

Dec. 9, 1952

R. W. WHITE

2,621,216

PRODUCTION OF ETHYLENE

Filed Aug. 17, 1950

2 SHEETS—SHEET 1

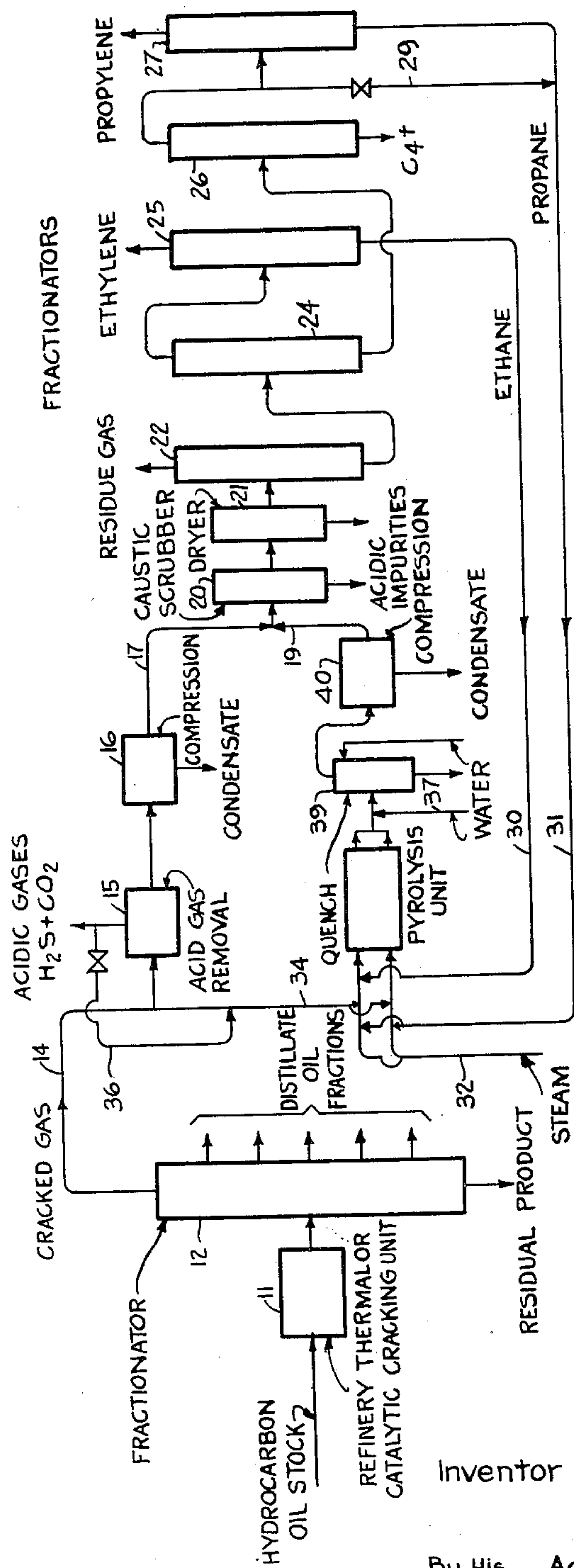


FIG. I

Inventor Robert W. White

By His Agent *John H. Colvin*

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2 SHEETS—SHEET 2

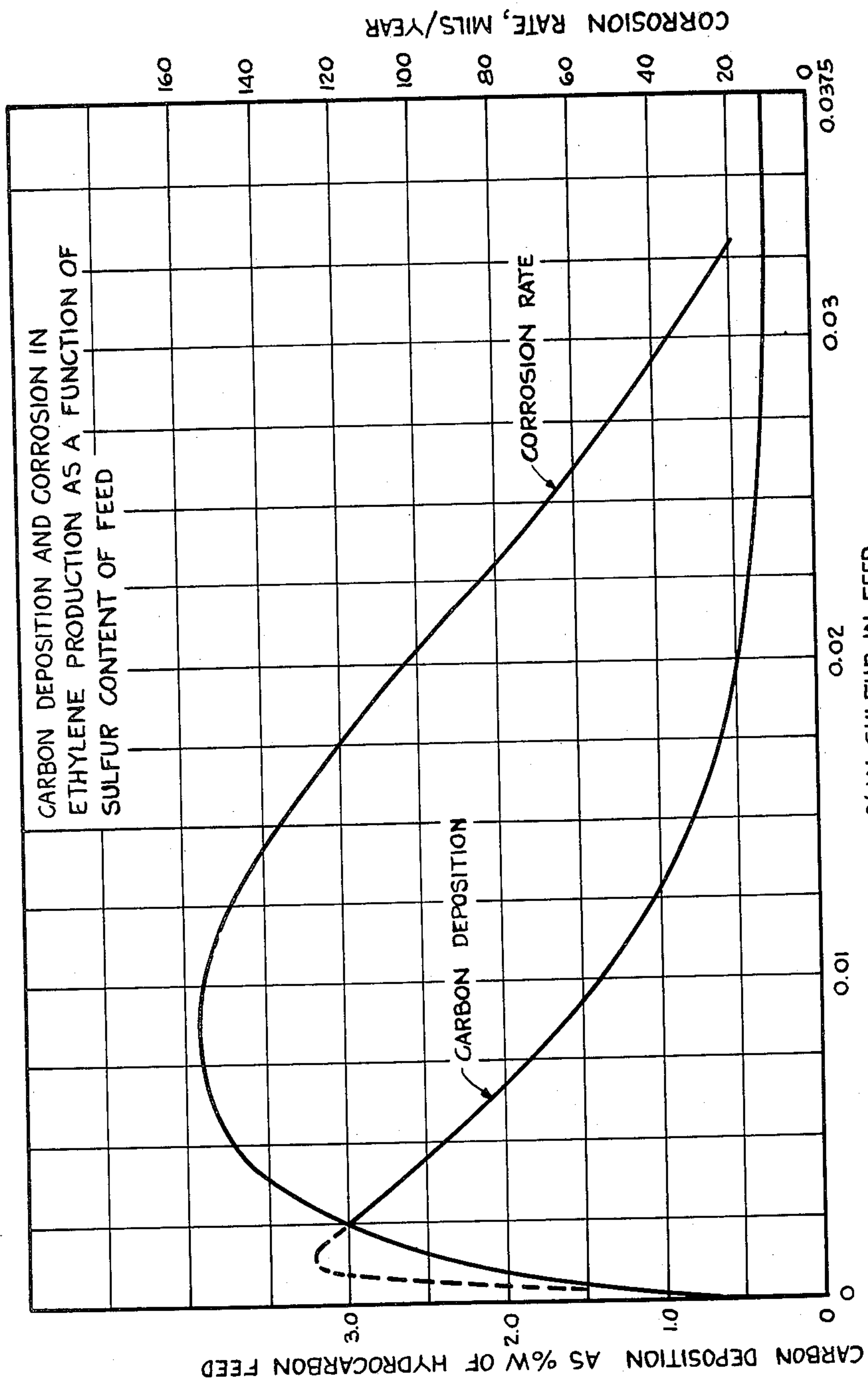


FIG. II

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By His Agent: *John H. Colvin*



## UNITED STATES PATENT OFFICE

2,621,216

## PRODUCTION OF ETHYLENE

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6 Claims. (Cl. 260—683.3)

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This invention relates to the production of ethylene, and more particularly to an improved process for the preparation of ethylene, involving the thermal cracking of ethane and/or propane.

Because of its reactivity, ethylene is coming into ever increasing demand as a raw material for the manufacture of an extremely wide variety of synthetic petroleum-derived chemical products, fuels and lubricants. Ethylene is available, as such, in refinery by-product gases, and also can readily be produced by pyrolysis (thermal cracking) of saturated light hydrocarbons, such as ethane and propane, as well as of their mixtures. The production of ethylene by pyrolysis of ethane, propane, or mixtures thereof, has been discussed in considerable detail, for example, by H. C. Schutt in the Transactions Section of the Chemical Engineering Progress, vol. 43, No. 3, March 1947, pages 103 et seq., and by C. K. Buell and L. J. Weber in Petroleum Processing, vol. 5, Nos. 3 and 4, March and April, 1950. According to H. C. Schutt, the cost of ethylene from destructive cracking of oil is appreciably higher than from mixtures of ethane and propane.

The prior art processes for the production of ethylene from light, saturated hydrocarbons, such as ethane and/or propane, involve essentially two phases of operation: the conversion of the charge by pyrolysis, and the separation by fractionation of the conversion product to recover the ethylene. Naturally, the recovered ethane and propane are recycled to the pyrolysis for more complete conversion of the available feed stock. Also, according to H. C. Schutt, it is the usual practice to admix a small amount of steam with the charge to the pyrolysis zone, even when the feed stock is absolutely sulfur-free, for the corrosion protection it affords if the charge contains small amounts of hydrogen sulfide or other impurities which may be present in the original feed. Without the presence of steam, sulfur corrosion may be acute under operating temperatures prevailing in the pyrolysis coil, especially in sections where no carbon scale forms on the tube wall. On the other hand, Buell and Weber, in discussing the effect of feed composition on the operations of the process, state that it will generally be desirable to dry the propane-ethane feed to the cracking furnaces.

