

Nov. 26, 1935.

F. W. SULLIVAN, JR
POLYMERIZATION OF OLEFINS

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2 Sheets-Sheet 1

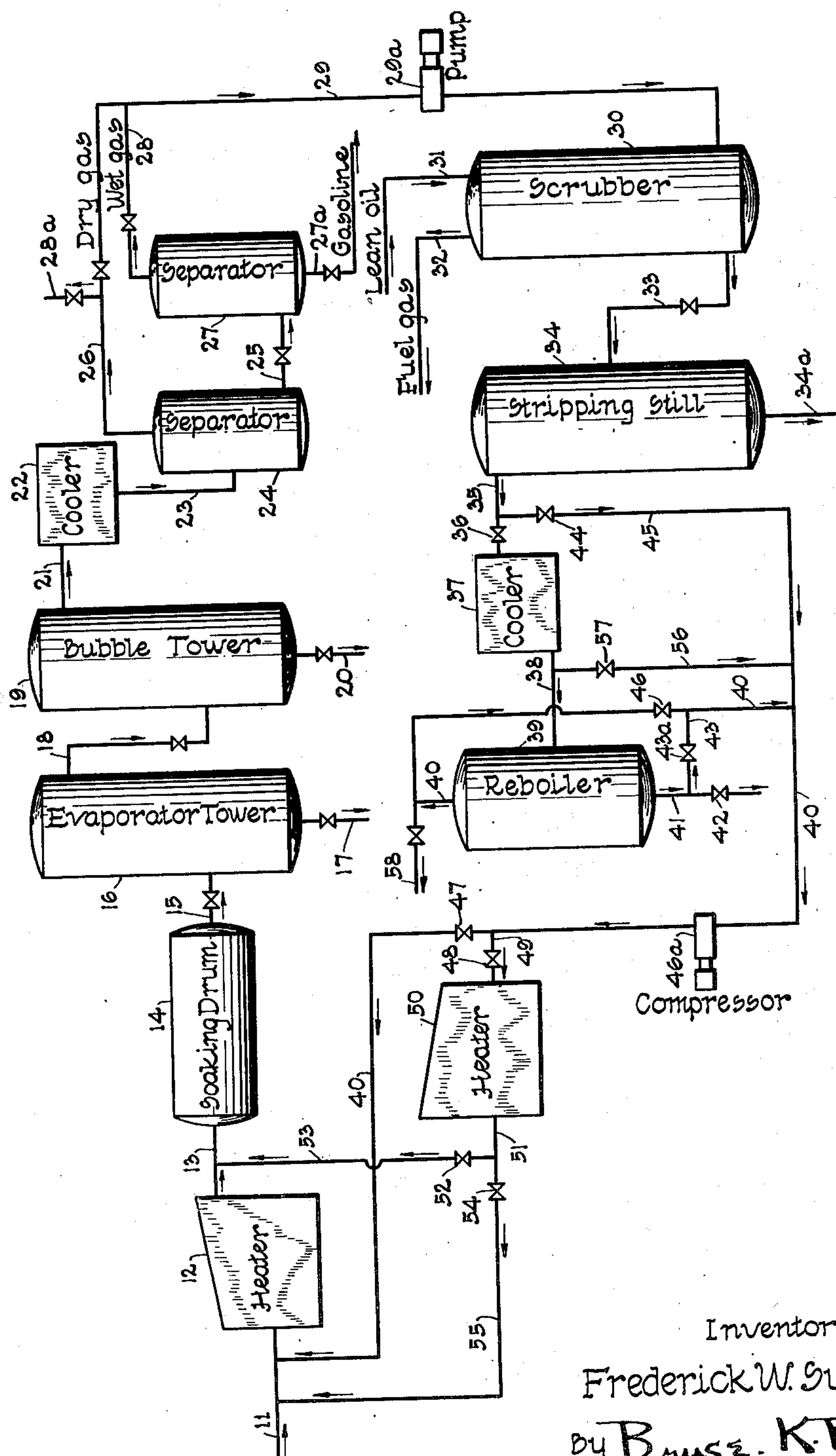


Fig. 1

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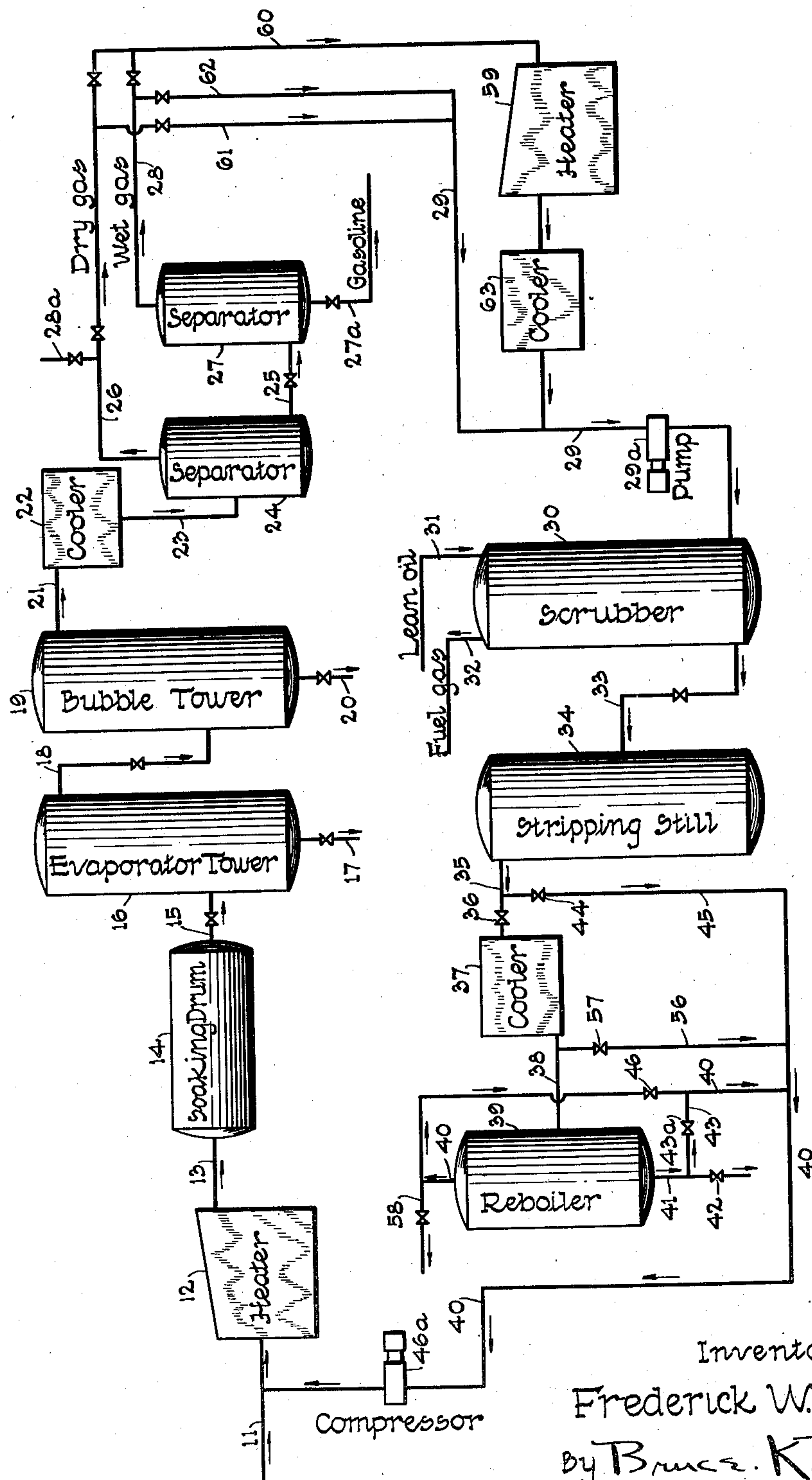


Fig. 2

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UNITED STATES PATENT OFFICE

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POLYMERIZATION OF OLEFINES

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7 Claims. (Cl. 196—66)

This invention relates to improvements in the art of cracking oils. Its particular object is to increase the yield of gasoline by effective re-use in the cracking system of certain of the gases produced in the system. Broadly speaking, this is accomplished by the separation of olefinic or unsaturated gases produced in the normal cracking reactions and returning said olefinic gases to the heating and reaction section of the cracking system.

