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METHOD OF SEPARATING THE CONSTITUENTS OF GASEOUS MIXTURES

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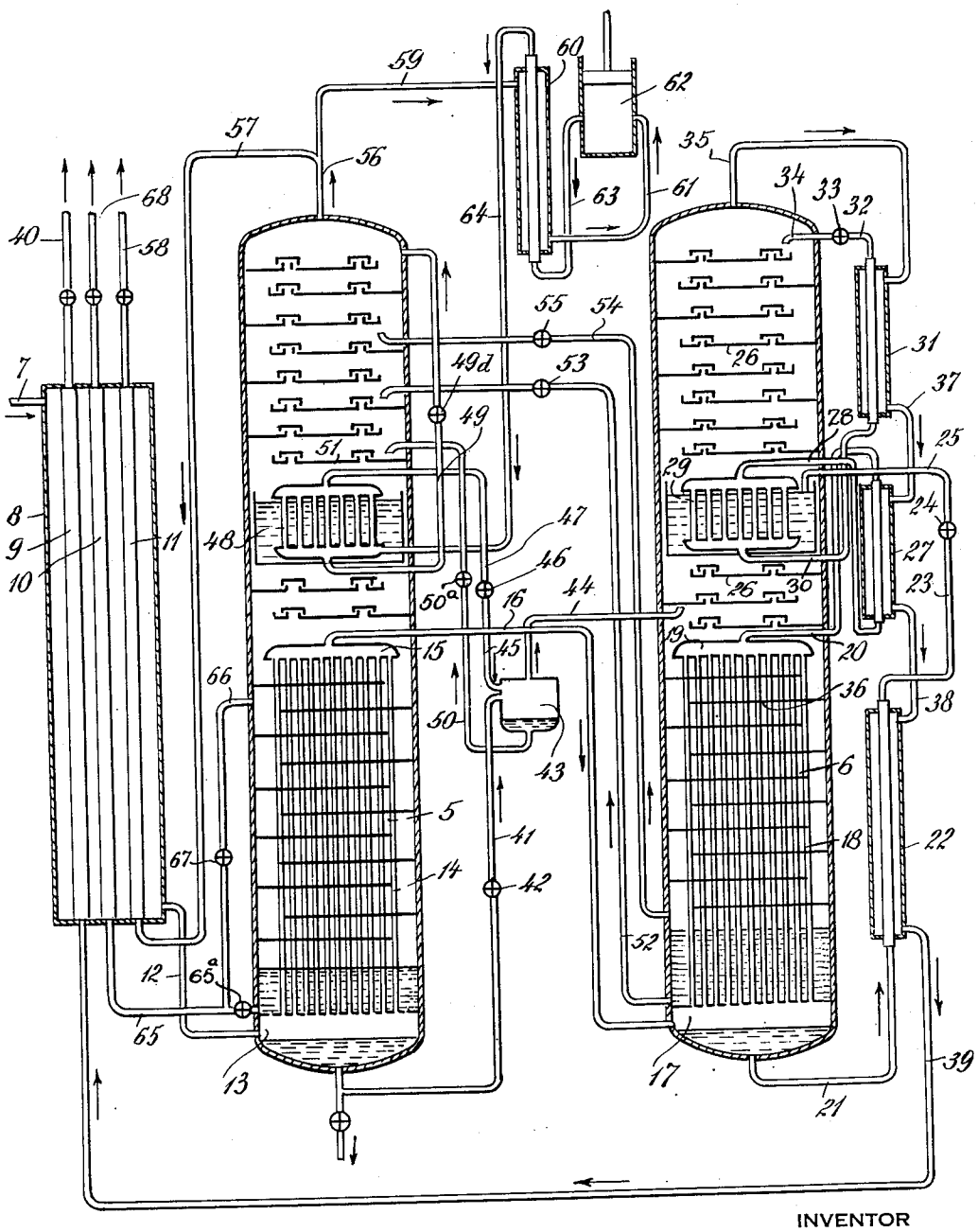

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METHOD OF SEPARATING THE CONSTITUENTS OF GASEOUS MIXTURES

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This invention relates to the separation and recovery of the constituents of gaseous mixtures, and particularly to the recovery of a constituent of intermediate boiling point in a condition of substantial purity by a continuous operation.

The invention may be utilized for the recovery of various constituents from complex gaseous mixtures, of which numerous examples are found in the art. It is especially useful in the recovery of products such as ethylene, which are produced admixed with various other hydrocarbon gases and hydrogen in the petroleum industry. By the application of the invention, ethylene can be recovered in a substantially pure condition and in an economical manner from various gaseous mixtures containing it.

It is the object of the invention, therefore, to provide a simple, efficient and economical method of separating the constituents of complex gaseous mixtures, and particularly of recovering a constituent of intermediate boiling point in a substantially pure condition.