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They also state that methane in the feed would simply be a diluent under the operating conditions of cracking ethane-propane to ethylene and, therefore, its presence would increase the size of the equipment and operating costs. Furthermore, since butane and heavier paraffinic hydrocarbons crack much more readily than propane or ethane, their concentration should be kept very low as some of their decomposition products degrade rapidly into tar and coke at the temperatures used for propane-ethane cracking. Still further, they state that the propylene and ethylene concentration in the feed should also be held as low as possible to prevent a loss in product since not only are these olefins partially decomposed in the cracking reaction, but also they "back out" additional fresh propane-ethane feed stock. Thus, it has been considered undesirable to subject the total cracked gas to a further thermal action to dehydrogenate saturates thereof to ethylene.

Regardless of the extensive studies which have been made on the cracking of light hydrocarbons for the production of ethylene, including commercial operations, operating and equipment costs are still higher than desired on account of insufficient tube life due to corrosive and/or erosive action, loss of operating time because of time required for decoking of the coked tubes, and the like.

It is a principal object of the present invention to provide an improved process for the production of ethylene by the cracking of hydrocarbons. Another object of the invention is to provide an improved process for the production of ethylene by cracking of hydrocarbons wherein coking of the reactor tubes is reduced to a minimum. A still further object is to provide such a process in which corrosion of the interior walls of the tubes is essentially eliminated. Another object of the invention is to provide an improved coordinated process for more efficacious production of ethylene from refinery cracked gases. These and other objects and the method of their attainment in accordance with the present invention will be better understood from the following detailed description of the invention, which will be made with reference to the accompanying drawings wherein:

Fig. I is a schematic flow diagram of an improved process for the production of ethylene



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from petroleum cracked gases involving the thermal cracking of ethane and/or propane constituents of said cracked gases and the recovery of ethylene from both the cracked gases as well as from the pyrolysis products of the thermal cracking of the ethane and/or propane; and

Fig. II shows the effect of hydrogen sulfide on carbon formation and on tube corrosion during the thermal cracking of propane to produce ethylene.

It has now been found that an improved coordinated process for the production of ethylene is provided when a cracked gas stream, as is obtained from the fractionation of products of refinery cracking operations of normally liquid hydrocarbon fractions, such as catalytic cracked gas and/or thermal cracked gas, and usually containing both saturated and unsaturated lighter hydrocarbons as well as other constituents such as nitrogen, carbon dioxide and hydrogen sulfide, is split into a major stream and a minor stream, the minor stream is blended with a major stream consisting essentially of ethane and/or propane (produced in the system as described later) and the blended feed is then pyrolyzed to produce unsaturates including ethylene as the principal unsaturate, while the first-mentioned major cracked gas stream is desulfurized, then blended with the pyrolysis product stream, the resulting mixture of cracked gas and pyrolysis gas is fractionated into separate ethane, ethylene, propylene and propane streams (as well as others), and the separated ethane and propane streams are used separately or together as feed streams in the pyrolysis operation.

Thus, whereas on the one hand the prior practices indicate that direct pyrolysis of the entire cracked gas stream should be avoided for various reasons, and on the other hand it has been the experience of the present inventor and of others that the pyrolysis of substantially pure ethane or of substantially pure propane or of mixtures thereof on a commercial scale in the production of ethylene, even in the presence of added steam for the prevention of corrosion and of coke formation, results in too much coking-up and/or corrosion of the pyrolysis tubes for desired production and operating economies, it has now been found that a coordinated process wherein a plurality of operations of fractionation, blending and pyrolysis (thermal dehydrogenation) are properly combined, overcomes the indicated difficulties associated with the separate pyrolysis of cracked gas or of pure ethane or propane, and results in a highly efficient process with practical elimination of reduced operating efficiency due to coke formation and corrosion in the pyrolysis tubes.

The invention will be better understood from the following description thereof, made with reference to Fig. I of the accompanying drawing. Referring to said Fig. I, the gaseous feed stock which provides the ethane and propane for the pyrolytic conversion to ethylene, is derived as a cracked gas product of the fraction of the mixture resulting from the thermal and/or catalytic cracking of hydrocarbon oil stocks, as normally practiced in petroleum refinery operations, for the production of various refinery products from crude petroleum, and from fractions thereof. Since in most complete refinery operations both thermal and catalytic cracking operations are practiced, both such streams are suitably used, the catalytic cracker gas generally being available at an initial higher pressure than the ther-

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mal cracked gas. Consequently, it is generally preferable to process the two streams separately through the deacidifying operation, after which they are advantageously combined. It will be understood that such parallel operations are contemplated in Fig. I as well as operations on a single product. Representative refinery cracked gas streams which are available have the approximate analyses as shown in the following Table I.