It is, of course, old to crack high boiling oils in the presence of hydrocarbon gases. Numerous proposals have been made to carry out such operations in the presence of natural gas or in the presence of fixed gases recycled from the system itself. In some cases the purpose of such addition of gases has been purely mechanical, i. e., to improve agitation, circulation, or heating conditions within the cracking system. In numerous of such processes it has been further claimed that the added gases exerted a "mass-action" effect and thus tended to repress the formation of fixed gases by the cracking reactions. In some cases it has been further claimed that the added gases actually reacted with the oil under treatment, or products thereof, with consequent enhancement of the yield and quality of low boiling products.

I have investigated the possibility of such processes and have found that no increased yield or improvement of product can be obtained by said means. In the early and inefficient forms of oil cracking apparatus, such as are no longer used, some improvement of physical conditions might be obtained by such circulation of gases, but no such improvement can be noted in cracking systems now in use. I have been unable to obtain any evidence of important or useful chemical reactions entered into by said gases under cracking conditions.

I have, however, discovered that this is due to the great dilution of the active unsaturated gases by hydrogen and saturated hydrocarbon gases present in the gas mixtures which have previously been used. My invention particularly resides in the discovery that if the active unsaturated gases are separated from inert gases and only the former are returned to the cracking system, very marked improvements in operating results are achieved.

My improved process may be briefly described. I take gases from a cracking system, compress said gases and contact them with a suitable scrubbing oil whereby methane and hydrogen remain undissolved while higher hydrocarbons, and predominately higher unsaturated hydrocarbons, are dissolved in the oil. The rich oil is then stripped by heating with or without direct contact with steam, and the evolved gases are condensed by cooling under elevated pressure. These gases are

returned to the heating and reaction section of the cracking system, with or without a high temperature treatment to still further increase their olefin content, or said condensed gases may be further separated in a reboiler wherein a butane-butylene fraction is separated and added to the gasoline produced by the cracking system, the remaining gases, other than butane-butylene, being returned to the heating and reaction section of the cracking system with or without preliminary high temperature treatment.

My invention will be more clearly understood from the detailed description and from the accompanying drawings, wherein:

Figure 1 shows a diagrammatic representation of one arrangement of apparatus for my process, and

Figure 2 illustrates a somewhat different arrangement to be used if gases are to be further cracked prior to separating and recycling desired fractions thereof.

Referring to Figure 1, charging stock, which may be suitably preheated by heat interchange, is introduced through pipe 11 into the heater 12 where it is raised to cracking temperatures (800–1000° F.) and is passed through transfer line 13 to soaking drum 14 (which is held at a pressure of 100–1000 lbs./sq. in. or thereabouts) whence, after conversion, it passes through valved line 15 to evaporator tower 16. Tar is eliminated at valved draw-off 17 and the overhead from tower 16 passes by valved pipe 18 to bubble tower 19, from the lower part of which recycle stock is eliminated through valved draw-off 20 and is returned for further cracking. Gaseous and undensified vapors from tower 19 pass through line 21 to cooler 22 and thence through line 23 to high pressure separator 24.

"Dry gas" is eliminated from separator 24 by line 26 while the liquid products pass through valved line 25 to low pressure separator 27. Gasoline is removed by line valved draw-off 27A and "wet gas" is removed through line 28. The dry gas, containing predominately methane plus hydrogen, may be eliminated from the system by valved off-take 28A, or the dry gas and the wet gas may be further treated separately, but preferably they are further treated together, being mixed in line 29. Pump 29A compresses these gases to a suitable elevated pressure of 50–300 pounds/square inch above atmospheric, following which they are contacted in scrubber 30 with oil or another suitable scrubbing medium introduced under pressure through inlet 31. Undissolved gases, consisting mainly of hydrogen and methane but containing varying small amounts of higher hydrocarbons and particularly of higher saturated hydrocarbons, are removed at off-take 32 and suitably consumed for fuel. The absorber oil charged with dissolved gases passes through line 60