Another object of the invention is to provide an efficient method of producing the refrigerative effect necessary for the accomplishment of the desired separation.

Further objects and advantages of the invention will be apparent as it is better understood by reference to the following specification.

The invention depends upon the treatment of the gaseous mixture by liquefaction and rectification, so that constituents having different boiling points are segregated. Thus the initial gaseous complex mixture, after compressing to a suitable pressure and primary cooling by heat exchange with products of the method, is subjected to selective liquefaction with backward return of the liquefied constituents. By this step the initial mixture is separated into a liquid portion containing a substantial fraction of the constituents of intermediate boiling point and the major portion of the constituents whose boiling points are higher, and a gaseous fraction containing the balance of the constituents of the initial gaseous mixture.

The gaseous mixture resulting from the first step of the procedure is then subjected to further liquefaction with backward return of the liquid produced, thus effecting a further separation into liquid and gaseous fractions. These fractions are then further separated by rectification so as to produce an effluent consisting substantially of the constituents of lowest boiling point and a liquid containing substantially only constituents of intermediate and higher boiling points.

The liquid fraction from the rectification is then returned and subjected to rectification with the first fraction produced in the initial separation, the rectification being completed with liquid consisting substantially of the constituents of intermediate boiling point so as to produce an effluent consisting of that constituent in a substantially pure condition. The residual liquid produced by the final rectification consists almost entirely of the constituents of higher boiling point. The several fractions into which the gaseous mixture is thus separated are withdrawn continuously and are thus recovered and may be utilized for any desired purpose.

In the application of the procedure to the recovery of ethylene from gases derived from the petroleum industry, the major product is ethylene which has a boiling point intermediate between the boiling points of other constituents making up the initial gaseous mixture. The remaining products recovered are usually hydrogen and various hydrocarbon gases.

The details of the procedure will be better understood by reference to the accompanying drawing and the following description. The drawing is a diagrammatic representation of an apparatus suitable for the practice of the method.

It is to be understood that in the drawing no attempt has been made to illustrate those details of liquefaction apparatus which are well known to those skilled in the art, the drawing being intended merely to elucidate the procedure as hereinafter described.

Referring to the drawing, 5 and 6 indicate columns in which the selective liquefaction and rectification of the gaseous mixture and the fractions thereof is accomplished. The initial gaseous mixture comprising the several constituents is compressed in a suitable compresser (not shown) to the pressure which may be necessary, and which will vary depending upon the nature of the gaseous mixture. The compressed gaseous mixture is introduced through a pipe 7 to an exchanger 8 wherein it is cooled by circulation about pipes 9, 10 and 11 through which the prod-

ucts of the separation at a lower temperature are delivered. The gaseous mixture thus cooled passes through a pipe 12 into a compartment 13 at the bottom of the column 5 and thence upwardly through pipes 14 which are surrounded by liquid produced in the rectification hereinafter described. The gaseous mixture passing through the pipes 14 at a higher pressure than that of the surrounding liquid is subjected to partial liquefaction and the liquid produced flows backwardly through the pipes and accumulates in the chamber 13. It consists of a large portion of the constituent of intermediate boiling point, for example, ethylene, and the major portion of a constituent or constituents having a higher boiling point.

The unliquefied residue is delivered to a head 15 and passes through a pipe 16 into a compartment 17 at the bottom of the second column 6. Thence the gaseous mixture passes upwardly through pipes 18 surrounded by liquid produced in the subsequent rectification and is subjected to partial liquefaction. The liquid returns through the pipes into the compartment 17. The balance of the gaseous mixture is delivered to a head 19 and escapes through a pipe 20.

Liquid accumulating in the compartment 17 is delivered by a pipe 21, passes upwardly through an exchanger 22, thence through a pipe 23 and pressure reducing valves 24 and is delivered through a pipe 25 into the rectifying section of the column 6, in which it flows downwardly over trays 26 of the type usually employed in rectification columns and in contact with rising vapors.

The gaseous fraction escaping through the pipe 20 passes through an exchanger 27, pipe 28 and condenser 29, within the rectification column, being thus condensed to a liquid which escapes through a pipe 30 to an exchanger 31 where the liquid may be sub-cooled. The liquid passes then through a pipe 32, pressure reducing valve 33 and pipe 34 into the upper end of the rectification column and flows downwardly over the trays 26 therein in contact with rising vapors.

By the rectification in the upper section of the column 6 a separation is effected so that the effluent which escapes through pipe 35 at the top of the column consists substantially of the constituents having a boiling point lower than that of the constituent of intermediate boiling point, such as ethylene. The liquid which flows downwardly becomes concentrated in the constituents of intermediate and higher boiling point, and this liquid flowing downwardly over the baffles 36 finally accumulates in the compartment surrounding the tubes 18 at the bottom of the column.