TABLE I  
REFINERY CRACKED GAS COMPOSITIONS

Component	Thermal Gas (Mol Percent)	Catalytic Gas (Mol Percent)
H <sub>2</sub>		18.7
H <sub>2</sub> +CO		22.3
CH <sub>4</sub>	47.2	21.8
CO <sub>2</sub>		2.2
H <sub>2</sub> S	1.2	5.0
C <sub>2</sub> H <sub>4</sub>	3.2	3.2
C <sub>2</sub> H <sub>6</sub>	31.8	12.6
C <sub>3</sub> H <sub>6</sub>	2.2	3.8
C <sub>3</sub> H <sub>8</sub>	4.4	0.7
C <sub>4</sub> <sup>+</sup>	1.2	0.4
H <sub>2</sub> O	0.8	0.3
Total	100.0	100.0

According to a preferred embodiment of the invention, the major portion of the refinery cracked gas stream(s) is treated to remove the acidic constituents thereof, i. e. H<sub>2</sub>S and CO<sub>2</sub>, compressed to a relatively high superatmospheric pressure as described in greater detail hereinafter, combined with an ethane and/or propane pyrolysis product gas stream, which ethane and/or propane is produced as product ethane and/or propane in the process as described hereinafter, the mixture is scrubbed with caustic for further purification, thoroughly dried as by contact with activated alumina, and then fractionated by any of the available suitable methods into a residue gaseous fraction boiling below ethylene, an ethylene fraction, an ethane fraction, a heavy fraction or fractions of C<sub>4</sub>'s and heavier materials and a propylene-propane fraction, or a separate propylene fraction and a separate propane fraction. The separated ethane and/or propane fractions are then admixed with the remaining minor portion of the cracked gas stream and with a minor proportion of steam, and the resulting mixed gas stream(s) is pyrolyzed in ferruginous metal pyrolysis tubes under conditions selected to give a satisfactory yield of ethylene. The pyrolyzed product stream is quenched with a suitable quenching medium, water being preferred, and the separated quenched product stream is compressed for subsequent low temperature fractionation, and resulting condensate is separated therefrom. A typical analysis of a representative pyrolysis product composite stream is given in Table II.

TABLE II  
PYROLYSIS PRODUCT

Component	Mol Percent
H <sub>2</sub>	
H <sub>2</sub> +CO	24.7
CH <sub>4</sub>	0.1
C <sub>2</sub> H <sub>4</sub>	14.0
C <sub>2</sub> H <sub>6</sub>	30.7
C <sub>3</sub> H <sub>6</sub>	20.2
C <sub>3</sub> H <sub>8</sub>	2.7
C <sub>4</sub> 's	3.0
C <sub>5</sub> <sup>+</sup>	1.2
H <sub>2</sub> O	2.8
	0.6

The compressed pyrolysis product gas stream is



then combined with the compressed cracked gas stream, as already indicated, and the combined stream is processed for separation of the desired olefin product(s) for conversion to desired chemical derivative product(s), and for recovery of the ethane and propane content thereof for subsequent pyrolysis to ethylene in the process.

Thus, it is seen that the process of the invention comprises a coordinated combination of interlocking operations. For example, the principal portion of the refinery cracked gas stream is combined with the ethane and/or propane pyrolysis product stream and the combined stream is fractionated for recovery of the indicated components thereof, some of each of said components being contained in both of the streams prior to combination, with unchanged ethane and propane from the pyrolysis product stream being separated, respectively, together with ethane and propane from the refinery cracked gas stream(s). At the same time a minor but significant and critical proportion of the refinery cracked gas stream (and/or a portion of the acidic gaseous components or acidic product stream separated therefrom) is combined with the composited ethane and/or propane feed to the pyrolysis operation. The thus coordinated combination process provides an efficient and economical process for the recovery of ethylene from refinery cracked gases together with the pyrolysis of the ethane content thereof to ethylene and the recovery of the thus produced ethylene.

Having broadly described the process of the invention, it will now be set forth in greater detail with reference to Fig. I, and, at the same time, details of a preferred embodiment thereof will be described as practiced in a commercial plant having a designed capacity to produce 200 short tons of ethylene gas per stream day at maximum economic conversion and recovery rates.