33, wherein suitable pumping means (not shown) may be inserted if desired, to stripping still 34 wherein it is heated by indirect means and wherein it may also be subjected to the direct action of live steam. Stripped oil is removed at 34A and recycled by suitable means (not shown) to scrubber inlet 31. The evolved gases which are at high pressure and elevated temperature pass through line 35, and valve 36 to cooler 37 wherein they are condensed. If direct stripping steam were used in 34 a water separator must be inserted at this point. The liquefied hydrocarbons pass through line 38 to reboiler 39 wherein suitable heating and fractionating means are provided. Gases lower than butane-butylene are evolved and removed through line 40 while butane-butylene is removed as liquid through line 41 and valve 42. If it is not desired to separate all butane-butylene for addition to the gasoline, a part of this fraction may be bypassed through line 43 and valve 43a, and returned to the system through line 40. If, on the other hand, it is desired to return all of the butane-butylene fraction to the system, the cooler 37 and reboiler 39 may be cut out of the system by opening valve 44 in line 45 and closing valves 46, 36 and 43a in lines 40, 35 and 43 respectively.

Regardless of which of these latter modifications or procedure is used, the recycled gases in line 40 are compressed by compressor 46A to a suitable pressure for reintroduction into the heating and reaction section of the cracking system. If valve 47 in line 40 be opened and valve 48 in line 49 be closed, these compressed gases will be reintroduced directly into the intake 11 of heater 12. On the other hand, under certain conditions it may be desired to heat these gases in order to further increase their olefine content. In this case valve 47 is closed and 48 is opened so that the compressed gases pass through heater 50 wherein they are subjected to temperatures in the vicinity of 1500° F. The cracked gases from heater 50 may be passed through line 51 and valve 52 in line 53 into the transfer line 13 leading to the soaking drum 14. On the other hand, by closing valve 52 and opening valve 54 in line 55 the gases may be passed to the inlet 11 of the heater 12.

As a modification of this procedure, I may operate cooler 37 so as to condense only propylene-propane-butylene butane and may remove uncondensed ethylene-ethane through line 56 and valve 57 and return only the latter to the cracking system through line 40. In this case if the propylene-propane is not to be returned to the oil cracking system it may be eliminated through valved line 58. It will be evident that the particular form and arrangement of apparatus used in the separation and fractionation of the cracked gases may vary considerably and in fact that entirely different types of apparatus might be used, including the use of somewhat higher pressures with resultant complete or partial liquefaction without use of solvents.

Figure 2 is a diagrammatic representation of the arrangement of apparatus if the gases from the cracking system are to be re-cracked at higher temperatures prior to the separation step wherein methane and hydrogen are eliminated and desired fractions are recycled to the cracking system. The system is the same as that shown in Figure 1, except that heater 50 and its accessory connections, etc. 47-55 (both inclusive) are omitted and an equivalent heater 59 is inserted in the system prior to the scrubber 30. Gases from

the cracking system are introduced into heater 59 through line 60 which is connected with gas lines 26 and 28 from the separators of the cracking system. Lines 61 and 62 by-pass the heater and connect with line 29, so that by suitable adjustment of the valves shown in lines 26, 28, 61 and 62 the dry gas and the wet gas may both be passed through heater 59 or either one may be by-passed around the heater. Following the heater is a cooler 63 from which the cracked gases are delivered thru pipe 29 to pump 29a and into scrubber 30. The arrangement of the system following scrubber 30 is unchanged and all of the previously described modifications of the operation thereof are possible. The gases in heater 59 will ordinarily be subjected to temperatures of 1400 to 1600° F. for a period of ten seconds or less, whereby the total amount of olefins present may be increased.

Whether or not my improved process is operated in accordance with the modifications of Figure 1 or Figure 2 will depend largely on the operating conditions and charging stock used in the cracking system, or in other words, on the olefine content of the gas from said system.

