries have been in deeper pay zones where the natural gas liquids content is much lower when compared with the content of oil well gas (see Figure 2).

Table 3 shows the volumes of butanes and isobutane, as such, as reported by the Bureau of Mines and the estimate of butanes production from natural gas liquid (NGL) plants which was used in deriving the gallons per Mcf of butanes recovered shown in Table 2. This is a modification of the

Bureau of Mines production data because their data do not break out the amount of butanes contained in the butane-propane mix and in natural gasolines. In making these modifications of the Bureau of Mines data, we have used the following factors:

1. Butane-propane mix. It is assumed that the reported volumes contained 65% butanes. This premise is the same as assuming that the butane-propane mix had an average Reid vapor pressure slightly in excess of 100 lb./sq. in.

2. Natural gasoline. The Bureau of Mines has for several years reported natural gasoline production in a range of vapor

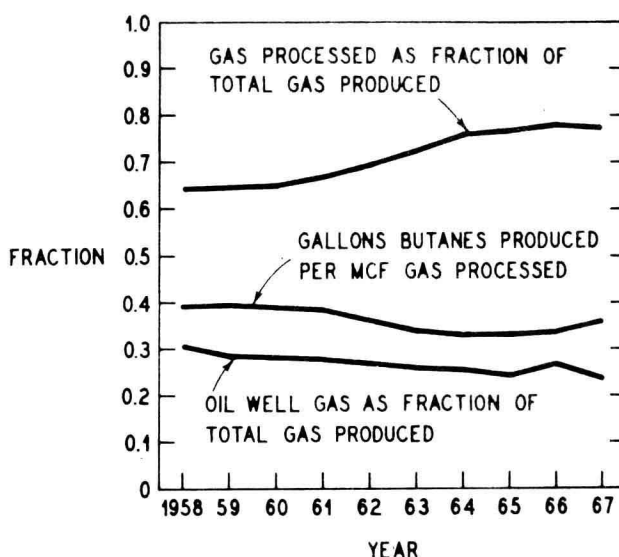


Fig. 2. Oil well gas-gas processed-butanes produced, United States (Bureau of Mines data, USA modified butanes data).

pressures. The ranges and the percentages of butanes which have been premised to be contained therein are as follows:

Natural gasoline vapor pressure	% butanes
12 lb. and below	0
Over 12 lb. but less than 14 lb.	2.5
14 lb. but less than 18 lb.	10.0
18 lb. but less than 22 lb.	20.0
22 lb. but less than 26 lb.	30.0
26 lb. and over	35.0

The tabulation of natural gasoline by grades was analyzed for a 4 yr. period to determine the percentage of butanes contained in natural gasoline, and this percentage was applied retroactively to 1958 to give an estimate of the total butanes actually recovered regardless of the product category which was reported to the Bureau of Mines. These factors are defined so that one may more clearly understand how this paper has approached the problem of estimating the amount of butanes



TABLE 3. TOTAL BUTANES PRODUCED FROM  
NGL PLANTS, UNITED STATES  
(Modified Bureau of Mines Data)

Year	Butanes volume shown by B.O.M.	Million barrels Iso-butane volume shown by B.O.M.	Total butanes reflected by B.O.M.*
1958	41	18	79
1959	48	16	87
1960	50	17	89
1961	51	19	93
1962	51	20	95
1963	56	22	101
1964	58	23	105
1965	62	25	110
1966	70	27	121
1967	75	29	132

\*Includes butanes from butane-propane mix and from natural gasoline.

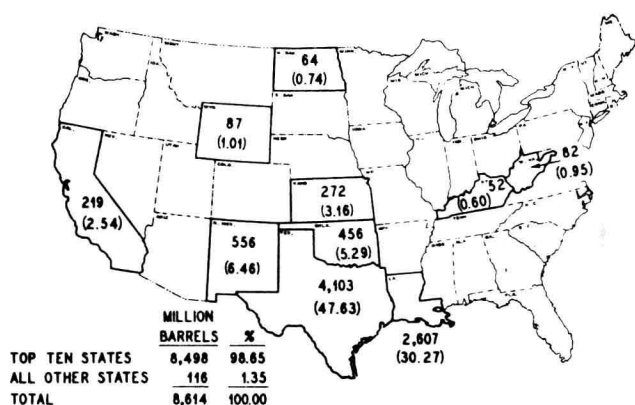


Fig. 3. Estimated total proved recoverable reserves of natural gas liquids, million barrels and percent as of 12/31/67 (data from AGA-API-CPA report).

recovered from the natural gas processed in the United States and so that one will not be surprised when this paper's estimate of the butanes production is compared with the butanes production as reported by the Bureau of Mines. No attempt has been made to estimate the quantity of butanes contained in the condensate reported by the Bureau of Mines as being delivered to gasoline plants.