As already described, the feed gases for the process are, for economic and operational reasons, residue gases from the well-known oil-refinery thermal and catalytic cracking operations, as applied to various petroleum oil fractions. One or more of such cracking operations are indicated by 11 in Fig. I, and the fractionations as usually obtained in such refinery operations are indicated as being withdrawn from unit 12. Analyses of representative thermal and catalytic cracked gases have been given in Table I.

#### Feed purification and compression

The residue feed gases, or major portions thereof [cracked gas in line 14] are separately treated with a suitable deacidifying medium, such as with a 20% diethanolamine-water solution (aqueous caustic or alkaline phosphate solutions may be used as well known), generally in an absorber-regenerator system indicated by 15, said operations being effected at their respective pressure levels, for the removal of hydrogen sulfide and carbon dioxide. The  $H_2S$  content is reduced thereby to a value of about 2 grains per 100 standard cubic feet. As practiced in usual operations, the thermal feed gas at this point is at a temperature of about 100° F. and a pressure of about 95 p. s. i. g., while the catalytic cracked gas is at 100° F. and about 260 p. s. i. g. The purified gas streams are then compressed at 16, as in a single stage, to about 560 p. s. i. g.

#### Mixed gas purification

The compressed feed gas(es) in line 17 is mixed with compressed pyrolysis gas (described later) from line 19, and the mixed gases are passed through a caustic scrubbing system 20, for complete removal of residual  $H_2S$  and  $CO_2$ . A 10% aqueous caustic solution, or aqueous  $K_3PO_4$  or the like, is a satisfactory medium for circulation in this system for this purpose. The mixed gases are then cooled to about 60° F., condensed water is separated in a separator (not shown), after which the mixed gases are passed through a drier unit 21 comprising a bed of solid desiccant, such as activated bauxite or activated alumina, to effect a minimum water dew point thereof.

#### Low temperature fractionation

The combined dried gas from 21 is fractionated into the desired fractions thereof by any suitable method or sequence of operations, such as low temperature fractional distillation, adsorption fractionation as by the so-called "hypersorption" fractionation process, absorption fractionation, and combinations thereof. Absorption with chemical reaction may be utilized to effect some separations between unsaturated and saturated hydrocarbons. Thus, propylene may be absorbed from propylene-propane mixture by treating the mixture with a suitable agent or agents for conversion of the propylene to isopropyl alcohol, as by dissolving the propylene content in sulfuric or phosphoric acid. Fig. I indicates schematically a suitable low temperature fractionation method. Since the placement and use of the required coolers, heat exchangers, boilers, valves, pumps, temperature, flow and liquid level control devices, etc., will be readily understood by those skilled in this art, they have been omitted for the sake of clarity. Reference may be made to "Petroleum Refiner," vol. 28, No. 9, September 1949, pages 298-9, for specific information in this connection.

The dry mixed gas is precooled to a temperature of -75° F. and separated in fractionator 22 (demethanizer) into an overhead residue gas consisting essentially of the methane, hydrogen, carbon monoxide and nitrogen contents of the mixed gas and a bottoms fraction. The residue gas is recovered at a column top temperature of about -145° F. at 485 p. s. i. g. pressure and the bottoms is withdrawn at about 65° F. Ethylene at 90° F. in a refrigerant system is suitably used to subcool the feed to fractionator 22, while ethylene at -160° F. serves to condense demethanizer reflux. The demethanizer bottoms is fractionated in fractionator 24 (deethanizer), at top conditions of 10° F. and 290 p. s. i. g. and bottom temperature of 125° F., into an ethane-ethylene overhead fraction and a deethanizer bottoms. The ethylene is separated from the ethane of the ethane-ethylene fraction by fractionation in fractionator 25 (ethylene fractionator), at fractionator top conditions of -26° F. and 238 p. s. i. g. pressure and bottom temperature of about 11° F. The deethanizer bottoms is separated in fractionator 26 (depropanizer) into an overhead propane-propylene fraction (at 112° F. and 238 p. s. i. g.) and a  $C_4^+$  bottoms fraction. The propane-propylene ( $C_3$ ) overhead may be fed through line 29 to the pyrolysis furnace, but it is preferably separated into separate propylene and propane fractions as in fractionator 27.

Typical analyses of representative separated fractions are given in Table III.



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TABLE III

ANALYSES<sup>1</sup> OF SEPARATED FRACTIONS

Component	Demeth- anizer Residue Gas	Ethylene	Ethane	Propylene- Propane
Hydrogen.....	35.2			
N <sub>2</sub> +CO.....	8.7			
Methane.....	53.0	0.53		
Ethylene.....	2.4	97.97	4.1	0.2
Ethane.....	0.7	1.50	94.2	3.1
Propylene.....			1.1	45.2
Propane.....			0.6	50.5
C <sub>4</sub> 's.....				1.0
Total.....	100.0	100.0	100.0	100.0

<sup>1</sup> Values are in mol percent.