The effluent escaping through the pipe 35 passes through the exchanger 31 where it serves to reduce the temperature of the liquid flowing in the opposite direction therethrough, thence through a pipe 37 to the exchanger 27, thence through a pipe 38 to the exchanger 22, and finally through a pipe 39 which delivers it to the pipe 9 in the exchanger 8. It is withdrawn after giving up its cold in the exchanger system through a pipe 40 as one of the products of the operation.

Liquid accumulating in the compartment 13 at the bottom of the column 5 is withdrawn through a pipe 41 and, after passing through a pressure reducing valve 42, is delivered to a separator 43. In the separator, vapors may escape from the liquid, and such vapors may be delivered through a pipe 44 to an intermediate point in the column 6. Uncondensed vapors leaving a condenser 48 through pipe 47 and valve 46 pass through pipe 45 to the separator 43, whence they pass out through pipe 44 to column 6 with the vapors previously mentioned.

The liquid from the separator 43 is delivered through a pipe 50 and valve 50*a* at an intermediate point in the rectification section of the column 5 wherein it flows downwardly over the usual trays 51 in contact with vapors rising through the column.

Liquid from the lower part of the column 6 is delivered through a pipe 52 and valve 53 to the rectification section of the column 5, or, as an alternative, vapors may be withdrawn also from a lower level of the column 6, above the liquid therein, through a pipe 54 and delivered through a valve 55 to the rectification section of the column 5.

There are thus flowing into the rectification section of the column 5 fluids consisting principally of the constituents of intermediate and higher boiling points. Those fluids which are liquid flow downward, tending to concentrate in the constituents of higher boiling point; those fluids which are gaseous flow upward and become concentrated in the constituent of intermediate boiling point, such as ethylene. The final rectification is accomplished with liquid flowing through the pipe 49, and the pressure reducing valve 49*d*, which consists substantially of the constituent of intermediate boiling point, so that the effluent escaping through the pipe 56 consists of the constituent of intermediate boiling point, for example ethylene, in substantial purity. This product may be delivered through a pipe 57 to the pipe 11 in the exchanger 8 and may be withdrawn through a pipe 58 and delivered to a suitable receptacle for storage, or it may be otherwise employed.

To facilitate the final rectification, a portion of the effluent is diverted from the pipe 56 through a pipe 59, and, after passing through an exchanger 60, it is delivered by a pipe 61 to compresser 62 where the pressure is materially increased. The compressed effluent which may at this point be partially liquid is returned through a pipe 63 and the exchanger 60 to a pipe 64 which delivers it to the condenser 48. The unliquefied portion of this effluent is partially liquefied in condenser 48 and is delivered through pipe 49 and pressure reducing valve 49*d* to the top of the rectifying section of the column 5. Thus the rectifying section is supplied continuously with a quantity of liquid consisting substantially of the constituent of intermediate boiling point, for example, ethylene. This liquid washes from the rising vapors all constituents of higher boiling point, which are thus returned to the liquid flowing downwardly through the column and accumulating therein about the pipes 14. The latter liquid is partially vaporized in cooling the initial gaseous mixture in the pipes 14, and the balance, if any, is withdrawn through a pipe 65 and valve 65*a* which delivers it to the pipe 10 in the exchanger 8. The lower end product of the rectification column 5, over and above that portion withdrawn in the liquid state through pipe 65, is withdrawn in the vapor state through pipe 66 and regulative valve 67, after which it is added to the liquid portion coming through valve 65*a*. These combined products then enter pipe 10 of exchanger 8 wherein the vaporization of the liquid is completed, and the resulting product, consisting of the constituent or constituents of higher boiling point, escapes through a pipe 68.

As examples of the practical application of the invention, I have utilized it to separate and recover ethylene from complex gaseous mixtures such as the following, in which the constituents are arranged in the order of their boiling points.

I

Gas	Percent
H_2	6–8
CH_4	23–35
C_2H_4	23–26
C_2H_6	10–12
C_3H_6	15–18
C_3H_8	2–4
C_4H_8	6–9

As well as small amounts of other constituents.

II

Gas	Percent
H_2	33.0
CH_4	12.5
C_2H_4	36.5
C_2H_6	14.0
C_3H_6	0.5–1.0
C_4H_8	0.3–0.7

As well as small amounts of C_2H_2 and other constituents.

III

Gas	Percent
H_2	17.5
CH_4	34.9
C_2H_4	27.2
C_2H_6	0.0
C_3H_6	6.1–9.6
C_3H_8	6.6
C_4H_8	.7

As well as small amounts of C_2H_2 and other constituents.

From such complex mixtures I have readily obtained ethylene of 98–99% purity with a yield of 80–85% and higher. The invention thus affords a convenient and economical method of separating ethylene from mixtures of hydrogen and hydrocarbons which are available in larger quantities. The ethylene thus obtained may be utilized for a variety of commercial purposes.