In forecasting the amount of butanes which will be recovered from natural gas in the future, the three basic trends which are revealed in Table 2 will probably continue through the period ending in 1980. Extrapolation has been made to the year 1980 of the gallons of butane recovered per thousand

cubic feet of gas processed, and it is concluded that the recovered gallons per Mcf of butanes will decline to approximately 0.3. The amount of oil well gas expressed as a percentage of total gas production will continue to decline, and the percentage of gas processed compared with total gas production will increase. It is probable that only a very modest increase in the depth of extraction of butanes will occur, along with a very modest increase in the percentage of gas processed, and a significant decrease in the percentage of oil well gas produced as compared with total gas production is foreseen. This has resulted in the conclusion, as shown in Table 4, that in 1980 approximately 160 million barrels of butanes will be recovered by NGL plants. This would compare with the calculated 132 million barrels of butanes recovered in 1967 based on this paper's modification of the Bureau of Mines data. As for the location of the current reserves of natural gas liquids, reliance is placed on the estimated total proven recoverable reserves of natural gas liquids contained in the December 31, 1967, report sponsored by the American Gas Association, the American Petroleum Institute, and the Canadian Petroleum Association. Reference will be made later to the butanes contained in crude to refineries. Table 5 shows the recoverable NGL reserves in mil-

TABLE 4. TOTAL PRODUCTION OF NATURALLY  
OCCURRING BUTANES, UNITED STATES  
Million barrels of butanes

Year	(1) From NGL plants	(2) Contained in crude to refineries	Total
1967	132	36	168
1980	160	66	226

- (1) 1967 — Modified Bureau of Mines data.  
1980 — Forecast based on the 24.6 TCF gas consumption projected by the Bureau of Mines.
- (2) 1% of the crude petroleum input at refineries reported by the Bureau of Mines.

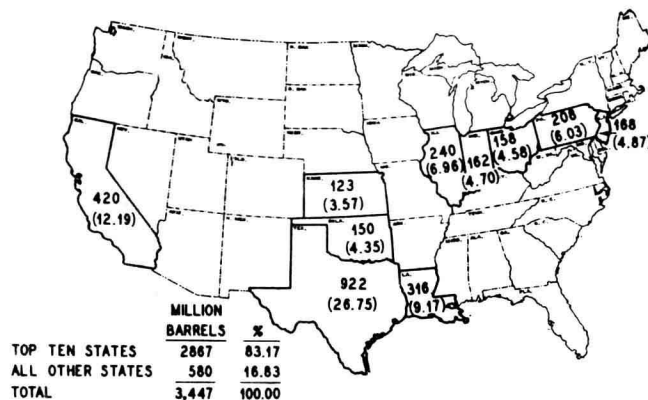
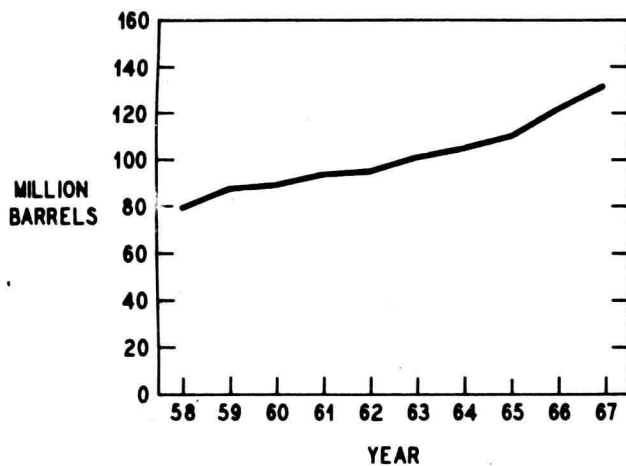


Fig. 4. Crude petroleum input at refineries, million barrels and percent in 1966 (Bureau of Mines data).

**TABLE 5. ESTIMATED TOTAL PROVED RECOVERABLE RESERVES OF NATURAL GAS LIQUIDS IN THE UNITED STATES AS OF 12/31/67**  
(Data from AGA-API-CPA report)

State	Recoverable NGL reserves	
	Million barrels	%
California	219	2.54
Kansas	272	3.16
Kentucky	52	.60
Louisiana	2,607	30.27
New Mexico	556	6.46
North Dakota	64	.74
Oklahoma	456	5.29
Texas	4,103	47.63
West Virginia	82	.95
Wyoming	87	1.01
All others	116	1.35
Total	8,614	100.00



**Fig. 5. Estimated total proved recoverable reserves of natural gas liquids, millions barrels and percent as of 12/31/67**  
(data from AGA-API-CPA report).

lions of barrels and the amount and percentage of these in each of the ten states having the largest reserves. Approximately 48% of the NGL reserves are located in Texas, slightly in excess of 30% of these reserves are located in Louisiana, New Mexico has approximately 6.5%, and Oklahoma has 5.3%. No other state has as much as 4% of the NGL reserves. Because it is close to the historical average, it has been estimated that approximately 20% of those NGL reserves are butanes (see Figure 3).