### Pyrolysis

Ethane and propane derived from the just-described fractionation, constituting those substances first separated from the feed refinery cracked gas(es) together with the ethane and propane recovered from the pyrolysis gas(es), thus being a recycle portion, are fed separately or together, by means of lines 30 and 31, in admixture with steam from line 32, and a minor proportion of sour refinery cracked gas from line 34, to the stainless steel tubes (such as type 316, preferably type 310—25/20 chrome-nickel), of a multiple (5) section tubular gas fired furnace of the equiflux type, indicated at 35, wherein they are thermally cracked (pyrolyzed), separately and/or in any desired mixed proportions. Details of conditions of operation, such as temperatures, pressures, residence times, and the like are discussed in detail in the literature already referred to. In general the operation is practiced at a pyrolysis coil outlet temperature of from about 1425° F. to about 1510° F., depending on the feed composition, with an outlet temperature of about 1465–1470° F. usually being utilized. The residence or contact time in the reaction zone is usually about 0.7–1.3 seconds at the coil outlet temperature. The feed inlet pressure is about 90–95 p. s. i. g. and the outlet pressure is about atmospheric to 15–20 p. s. i. g.

In similar operations as practiced heretofore, except that none of the sour refinery cracked gas was included directly in the pyrolysis feed, a major problem of operation was excessive coke formation in the pyrolysis tubes. Average run lengths on ethane cracking were in the order of 250–300 hours, while those on propane averaged 500–600 hours. In order to obtain even those run lengths it was necessary to double usual steam feed rates on propane cracking and nearly triple this flow on ethane cracking. Thus, the problem not only causes a considerable decrease in pyrolysis capacity of a given installation, but increases maintenance costs several-fold. Thus, numerous startups and shutdowns of coked tubes result in more than normal warpage and flange and header leaks.

In contrast, by blending a small proportion of the acidic refinery cracked gas, such as from about 0.2% to about 5% by volume, depending on the content of acidic constituents of the gas, the proportion generally being chosen so that the acidic content of the pyrolysis feed admixture is from about 0.01% to about 0.3% by volume (mol per cent), preferably about 0.02% to about 0.1%, it has been found that coking in the pyrolysis tubes is greatly reduced and that on-stream times between required decoking are multiplied many-fold. Thus, in a test plant run

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in one coil, as follows: ethane feed rate—80,000 standard cubic feet per hour; steam feed rate—1,400 pounds per hour; sour catalytic cracked gas feed rate—1,000 standard cubic feet per hour (per cent volume H<sub>2</sub>S in catalytic cracked gas—2 to 6 conc.), radiant outlet temperature—1465°–1470° F., operation was on stream for 1355 hours and was stopped then only for inspection, although the pressure drop across the coil still remained low. There was no corrosion of the tube due to the added normally corrosive sulfur compound. By this practice, on-stream times between decoking have been increased to 5–6 months and more, with no deleterious effect due to feeding a part of the refinery cracked gas directly into the pyrolysis tubes along with the ethane and/or propane feed.

Instead of mixing a portion of the sour refinery cracked gas with the ethane and/or propane pyrolysis feed, an appropriate portion of the acidic gases removed therefrom in 15 may be sufficiently pressured and incorporated with the pyrolysis feed, as indicated by line 36. Thus, as an illustration, it will be seen that when the feed gas for the process is the sour catalytic cracked gas of Table I, the process in effect removes the 5 mol parts of H<sub>2</sub>S and 2.2 mol parts of CO<sub>2</sub> from 100 mol parts of the feed, recovers the 9.2 mol parts of ethylene as substantially pure ethylene, separates the 12.6 mol parts of ethane, combines the 12.6 mol parts of ethane with a minor portion (0.001 to 0.03 mol part, preferably about 0.005 mol part) of the H<sub>2</sub>S or the acidic product recovered from the deacidifying step, and with a minor proportion of steam, say 1 to 2.5 mol parts, pyrolyzes the admixture to produce ethylene, and recovers the ethylene and ethane from the pyrolysis product while in admixture with another portion of deacidified catalytic cracked gas. The conversion product stream(s) from the pyrolysis unit 35 is quenched to about 700° F. upon leaving the cracking coil, by water injection through line 37, passed through coke or scale traps (not shown) and then through a quench tower 39, where the temperature is reduced to 130° F. by further injection of water. Heavier hydrocarbons formed during the cracking and light oils are removed with the quench water while the quench tower overhead vapor comprising most of the conversion products, saturated with steam, is cooled and compressed in three stages at 40 to 560 p. s. i. g. pressure and then combined with the compressed refinery gas stream(s) for separation into the constituent components.