From the foregoing description, it will be evident that the successive steps of separating the several constituents of the initial gaseous mixture are accomplished in a continuous manner, so as to effectively eliminate the constituents of lower boiling point and then to separate the constituents of higher boiling point, especially from the constituent of intermediate boiling point. The primary purpose of the invention is the recovery of the constituent of intermediate boiling point in a condition of substantial purity, and this is readily and economically accomplished by the procedure as described.

Various changes may be made in the details of the operation, particularly in view of the special characteristics of the mixture treated, without departing from the invention or sacrificing any of the advantages thereof.

I claim:

1. The method of separating and recovering ethylene from complex gaseous mixtures which comprises initially separating, by selective liquefaction and backward return of the liquid, a fraction containing ethylene and other constituents of higher boiling point, subjecting the balance of the gaseous mixture to further separation by selective liquefaction with backward return of the liquid followed by rectification so as to separate it into two portions, the first containing only constituents of boiling points lower than that of ethylene, and the second or lower product containing only ethylene and constituents of higher boiling points, withdrawing the vapors of lower boiling point as the upper effluent from this rectification, subjecting the second or lower product of the rectification to further and combined rectification with the liquid product of the initial separation, and withdrawing as the upper effluent of the combined rectification a vapor consisting substantially of ethylene.

2. The method of separating and recovering ethylene from complex gaseous mixtures which comprises initially separating, by selective liquefaction and backward return of the liquid, a fraction containing ethylene and other constituents of higher boiling point, subjecting the balance of the gaseous mixture to further separation by selective liquefaction with backward return of the liquid followed by rectification of the liquid to separate constituents having boiling points lower than that of ethylene, withdrawing the vapors of lower boiling point, subjecting the remaining products of the rectification to further and combined rectification with the liquid product of the initial separation, withdrawing as the effluent of the combined rectification a vapor consisting substantially of ethylene, and liquefying and returning a portion of the effluent from the combined rectification to facilitate the separation of ethylene in a condition of substantial purity.

3. The method of separating and recovering ethylene from complex gaseous mixtures which comprises initially separating, by selective liquefaction and backward return of the liquid, a fraction containing ethylene and other constituents of higher boiling point, subjecting the balance of the gaseous mixture to further separation by selective liquefaction with backward return of the liquid followed by rectification of the liquid to separate constituents having boiling points lower than that of ethylene, withdrawing the vapors of lower boiling point, subjecting the remaining products of the rectification to further and combined rectification with the liquid product of the initial separation, withdrawing as the effluent of the combined rectification a vapor consisting substantially of ethylene, and recompressing and liquefying and returning a portion of the effluent from the combined rectification to facilitate the separation of ethylene in a condition of substantial purity.

4. In the method of separating and recovering ethylene from complex gaseous mixtures, the steps of initially separating the gaseous mixture into liquid and gaseous fractions by selective liquefaction and backward return of the liquid, conducting the liquid at reduced pressure to a compartment, separating vapors from the liquid in the compartment, subjecting the liquid to rectification, liquefying at least a portion of the gaseous fraction from the initial separation and utilizing the vapors from the compartment in a separate rectification of liquefied constituents of the gaseous fraction from the initial separation.

5. The method of separating and recovering ethylene from complex gaseous mixtures, which comprises initially separating, by selective liquefaction and backward return of the liquid, a fraction containing ethylene and other constituents of higher boiling point, subjecting the balance of the gaseous mixture to further separation by selective liquefaction and backward return of the liquid, followed by rectification of the liquid to separate constituents having boiling points lower than that of ethylene, withdrawing the vapors of

the lower boiling point, subjecting the liquid product of the initial separation to reduced pressure and separating vapors therefrom, utilizing the vapors thus separated in a rectification of liquid resulting from the liquefaction of the gaseous fraction of the initial separation, and subjecting the liquid remaining after the separation of vapors therefrom to rectification.

6. The method of separating and recovering ethylene from complex gaseous mixtures, which comprises initially separating, by selective liquefaction and backward return of the liquid, a fraction containing ethylene and other constituents of higher boiling point, subjecting the balance of the gaseous mixture to further separation by selective liquefaction and backward return of the liquid, followed by rectification of the liquid to separate constituents having boiling points lower than that of ethylene, withdrawing the vapors of the lower boiling point, subjecting the liquid product of the initial separation to reduced pressure and separating vapors therefrom, utilizing the vapors thus separated in a rectification of liquid resulting from the liquefaction of the gaseous fractions of the initial separation, subjecting the liquid remaining after the separation of vapors therefrom to combined rectification with the liquid resulting from the liquefaction of the gaseous fraction of the initial separation, and withdrawing as the effluent of the combined rectification a vapor consisting substantially of ethylene.

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