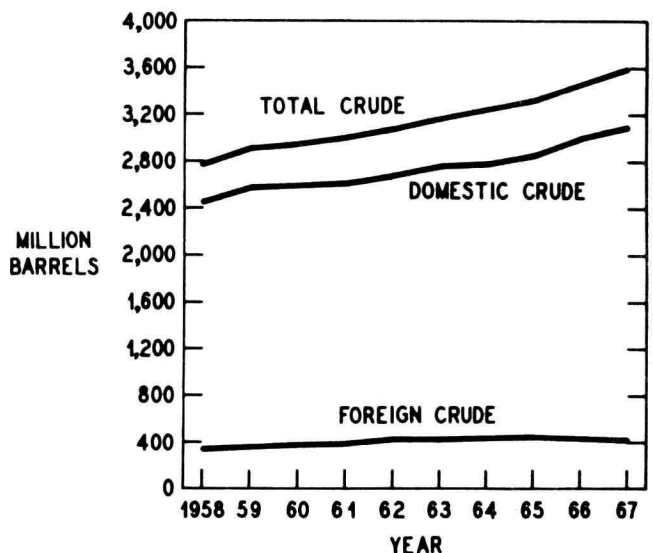
#### BUTANES FROM CRUDE

The amount of butanes that is naturally occurring in crude oil is very difficult to document from published sources. Considerable work has undoubtedly been done by individual companies on individual crudes. This paper relies on an estimate which was secured from a study commissioned by the API

titled "U.S. Motor Gasoline Economics," prepared by Bonner, Moore and Associates, Inc. Although this study was undertaken for other purposes, it indicated that butanes contained in crude charged to refineries would probably average 1%. This value is credible in the light of experience. The reader is reminded again that this paper does not attempt to analyze the effect of refinery operations, such as cracking and reforming, which would produce butanes from some of the heavier hydrocarbons in crude, but only attempts to assess the amount of naturally occurring butanes that are contained in crude charged to refineries. The crude petroleum input to refineries in the United States, based on Bureau of Mines data, is shown in Table 6 in millions of barrels per year. As shown in this table, crude refined has increased from 2.789 trillion barrels in 1958 to 3.583 trillion barrels in 1967. Table 7 shows the amount and percentage of crude refined in the top ten states during 1966. This table is designed to indicate the probable location of naturally occurring refinery butanes. There is a considerable

**TABLE 6. CRUDE PETROLEUM INPUT AT REFINERIES, UNITED STATES**  
(Bureau of Mines data)

Year	Million barrels		Total
	Domestic	Foreign	
1958	2,444	345	2,789
1959	2,566	352	2,918
1960	2,582	371	2,953
1961	2,604	383	2,987
1962	2,660	410	3,070
1963	2,758	412	3,170
1964	2,786	437	3,223
1965	2,848	453	3,301
1966	3,001	446	3,447
1967	3,174	409	3,583



**Fig. 6. Crude petroleum input at refineries, United States**  
(Bureau of Mines data).

TABLE 7. CRUDE INPUT, BY STATES, AT REFINERIES  
IN 1966, UNITED STATES  
(Bureau of Mines data)

State	Million barrels	%
California	420	12.19
Illinois	240	6.96
Indiana	162	4.70
Kansas	123	3.57
Louisiana	316	9.17
New Jersey	168	4.87
Ohio	158	4.58
Oklahoma	150	4.35
Pennsylvania	208	6.03
Texas	922	26.75
All others	<u>580</u>	<u>16.83</u>
Total	3,447	100.00

difference in the location of the refinery butanes as compared with the natural gas liquid reserves. Although Texas leads the list in volume of crude refined with approximately 27%, California is second in crude refined with slightly more than 12%, and Louisiana is third. This amounts to a considerably wider dispersion in butanes available from refineries as compared with butanes available from natural gas processing facilities (see Figure 4). Using an estimate of 1% of crude charged to refineries as being naturally occurring butanes, we conclude that the 1967 production of such butanes would be 36 million barrels and would increase in 1980 to 66 million barrels. As noted in Table 4, the total production of naturally occurring butanes in the United States in 1967 was 168 million barrels, and this is anticipated to increase to 226 million barrels in 1980.

## SUMMARY

The forecasted rate of growth of butanes produced by NGL plants for the period 1967 through 1980 is approximately 1.5%/yr. This compares with a growth rate averaging almost 6%/yr. for the period 1958 through 1967. During the earlier period, butanes from NGL plants increased from 79 million barrels in 1958 to 132 million barrels in 1967, for a gross increase of 67%. During this same period, gross gas production increased 53%, and the average butanes content of the gas processed was declining. This healthy rate of growth was the result of two factors: the gas processing industry increased the volume of gas processed by 83.5%, and the percentage of butanes extracted was increased. Since it is anticipated that the rate of growth rate of gas available for processing will decline and that the percentage of gas which will be processed will tend to level off at about 85% of the gas produced with only minor increases in the depth of extraction of butanes, it seems unlikely that the historical rate of growth can be maintained.

Crude oil charges to refineries were estimated to contain 1% butanes both in 1967 and 1980. The annual volumes of naturally occurring butanes produced from this source are forecast to increase 30 million barrels, or about the same volumetric increase forecasted for butanes from NGL plants.

The forecasted growth rate of total naturally occurring butanes produced from both NGL plants and refineries between 1967 and 1980 averages slightly less than 2%/yr. This represents an increase from 168 million barrels in 1967 to 226 million barrels in 1980. It should be emphasized that this paper has limited its attention to the naturally occurring butanes and consequently has excluded consideration of those butanes which might be produced from refineries by cracking or reforming operations, which could well represent a significant portion of the butanes available in 1980.