The influence of added hydrogen sulfide to the pyrolysis feed, on both coke formation and corrosion, is shown graphically by the curves in Fig. II. The curves in Fig. II are based on results of thermally cracking propane in a type 310 stainless steel tube, under the usual conditions employed for the production of ethylene, in the presence of added amounts of hydrogen sulfide. The effect of sulfur content of the feed is interesting. With a very low sulfur content (0.0003% by weight S), the corrosion (Fig. II) was a very low value. But, with a sulfur content of the feed of about 0.003% by weight, which is that of a commercial grade of "Shellane" (liquefied petroleum gas—principally propane), the corrosion was greatly increased; addition of H<sub>2</sub>S to a sulfur content of 0.01% gave about the same high corrosion value. Nevertheless, the addition of still larger amounts of hydrogen sulfide markedly reduced the corrosion so that at 0.03% by weight



sulfur (as  $H_2S$ ) the corrosion was brought down to a very low value. The results show that when hydrogen sulfide is added alone, the amount should be appreciably greater than 0.01% by weight (with ethane the weight per cent and mol per cent are substantially equivalent, while with propane the mol per cent is about three-fourths of the weight per cent), such as about 0.02%, and preferably 0.03% by weight. Because of the necessity of removing added  $H_2S$  from the product gases, both because of adverse effect on conversion reactions of components thereof (ethylene, propylene) and on equipment utilized in the subsequent fractionation of the product gases into components thereof, it is essential that the  $H_2S$  content of the pyrolysis feed be kept as low as feasible, preferably not greater than about 0.3 mol per cent. Furthermore, for reasons already referred to, it is preferred to minimize the amount of the refinery cracked gases passed directly to the pyrolysis coils on account of the diluent methane and the unstable olefins present. Nevertheless, the proportion must be such as to be greater than the value corresponding to increased corrosion and carbon formation.

The advantage of adding steam to the pyrolysis feed, along with hydrogen sulfide, is that lower concentrations of  $H_2S$  may be utilized in combination with steam, with reduced corrosion and coking, than with  $H_2S$  alone; proportions of  $H_2S$  even as low as about 0.01% by weight may be utilized to advantage, although it is still preferred to use an amount corresponding to at least about 0.02%. As already indicated in the prior art, the proportion of steam may vary over a wide range, from a relatively small proportion, such as about 3-5% by weight to a value of about 25-30% by weight, while a value of from about 6% to about 20% by weight is generally preferable, corresponding to a mol or volume proportion of from about 10 to about 35 per cent of the volume of ethane.

I claim as my invention:

1. A process for the production of ethylene, which comprises in combination the steps: dividing a sour refinery cracked gas stream containing  $C_1$  and  $C_2$  hydrocarbons as the principal hydrocarbon components thereof and with only a negligible portion of  $C_4^+$  hydrocarbons and containing hydrogen sulfide in a minor proportion as essential sour constituent, into a minor stream and a major stream; subjecting the minor stream in admixture with an ethane stream as produced in the process and described hereinafter and with a minor proportion of steam, to pyrolysis in a tubular ferruginous metal vessel under conditions adapted to produce ethylene as principal conversion product; deacidifying said major cracked gas stream; combining the deacidified cracked gas stream and the pyrolysis product stream; fractionating the resulting mixed gas stream and recovering therefrom a light residue gas stream containing substantially all of the methane content thereof, a substantially pure ethylene stream and an ethane stream containing substantially all of the ethane content thereof; and cycling the separated ethane stream to the pyrolysis operation as the ethane feed stream thereto.

2. A process for the production of ethylene, which comprises in combination the steps: deacidifying a sour refinery cracked gas stream containing  $C_1$  and  $C_2$  hydrocarbons as the principal hydrocarbon components thereof and with

only a negligible portion of  $C_4^+$  hydrocarbons and containing hydrogen sulfide in a minor proportion; combining the deacidified cracked gas stream with a pyrolysis product stream as produced in the process and described hereinafter; fractionating the resulting mixed gas stream and recovering therefrom a light residue gas stream containing substantially all of the methane content thereof, a substantially pure ethylene stream and an ethane stream containing substantially all of the ethane content of said mixed gas stream; subjecting the separated ethane stream in admixture with a minor proportion of steam and with a minor proportion of the acidic product stream recovered from the deacidifying of said sour refinery cracked gas stream, to pyrolysis in a tubular ferruginous metal vessel under conditions adapted to produce ethylene as principal conversion product; and combining the resulting pyrolysis product stream with a further portion of said stream of deacidified refinery cracked gas.