By the aforescribed process I reintroduce into the cracking system only the hydrocarbon gases having two, three or four carbon atoms in their molecule, and predominately only the unsaturated hydrocarbons in this range. By eliminating the hydrogen and methane which are ordinarily present in large volume in gases from cracking systems and by eliminating to as large an extent as possible all saturated hydrocarbons, I eliminate the diluent and retarding effect which the latter customarily exerts upon the polymerization of the unsaturated constituents and obtain markedly increased yields of gasoline.

While the foregoing is a full and complete description of my invention it is understood that I am not limited therein except as defined in the claims as follows.

I claim:

1. A method of converting hydrocarbon oils into gasoline-like products which comprises flowing a stream of oil through an elongated passageway while maintaining the oil under a high super-atmospheric pressure, cracking the stream of oil during its flow through said passageway, in the presence of recycled unsaturated normally gaseous hydrocarbons formed in the process and from which substantial amounts of hydrogen and methane have been removed, to produce products including gasoline-like products and a mixture of light normally gaseous hydrocarbon products comprising hydrogen, methane and heavier normally gaseous unsaturated hydrocarbons, passing the stream of reaction products from said passageway to a separating zone wherein heavy tarry residues are separated in liquid form and lighter products are separated in vapor form, collecting said tarry residues without returning any of them to the oil undergoing cracking, separately withdrawing vapors from said separating zone and fractionating them to separate therefrom as separate fractions desired gasoline-like products and a mixture of light normally gaseous hydrocarbon products comprising hydrogen, methane and heavier unsaturated normally gaseous hydrocarbons, fractionating the said mixture of normally gaseous hydrocarbon products to separate hydrogen and methane constituents therefrom and discharging such separated constituents from the system, thereby forming a normally gaseous mixture of materially increased concen-

tration of unsaturated hydrocarbons, introducing as the aforescribed recycled gaseous hydrocarbons at least a portion of the resulting concentrated heavier normally gaseous hydrocarbons into the first mentioned stream of oil and subjecting the unsaturated constituents of said gaseous hydrocarbons to a polymerization reaction for the first time subsequent to said concentrating operation to form normally liquid gasoline-like products in the presence of the oil stream undergoing cracking into gasoline-like products, with the result that a marked increase in gasoline-like products is effected in the process and there is produced a gasoline product having relatively high anti-knock properties.

2. The method of converting hydrocarbon oils into gasoline-like products which comprises heating a flowing stream of oil during its flow through an elongated passageway to a cracking temperature while maintaining it under a high superatmospheric pressure, maintaining the oil stream at said temperature and under said pressure until the desired conversion into gasoline-like products is effected, thereafter passing the stream of reaction products from said passageway to a separating zone wherein heavy tarry residues are separated in liquid form and lighter products are separated in vapor form, collecting said tarry residues without returning any of them to the oil stream undergoing cracking, separately withdrawing vapors from said separating zone and fractionating them to separate therefrom as separate fractions desired gasoline-like products and a mixture of light normally gaseous hydrocarbon products comprising hydrogen, methane and heavier unsaturated normally gaseous hydrocarbons, fractionating the said mixture of normally gaseous hydrocarbon products to separate hydrogen and methane constituents therefrom and discharging such separated constituents from the system, thereby forming a normally gaseous mixture of materially increased concentration of unsaturated hydrocarbons and directly introducing at least a portion of the said concentrated heavier normally gaseous mixture into the said elongated passageway to admix with the oil therein subjected to cracking and be subjected to thermal conversion for the first time following said concentrating operation, whereby the unsaturated constituents of said gaseous hydrocarbons undergo a polymerization reaction to form normally liquid gasoline-like products in the presence of the oil stream undergoing cracking into gasoline-like products, with the result that a marked increase in gasoline-like products is effected in the process and there is produced a gasoline product having relatively high anti-knock properties.