# FIELD PROCESSING FOR BUTANE RECOVERY

J. F. Wolfe

The field separation of butane from associated and nonassociated natural gases is accomplished through the single or combined use of absorption, adsorption, or equilibrium separation. Advantages and design considerations of each mass transfer method are discussed, and their current utilization by the petroleum industry is described.

Natural gas, as produced in the field, is primarily a mixture of light (methane-decane) paraffin hydrocarbons saturated with water vapor. In addition, varying amounts of nonhydrocarbon gases are present such as nitrogen, carbon dioxide, helium, and hydrogen sulfide, as well as small quantities of aromatics and naphthenes. The field processing of natural gas involves the removal from methane of all or part of these compounds which are more valuable as separate products, or which are considered contaminants in terms of contractual requirements imposed by the gas buyer. Discussions of methods for removing contaminants will be omitted here so that emphasis can be given to reviewing those current processing cycles used to recover light hydrocarbons as products.

## SEPARATION METHODS

Ethane, propane, butane, pentane, and heavier gas components are those normally considered for field recovery. Their relative composition in a typical natural gas is shown in Table 1. Liquid equivalent values at standard conditions are also given. Since butanes are in the middle ranges of recoverable component volatilities, their separation from the gas mixture must involve other components as well. Designing a process to treat such a gas as shown in Table 1 requires a decision as to which and how much of the lightest component is to be separated from the gas; the lighter or higher in the mixture the de-

sign cut is made, the more expensive the process. Once the design recovery component is chosen, the heavier fractions will also be removed by the process as established by the gas composition, relative component volatilities, and to a lesser degree, process type.

Current gas processing plants, for example, are typically designed to recover 25 to 60% of the ethane, 60 to 95% propane, and in excess of 95% of the butanes and pentane plus fractions.

Although many process variations and types are prevalent in the gas industry, this primary separation is always accomplished by single or repeated application of the following two techniques: alteration of the mixture temperature, pressure, or composition to form a vapor-liquid phase system having the product fractions most concentrated in the liquid phase; putting the mixture in contact with an adsorbent which has preferential adsorption characteristics to the higher molecular components. Following the principal separation, major field plants also fractionate the recovered light hydrocarbons into pure or combined products for storage and transmission.

Table 2 gives the product breakdown and rates for the United States gas processing industry as of January 1, 1968. As shown in the table, normal butane and iso-butane are produced in several product streams. In addition to pure iso-butane and

TABLE 1. TYPICAL NATURAL GAS FEED COMPOSITION

Component	Mole %	Liquid equivalent in gallons* at standard conditions per million standard cubic feet feed gas
N <sub>2</sub> & CO <sub>2</sub>	1.10	
Methane	93.00	
Ethane	3.50	880
Propane	1.50	410
i-Butane	0.35	110
n-Butane	0.30	94
Pentane +	0.25	92
	100.00	

Esso Production Research Company, Houston, Texas

TABLE 2. UNITED STATES GAS PROCESSING,  
JANUARY 1, 1968\*

Number of Plants: 836

Natural gas throughput: 53,090 million std. cu. ft./day

Products	gal./day
Propane	15,496,045
Iso-butane	2,299,435
N-butane and Normal iso Mix	7,351,480
Gasoline + LPG	26,953,775
Debutanized Gasoline	7,561,615
Other †	8,958,345
	71,521,685

\* *Oil & Gas Journal*, March 25, 1968.

† Includes condensate and ethane.

a normal iso mix, butanes are mixed with propane to form liquefied petroleum gas (LPG), both as an LPG product and as a gasoline-LPG product mix. The other product consisting mainly of condensate and ethane contains small amounts of butane in the condensate portion. Total butane production is about 14 million gal./day.

Table 3 illustrates the different types of processes which are used to process the gas for the products listed in Table 2. With the exception of adsorption, all the processes rely on the development of vapor-liquid phase systems to affect product separation from the primary gas stream. Reasons for the predominance of one technique over another will be discussed as each is reviewed in terms of its operation and advantages.

## REFRIGERATION

The use of refrigeration alone for gas separation implies that cooling is added from some external source, or some form of autorefrigeration is used. Figure 1 shows the cycle for a typical low temperature separator (low in this case refers to temperatures of about 0° to 50°F.) which utilizes the Joule-Thompson expansion for refrigeration to produce a condensate product.

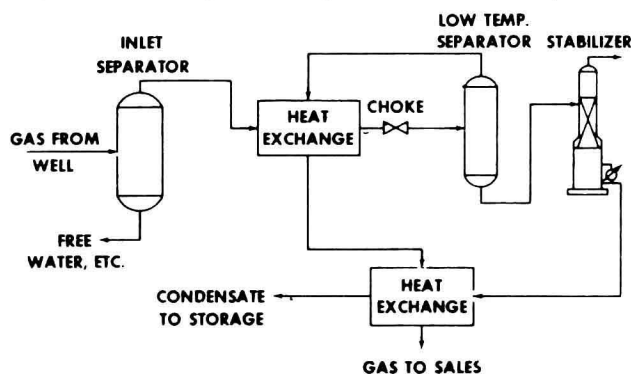


Fig. 1. Low temperature separation of condensate.