3. A process for the production of ethylene, which comprises in combination the steps: dividing a sour refinery cracked gas stream containing methane, ethylene and ethane as the principal hydrocarbon components thereof and with only a negligible portion of  $C_4^+$  hydrocarbons and containing a minor proportion of an acidic material, into a minor stream and a major stream; subjecting an ethane stream as produced in the process and described hereinafter in admixture with said minor stream in proportions to provide a  $H_2S$  content of the admixture of from about 0.01 to 0.3 mol per cent and with a minor proportion of steam of from about 6 to about 20 weight per cent of the ethane stream, to pyrolysis in a tubular ferruginous metal vessel under conditions adapted to produce ethylene as principal conversion product; deacidifying said major cracked gas stream; combining the deacidified cracked gas stream and the pyrolysis product stream; fractionating the resulting mixed gas stream and recovering therefrom a substantially pure ethylene stream containing substantially all of the ethylene content thereof and an ethane stream containing substantially all of the ethane content thereof; and cycling the separated ethane stream to the pyrolysis operation as the ethane feed stream thereto.

4. A process for the production of ethylene, which comprises in combination the steps: dividing a sour refinery catalytic cracked gas stream containing methane, ethylene and ethane as the principal hydrocarbon components thereof and with only a negligible portion of  $C_4^+$  hydrocarbons and containing a minor proportion of about 2 to 6 volume per cent of  $H_2S$ , into a minor stream and a major stream; subjecting an ethane stream as produced in the process and described hereinafter in admixture with said minor stream in proportions to provide a  $H_2S$  content of the admixture of from about 0.02 to about 0.1 volume per cent and with a minor proportion of steam of from about 10 to about 35 per cent by volume of the ethane stream, to pyrolysis in a tubular ferruginous metal vessel under conditions adapted to produce ethylene as principal conversion product; deacidifying said major cracked gas stream; combining the deacidified cracked gas stream and the pyrolysis product stream; fractionating the resulting mixed gas stream and recovering therefrom a substantially pure ethylene stream containing substantially all of the ethylene content thereof and an ethane stream



containing substantially all of the ethane content thereof; and cycling the separated ethane stream to the pyrolysis operation as the ethane feed stream thereto.

5. In a process for the production of ethylene by the thermal vapor phase dehydrogenation of ethane while being passed through a heated ferruginous metal tube, wherein the resulting pyrolysis product stream is separated by fractionation to produce a substantially pure ethylene stream of substantially all of the ethylene content thereof and an ethane stream containing substantially all of the ethane content thereof, and the ethane stream is cycled to the thermal vapor phase dehydrogenation operation together with additional ethane from another source as further feed thereto, the improvement which comprises providing the additional ethane from the other source by admixing the pyrolysis product stream prior to fractionation with a deacidified cracked gas stream containing methane, ethylene and ethane as the principal hydrocarbon components thereof, in proportions sufficient to provide said additional ethane, and admixing a minor proportion of acidic constituents consisting essentially of H<sub>2</sub>S which were present in said deacidified cracked gas stream prior to being deacidified, with the feed to the thermal vapor phase dehydrogenation operation.

6. A process for the production of ethylene, which comprises in combination the steps: dividing a sour cracked gas stream containing C<sub>1</sub>-C<sub>3</sub> hydrocarbons as the principal components thereof, including ethylene, and with only a

negligible portion of C<sub>4</sub>+ hydrocarbons and containing a minor proportion of H<sub>2</sub>S as acidic contaminant, into a minor stream and a major stream, subjecting C<sub>2</sub>-C<sub>3</sub> alkanes as separated in the process and described hereinafter in admixture with said minor sour cracked gas stream in proportions to provide a H<sub>2</sub>S content of the admixture of from about 0.01 to 0.3 mol per cent and with a minor proportion of steam of from about 6 to about 20 weight per cent of the alkanes, to pyrolysis in a tubular ferruginous metal vessel under conditions adapted to produce ethylene as principal conversion product; deacidifying said major cracked gas stream; combining the deacidified cracked gas stream and the pyrolysis product stream; fractionating the resulting mixed gas stream and recovering therefrom a substantially pure ethylene stream containing substantially all of the ethylene content thereof and separate therefrom substantially all of the C<sub>2</sub>-C<sub>3</sub> alkane content thereof; and cycling the separated C<sub>2</sub>-C<sub>3</sub> alkanes to the pyrolysis operation as C<sub>2</sub>-C<sub>3</sub> alkane feed thereto.

ROBERT W. WHITE.

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