3. The method of converting hydrocarbon oils into gasoline-like products which comprises heating a flowing stream of oil during its flow through an elongated passageway to a cracking temperature while maintaining it under a high superatmospheric pressure, maintaining the oil stream at said temperature and under said pressure until the desired conversion into gasoline-like products is effected, thereafter passing the stream of reaction products from said passageway to a separating zone wherein heavy tarry residues are separated in liquid form and lighter products are separated in vapor form, collecting said tarry residues without returning any of them to the oil stream undergoing cracking, separately withdrawing vapors from said separating zone and fractionating them to separate therefrom as separate fractions desired gasoline-like products,

reflux condensate comprising constituents heavier than the desired gasoline-like products and a mixture of light normally gaseous hydrocarbon products comprising hydrogen, methane and heavier unsaturated normally gaseous hydrocarbons, fractionating the said mixture of normally gaseous hydrocarbon products to separate hydrogen and methane constituents therefrom and discharging such separated constituents from the system thereby forming a normally gaseous mixture of materially increased concentration of unsaturated hydrocarbons, returning reflux condensate from the aforesaid fractionating operation to said elongated passage for further cracking therein, and directly introducing at least a portion of the said concentrated heavier normally gaseous mixture into the said elongated passageway to admix with the oil therein subjected to cracking and be subjected to thermal conversion for the first time following said concentrating operation, whereby the unsaturated constituents of said gaseous hydrocarbons undergo a polymerization reaction to form normally liquid gasoline-like products in the presence of the oil stream undergoing cracking into gasoline-like products, with the result that a marked increase in gasoline-like products is effected in the process and there is produced a gasoline product having relatively high anti-knock properties.

4. The method of converting hydrocarbon oils into gasoline-like products which comprises heating a flowing stream of oil during its flow through an elongated passageway to a cracking temperature of about 800° F. to about 1000° F. while maintaining it under a high superatmospheric pressure of from 100 to as much as 1000 pounds per square inch, maintaining the oil stream at said temperature and under said pressure until the desired conversion into gasoline-like products is effected, thereafter passing the stream of reaction products from said passageway to a separating zone wherein heavy tarry residues are separated in liquid form and lighter products are separated in vapor form, collecting said tarry residues without returning any of them to the oil stream undergoing cracking, separately withdrawing vapors from said separating zone and fractionating them to separate therefrom as separate fractions desired gasoline-like products and a mixture of light normally gaseous hydrocarbon products comprising hydrogen, methane and heavier unsaturated normally gaseous hydrocarbons, fractionating the said mixture of normally gaseous hydrocarbon products to separate hydrogen and methane constituents therefrom and discharging such separated constituents from the system, thereby forming a normally gaseous mixture of materially increased concentration of unsaturated hydrocarbons, and directly introducing at least a portion of the said concentrated heavier normally gaseous mixture into the said elongated passageway to admix with the oil therein subjected to cracking and be subjected to thermal conversion for the first time following said concentrating operation, whereby the unsaturated constituents of said gaseous hydrocarbons undergo a polymerization reaction to form normally liquid gasoline-like products in the presence of the oil stream undergoing cracking into gasoline-like products, with the result that a marked increase in gasoline-like products is effected in the process and there is produced a gasoline product having relatively high anti-knock properties.

5. The method of converting hydrocarbon oils into gasoline-like products which comprises heating a flowing stream of oil during its flow through an elongated passageway to a cracking temperature while maintaining it under a high superatmospheric pressure, maintaining the oil stream at said temperature and under said pressure until the desired conversion into gasoline-like products is effected, thereafter passing the stream of reaction products from said passageway to a separating zone wherein heavy tarry residues are separated in liquid form and lighter products are separated in vapor form, collecting said tarry residues without returning any of them to the oil stream undergoing cracking, separately withdrawing vapors from said separating zone and fractionating them to separate therefrom as separate fractions desired gasoline-like products and a mixture of light normally gaseous hydrocarbon products, subjecting at least a portion of said normally gaseous hydrocarbon products to thermal treatment to crack unsaturated constituents thereof into normally gaseous olefines, fractionating the resulting converted gases to separate hydrogen and methane constituents therefrom and discharging such separated constituents from the system, thereby forming a normally gaseous mixture of materially increased concentration of unsaturated hydrocarbons, and directly introducing at least a portion of the said concentrated heavier normally gaseous mixture into the said elongated passageway to admix with the oil therein subjected to cracking and be subjected to thermal conversion for the first time following said concentrating operation, whereby the unsaturated constituents of said gaseous hydrocarbons undergo a polymerization reaction to form normally liquid gasoline-like products in the presence of the oil stream undergoing cracking into gasoline-like products, with the result that a marked increase in gasoline-like products is effected in the process and there is produced a gasoline product having relatively high anti-knock properties.