Condensate is a colloquial term applying to any liquid phase which is easily and readily achieved from a produced natural gas near the wellhead. Most wellhead gas which flows into ambient temperature surface separators will produce some condensate owing to the temperature drop from reservoir conditions. Although the pressure loss encountered by the gas in flowing to the surface tends to retard the amount of condensate produced by temperature effects, some high pressure gas mixtures exhibit a retrograde behavior where the pressure loss contributes to the formation of condensate. In either case, the amount of liquid product produced in this manner at the surface can be increased by surface cooling. Condensate, whether produced in an ambient temperature surface separator or a low temperature separator, contains most of the pentane and heavier components in the gas. Quantities of butane and higher fractions present are frequently lost through vaporization when the condensate is stored under atmospheric pressure and temperature conditions.

The low temperature separator schematic in Figure 1 is a representative process for recovering condensate from high

pressure gas. The inlet gas is precooled and expanded across the Joule-Thompson valve from its available pressure to the pressure level consistent with the sale system. Generally, the sales gas line is near 1,000 lb./sq. in. By assuming an inlet temperature of 100°F. and an inlet pressure of 2,000 lb./sq. in. abs., expansion to 1,000 lb./sq. in. abs. in this arrangement will achieve a temperature around 30°F. in the low temperature separator. Hydrate formation is usually prevented by glycol or methanol injection with the feed gas. Liquid from the separator is sometimes fed to a small stabilizing column as shown to remove most methane, ethane, and propane that has condensed with the liquid. The stabilizing column itself is usually a small packed tower with no reflux which operates at a pressure near 250 lb./sq. in. abs. Failure to stabilize the separator liquid prior to storing under atmospheric conditions will result in a smaller volume of product because the presence of very light components accelerates the loss of pentane and butane during storage weathering.

Low temperature separator units are small, often skid mounted, and are suitable for remote locations. They are used when major plant facilities are infeasible or under conditions where so much condensate is present in the wellhead gas that treatment is necessary prior to sending the gas to a major processing plant.

## ADSORPTION

The use of adsorbents (silica gel, alumina, charcoal, etc.) in gas processing was formerly limited to water dehydration. Later, these general adsorbents were conveniently utilized to remove condensate from small flow gas streams which were too lean to be effectively treated by low temperature separation methods. These small, condensate recovery systems were called *short cycle units*. They are still widely used throughout the industry, generally on gas streams of less than 50 million std. cu. ft./day. They contribute little to butane production, but the principles used in short cycle plants are currently being applied in larger processes for recovering propane and butane, with charcoal used as the adsorbent.

The flow schematic in Figure 2 illustrates the principle of separating gas mixtures by adsorption. Adsorption operations may be divided into two main phases: adsorption and regeneration. First, one column is used to adsorb, while the other columns are being regenerated; then the roles are reversed. Two and three tower configurations are the most common. The three tower system shown in Figure 2 permits the regeneration phase to operate cooling and heating cycles simultaneously on the two regenerating columns. Two regeneration schemes are used: closed and open cycle. In a closed cycle unit, the regeneration gas travels in a loop and is used over and over again. In an open cycle (Figure 2), a portion of the inlet gas is used to regenerate the saturated bed. This gas is used only once, and then it is returned to the main stream. The open cycle has the advantage that its operation requires no regeneration gas pump, but it has the disadvantage of causing some bed presaturation during cooling.



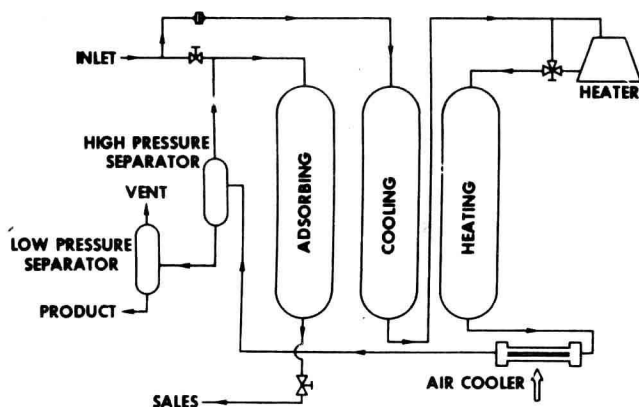


Fig. 2. Adsorption recovery unit.

Inlet gas enters the top of a cool bed of adsorbent, and the heavier components in the natural gas mixture are adsorbed in a narrow band. Since the adsorbent has a greater affinity for heavier hydrocarbons than light ones, the adsorbent at the top of the column becomes saturated with ethane more quickly than it does with propane and saturated sooner with propane than with butane, etc. As more gas enters the column there is no more room at the top for, say, ethane, so that component is carried downward until it encounters fresh adsorbent. This process is repeated continuously for all components of the mixture. Consequently, inside the column there are waves or bands of components traveling down the column at different speeds. The speeds are dependent on the capacity of the adsorbent for different components. These adsorption bands do not have sharp distinct fronts but rather have diffuse boundaries due to nonuniform velocity profiles and transient mass transfer rates. Since the lightest component reaches the bottom of the adsorbing column first, the adsorbing cycle is terminated when the lightest component desired to be recovered begins to emerge as effluent from the bottom of the tower. At that time, the adsorbing tower is put on regeneration, the cooling tower is put on adsorbing, and the heating tower is put on cooling. Hot gas forced downward through the column saturated with product desorbs this material which is condensed and separated for subsequent storage or fractionation.

If pentane-plus recovery only is desired from an adsorbing system, then, as with low temperature saturators, the product can be transferred directly to atmospheric storage with only nominal loss due to vaporization. Also, cycle times are reasonable, and equipment and energy requirements are sufficiently low for the relatively small amount of condensate produced. On the other hand, if the adsorbing system is to recover propane-plus components, product fractionation and pressure storage will be required. Cycle times will be accordingly shorter (or the amount of adsorbent must be increased) and regeneration heat loads higher. These increased costs are offset by higher product volumes. There is current industry interest in processes using charcoal for recovering propane-plus components at gas flows up to 300 to 500 million std. cu ft./day. There has not been enough experience with this technique, however, to

determine its competitive position with absorption recovery plants.

## ABSORPTION AND REFRIGERATED ABSORPTION

As shown in Table 3, absorption processes accept about 86% of all gas processed in the United States. Absorption plants are large expensive facilities that have favorable economics for high gas throughputs (100 to 1,000 million std. cu. ft./day) and where butane, propane, and ethane are to be removed from the gas. Because of their size, absorption plants usually incorporate fractionating capability in addition to the basic separation unit operations.

TABLE 3. RELATIVE USE OF MAJOR PROCESSES

Process method	Approximate percent of total gas processed
Absorption — refrigeration	48
Absorption	38
Adsorption	8
Refrigeration	3
Other	3
	100

Absorption implies the closed loop circulation of a hydrocarbon stream called an *oil*. This oil is the stripping medium which removes or absorbs the natural gas product components. The oil is called *lean oil* without any gas components present and *rich oil* when it contains light gas hydrocarbons.

Contacting between the oil and the feed gas is done at high pressure in a countercurrent flow column. Early major gas plants operated these absorption towers near ambient temperature with approximately 200 molecular wt. oil and were designed to remove some propane and most of the butane-plus components from the gas. Emphasis in the last 10 yr., however, has been to near total recovery of propane and significant recovery of ethane. The most feasible process alteration for accomplishing this more difficult separation was to lower the temperature of absorption by refrigerating the oil and gas and by reducing the oil's molecular weight to the 100 mw. range. Most recent major gas facilities are of this refrigerated absorption type, as illustrated in Figure 3.

Absorption towers usually operate between 800 and 1,200 lb./sq. in. abs. and at temperatures between 0° and -40°F. Refrigeration is most often provided by closed loop propane systems. A typical plant with a gas throughput of 500 million std. cu. ft./day having the composition given in Table 1, designed to recover 25% ethane, 80% propane, and essentially all butane-plus, would cost about \$8,000,000.

After it is dried and cleaned, the inlet gas is chilled by cold residue gas and propane refrigeration prior to absorption. Cold lean absorption oil enters the top of the absorber column and flows countercurrently with the feed gas. The column is

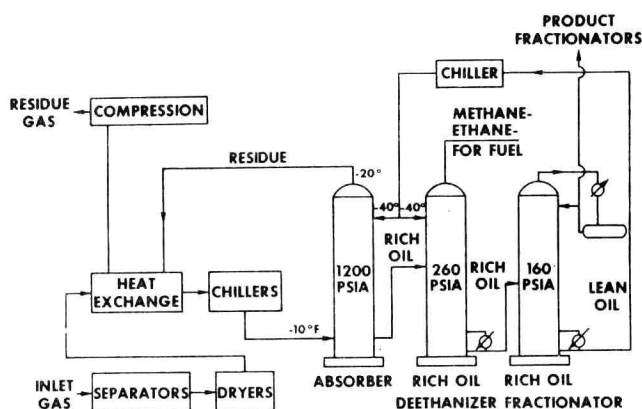


Fig. 3. Refrigerated lean oil absorption cycle.

not refluxed, nor does it use reboilers. Rich oil from the bottom of the absorber will contain, in addition to the desired products, excessive amounts of methane and possibly ethane. These excess light components are removed from the rich oil in a fractionating column called a *deethanizer* operating at a lower pressure level and refluxed with lean oil. Frequently some demethanization is incorporated at higher pressure levels before deethanization so as to minimize compression requirements on methane. Following deethanization, the rich oil is fractionated at a reduced pressure, with gasoline and lighter fractions taken overhead, and lean oil from the bottoms is recirculated for chilling and return to the absorption towers.

Components in the inlet gas which are in the same molecular weight range as the circulating lean oil are picked up in the bottom of the rich oil fractionator and serve as a makeup source of oil. This replenishing of the oil tends to offset oil losses at the top of the absorber due to the oil's light molecular weight and relatively high volatility. This means that the oil will assume a different composition characteristic with time as determined by the heavy components in the inlet gas. If significant amounts of naphthenes or aromatics are involved, the resulting oil composition change can affect recovery in the primary absorber. If lean oil losses in the absorption overhead are excessive, an additional oil cycle (requiring an additional tower) with a slightly heavier oil (called *sponge oil*) may be employed to recover the primary lean oil loss.