6. The method of converting hydrocarbon oils into gasoline-like products which comprises heating a flowing stream of oil during its flow through an elongated passageway to a cracking temperature of the order of from about 800° F. to as high as 1000° F. while maintaining it under a high superatmospheric pressure of the order of from about 100 to as high as 1000 pounds per square inch, maintaining the oil stream at said temperature and under said pressure until the desired conversion into gasoline-like products is effected, thereafter passing the stream of reaction products from said passageway to a separating zone wherein heavy tarry residues are separated in liquid form and lighter products are separated in vapor form, collecting said tarry residues without returning any of them to the oil stream undergoing cracking, separately withdrawing vapors from said separating zone and fractionating them to separate therefrom as separate fractions desired gasoline-like products and a mixture of light normally gaseous hydrocarbon products, subjecting at least a portion of said normally gaseous hydrocarbon products to thermal treatment at temperatures of the order of about 1400° F. to about 1600° F. to crack unsaturated constituents thereof into normally gaseous olefines, fractionating the resulting converted

gases to separate hydrogen and methane constituents therefrom and discharging such separated constituents from the system, thereby forming a normally gaseous mixture of materially increased concentration of unsaturated hydrocarbons, and directly introducing at least a portion of said concentrated heavier normally gaseous mixture into the said elongated passageway to admix with the oil therein subjected to cracking and be subjected to thermal conversion for the first time following said concentrating operation, whereby the unsaturated constituents of said gaseous hydrocarbons undergo a polymerization reaction to form normally liquid gasoline-like products in the presence of the oil stream undergoing cracking into gasoline-like products, with the result that a marked increase in gasoline-like products is effected in the process and there is produced a gasoline product having relatively high anti-knock properties.

7. A method of converting hydrocarbon oils into gasoline-like products which comprises flowing a stream of oil through an elongated passageway while maintaining the oil under a high superatmospheric pressure, cracking the stream of oil during its flow through said passageway, in the presence of recycled unsaturated normally gaseous hydrocarbons formed in the process and from which substantial amounts of hydrogen and methane have been removed, to produce products including gasoline-like products and a mixture of light normally gaseous hydrocarbon products comprising hydrogen, methane and heavier normally gaseous unsaturated hydrocarbons, passing the stream of reaction products from said passageway to a separating zone wherein heavy tarry residues are separated in liquid form and lighter products are separated in vapor form, collecting said tarry residues without returning any of them to the oil undergoing cracking, separately withdrawing vapors from said separating zone and fractionating them to separate therefrom as separate fractions desired gasoline-like products and a mixture of light normally gaseous hydrocarbon products comprising hydrogen, methane and heavier unsaturated normally gaseous hydrocarbons, fractionating the said mixture of normally gaseous hydrocarbon products to separate hydrogen and methane constituents therefrom and discharging such separated constituents from the system thereby forming a normally gaseous mixture of materially increased concentration of unsaturated hydrocarbons and comprising ethylene and propylene and their saturated analogs substantially free from higher or lower boiling materials, introducing as the aforescribed recycled gaseous hydrocarbons at least a portion of the resulting concentrated heavier, normally gaseous hydrocarbons into the first mentioned stream of oil and subjecting the unsaturated constituents of said gaseous hydrocarbons to a polymerization reaction for the first time subsequent to said concentrating operation to form normally liquid gasoline-like products in the presence of the oil stream undergoing cracking into gasoline-like products, with the result that a marked increase in gasoline-like products is effected in the process and there is produced a gasoline product having relatively high anti-knock properties.

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