Once product recovery specifications are established, the most important design parameters are absorption temperature and pressure levels, oil molecular weight, and the associated refrigeration, compression, and oil pumping requirements. These factors strongly control initial investment and also affect fuel gas consumption which is usually the largest single operating expense cost in a refrigeration absorption plant. Fuel requirements are normally about 1% of inlet gas. In a typical large facility, oil circulation rates of 2 to 3 gal./min. for every million standard cubic foot inlet gas are required. Plant pressure drops are usually small, and major compression requirements are usually established by feed gas pressure and

residue pressure requirements.

Absorption temperature levels are normally set near  $-40^{\circ}\text{F}$ . because this has proven to be a near optimum condition for minimum fuel consumption, minimum oil circulation, and hydrate inhibition. This temperature is also the practical lower limit for the use of carbon steels and, additionally, is well suited for propane refrigeration.

Overhead products condensed at the rich oil fractionator are separated into desired product streams by conventional fractionating techniques. A typical three-column sequence is shown in Figure 4. In this example, LPG and gasoline fractions

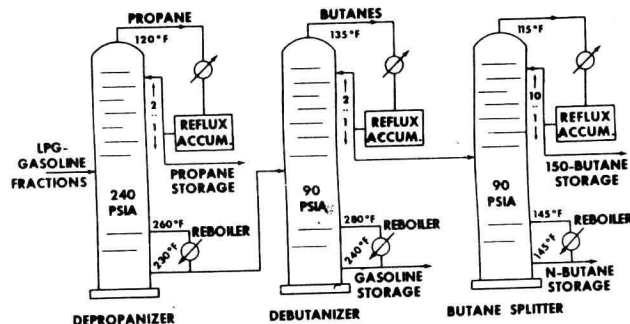


Fig. 4. Typical product fractionators.

are first depropanized and debutanized to produce propane and gasoline. Butanes taken overhead in the debutanizer can be separated into iso and normal components at the temperatures and pressures shown with a highly refluxed fractionator.

## CRYOGENIC FRACTIONATION

A process having the potential of competing with refrigerated absorption for separating ethane-plus components is called *cryogenic fractionation*. This cycle is illustrated in Figure 5 and is similar in concept to the low temperature separation units previously discussed. The principal difference is the method of expanding the gas to produce refrigeration. This scheme

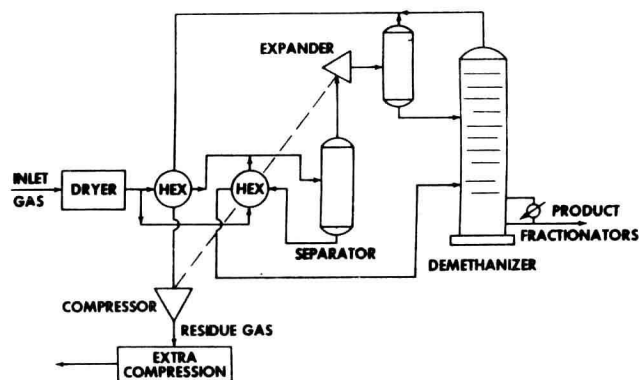


Fig. 5. Cryogenic fractionation cycle.

utilizes a highly efficient expansion turbine instead of a Joule-Thomson choke. Consequently, much lower temperatures are

achieved for a given pressure drop. Turbine expansion also produces mechanical work which can be utilized in the process to drive a centrifugal compression wheel mounted on the same shaft as the expander wheel. Thus, gas can be expanded to pressures below those required for sales and the residue gas recompressed by some fraction of the energy given up by expansion.

In a typical application, the inlet gas is dried and precooled prior to expansion. Turbines can handle large pressure ratios, and pressure drops from 2,000 to 300 lb./sq. in. abs. are representative. Adiabatic expansion efficiencies of about 80% can be expected. Such an expansion will result in temperatures near  $-150^{\circ}\text{F}$ ., with condensation of significant quantities of ethane, propane, and heavier components. As indicated in Figure 5, this cold, raw product can be stabilized with respect to excess methane and ethane in a nonrefluxing column operating at about 300 lb./sq. in. abs. As in the case with refrigerated absorption, the demethanized product is subsequently treated by product fractionators.

Cryogenic fractionation has the advantages of high thermodynamic efficiency and simplicity. The lean oil circulation system and high pressure absorption columns are eliminated. Although the cycle employed is simple and well known (it has been utilized in the separation of simple air type mixtures for many years), it has not been widely used with natural gases, mainly because their broad composition range causes condensation during expansion to almost any lower pressure. This condensation occurs inside the turbine and the blade erosion and dynamic imbalances that can be created by a condensing gas made turbine reliability a concern.

Offsetting the stated advantages, however, are increased costs resulting from special materials of construction, increased process sensitivity, difficult water dew-point requirements, and in many cases a need for additional compression. Future growth of cryogenic fractionation relative to refrigerated

absorption will depend in large measure on industry experience during the next few years.

## FUTURE TRENDS

Recapitulating, the United States gas industry is producing about 72 million gal./day of light hydrocarbon products, of which some 14 million gal. are butanes. Field processes used to obtain these products employ refrigeration, adsorption, absorption, or various combinations. By far, the most important to butane production are the major absorption and refrigerated absorption plants which handle about 86% of all natural gas treated. Recent trends have been toward increasing recovery of propane and ethane and the attendant lower processing temperatures. These trends alter the kinds of processes used for butane recovery but do not measurably change butane recovery amounts. Two new such processes, charcoal adsorption and cryogenic fractionation, are currently being applied by the gas industry.

Because natural gases are such complex mixtures and because processing conditions are conducive to very nonideal mixture behavior, the ability to predict accurately the fundamental thermodynamic properties of two-phase hydrocarbon mixtures is critically important in the design of all gas recovery processes. The gas industry has benefited from development of increased capability in this regard in the last 5 yr. The most contributing factor has been the emerging availability of digital computers. Computers have enabled complex rigorous thermodynamic relationships to be used in practical process designs. In addition, total simulation of all unit operations and their interrelationships in gas complexes are now routinely handled via computers. Future research at both the industrial and academic levels on the mathematics of unit operations, process systems, and their optimum arrangements in conjunction with continued studies of basic hydrocarbon thermodynamics should enable the gas industry to continue developing more efficient recovery processes.

# STEAM CRACKING: YESTERDAY, TODAY, AND TOMORROW

Maurice Spielman

This paper traces the development of steam cracking technology at Esso from pre World War II beginnings to the present time and takes a brief look into the future.

With the near approach of the seventy-fifth birthday of steam cracking, this paper celebrates the event by giving a brief history of the commercialization of steam cracking among the affiliates of the Standard Oil Company of New Jersey. Major emphasis will be placed on the cracking coil and furnace. The state of the art leading up to commercialization is shown. The present state of this massive industrial process is described, and some of the problems solved are discussed along with the progress made during almost 30 yr. of commercial operation. The paper concludes with a Brief look into the future.

Figure 1 shows an 1897 German patent which describes the production of aromatics from petroleum oil by retorting the oil at a bright red heat in the presence of steam (1). The noncondensable gases resulting can be used for gas lighting (which means that the gases are unsaturated), and the yield pattern depends upon the steam to hydrocarbon ratio. This German patent is right on the heels of a British patent with similar disclosures but where the red hot retort is packed with coke (2). The patent

literature from 1897 onward is dotted with steam cracking processes.

A vapor phase cracking process using steam was commercialized in Great Britain in 1908. It was called the "New Oil Refining Process." A 2/1 oil/steam mixture was fed to furnace tubes, which were packed with scrap iron and heated to a dull red heat (3, 4).

Next came the Greenstreet process, cracking oil vapors with steam and operating above 75 lb./sq. in. and up to 1,200°F. Several commercial units were built in the United States between 1911 and 1923, the largest having a feed rate of 1,500 barrels/day (4 to 6).

And, in the nineteen twenties, the I.G. Farbenindustrie received patents on the production of olefin gases from mineral oils and superheated steam by passage through a heated reaction zone at 1,450°F. (7 to 9).

By the mid nineteen thirties the petrochemical industry in the United States was in an early stage of development. Isopropanol was produced from refinery propylene. Butyl and amyl alcohols were also being made from refinery gas. The motor vehicle population had grown past twenty-five million, and there was a big market for better automotive fuels and for anti-freeze. More uses were being sought for refinery off gases other than just for refinery fuel.

New cracking and refining processes were being developed. The reactivity and potential availability of low molecular weight olefins in refinery processing were recognized. Suitable processes were sought to make the olefins.

Thermal cracking processes popular in the mid thirties are listed in Table 1. This was the era of patent wars in the refining industry, and it is difficult for any one but an attorney to distinguish between many of the processes. Most ran at 1,000 to 2,000 lb./sq. in. and around 900°F. They represented practically all the United States cracking capacity, just under two million barrels of feed per day.

Only a minor portion of this was vapor phase. Vapor phase was in disfavor because of high gas yields and the unsaturated nature of the gasoline product (gum), even though the gasoline had a satisfactory octane rating.

A feature common to all these cracking processes was the formation of coke deposits and the consequent fouling and plugging of equipment. While this may be bearable for batch processes, it was (and is) a major headache for anything claiming to be a continuous process. One well-known researcher

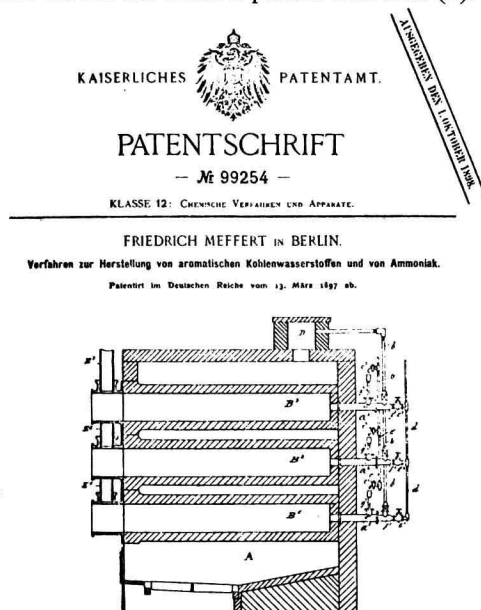


Fig. 1. An early patent claiming formation of aromatics and illuminating gas by retorting petroleum oil with steam.

\*Esso Research and Engineering Company, Florham Park, New Jersey. Now with Israel Chemicals, Ltd., Haifa.