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PROCESS FOR RECOVERING LOW BOILING POINT HYDROCARBONS, ESPECIALLY ETHYLENE

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1 Claim. (Cl. 260—683)

This application is a continuation-in-part of a co-pending application Ser. No. 554,814, filed December 22, 1955 in the names of Josef Schmidt and Heinrich Weber.

The present invention relates to processes for recovering certain low boiling point hydrocarbons, and more particularly to processes for enhancing the recovery of ethylene from a mixture of different low boiling hydrocarbons.

It is an object of the present invention to provide means facilitating recovery of low boiling hydrocarbons and especially of ethylene through novel and highly efficacious procedures which are easily carried out and result in considerably larger yields of said hydrocarbons as well as of ethylene than have heretofore been obtained with known procedures.

It is another object of the present invention to provide means contributing to a greatly improved and extremely efficient process for recovering desired hydrocarbons from a crude gas mixture containing the same in conjunction with other undesired gaseous products, which process requires a minimum of power input and expenditure of energy, time and money, whereby the entire process is rendered very economical.

Still another object of the present invention is to provide means conducive to an integrated, continuous and highly practical process of isolating valuable hydrocarbons, and in particular ethylene, in substantially pure form through sequential application of a quantity of said hydrocarbons to both a fluid absorption medium and a solid absorption medium and by means of a low temperature fractionation subsequent to liberation of said hydrocarbons from said absorption media.

Yet another object of the present invention is the provision of means conducive to an advantageous process of the aforesaid type in which the ultimate quantity of ethylene obtained results from the recovery of already existing ethylene and also from the recovery of ethylene created by transformation, for example, through cracking, of ethane or of mixtures of ethane and higher hydrocarbons into ethylene.

It is yet another object of the present invention to provide means enabling the aforesaid process to be carried out in a part of the same installation as is employed for the production of the crude gas mixture from which the ethylene is to be extracted, whereby the process is rendered still more economical.

More particularly, industrial requirements for ethylene to serve as a starting product or raw material in chemical syntheses and other applications are so great that it has recently become economically profitable to isolate this hydrocarbon from mixtures of gases in which it is found only to a relatively small extent. The most commonly encountered gas mixture of this type is coke oven gas, which generally contains between 1.5% and 2.5% by volume ethylene (C_2H_4) besides 0.5% to 2% ethane (C_2H_6), and like small quantities of propene (C_3H_6), propane (C_3H_8) and C_4 -hydrocarbons.

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Quantities of such hydrocarbons in the same order of magnitude are found in gas mixtures resulting from low temperature carbonizations and destructive distillations carried out under pressure and in gas mixtures resulting from other gasification or dry-distillation processes.

Within certain limits it is possible to enhance the ethylene content of coke oven gas by adding to the coking coal cheap oil residues which are split or cracked into ethylene and other lighter hydrocarbons at the temperatures existing in the coke oven. In accordance with a number of known procedures, such oil residues are not added to the coking coal but rather are introduced directly into the coke oven at a suitable location and in a predetermined form.

By means of such oil additions, it is possible to increase the ethylene content in the coke oven gas to a maximum value of about 3% by volume. The content of the other light hydrocarbons, and especially ethane, rises proportionately, the ethane content increasing by means of addition of oil from about 0.6% by volume to a maximum value of about 1.2% by volume.

The separation or recovery of ethylene and the other above-mentioned hydrocarbons, the mixture of which may be called "crude ethylene," is preferably effected, in accordance with the teaching of the above-mentioned co-pending application, on a large scale and in an economically satisfactory manner by virtue of the fact that the crude ethylene is extracted from the coke oven gas by means of an absorption procedure.

Certain fluids, such as benzene (C_6H_6), have proved to be suitable for use as an absorption medium for such crude ethylene. Activated carbon, which has a definite affinity or absorptive capacity for hydrocarbons, and especially for unsaturated hydrocarbons, has also been proposed for this purpose.

In each case, however, the other hydrocarbons are absorbed from the coke oven gas together with the ethylene, including a certain, usually large quantity of methane. The desired hydrocarbons are then separated from the absorption medium by suitable expelling procedures, such as expansion or pressure reduction, as a result of which the above-mentioned crude ethylene is isolated.

Alternatively, the crude ethylene and the absorption medium are cooled to a low temperature, whereby the crude ethylene is isolated through liquification. The concentration of the desired ethylene in the gas mixture which is designated by the term "crude ethylene" generally ranges from about 20% to about 35%, and on occasions may be even higher, while the remainder of the gas mixture consists mostly of methane (CH_4) in conjunction with certain amounts of ethane and small quantities of C_3 - and C_4 -hydrocarbons. The crude ethylene recovered by means of such procedures is thereafter split into its individual components through a low temperature fractionation.

The use of a fluid such as crude benzene as an absorption medium to aid in the recovery of ethylene and the other hydrocarbons has the advantage that the absorption medium is itself produced together with the desired hydrocarbons in the same operation. Saturation of the crude ethylene mixture with benzene subsequent to the absorption operation presents no additional problem, since coke oven gas under any circumstances contains benzene which can be subsequently removed by means of a suitable washing oil.

A further advantage attendant the use of benzene as the absorption medium resides in the fact that hydrogen sulfide and naphthalene are absorbed together with the desired hydrocarbons and can thereafter be separated from the medium in utilizable condition.

The use of activated carbon as the absorption medium, on the other hand, has the advantage that the latter is,

to a large extent, selectively absorptive with respect to the components of the crude ethylene. The gas mixture liberated from the activated carbon is relatively rich in ethylene and higher hydrocarbons, so that a subsequent transformation of said mixture into its pure fraction may be effected with a minimum of expense.

A disadvantage of absorption by means of activated carbon, however, is the substantial sensitivity or receptivity of this absorption medium to hydrogen sulfide and higher hydrocarbons such as naphthalene. Both of these last mentioned compounds are generally found in coke oven gas and in similar gas mixtures. Hydrogen sulfide and other sulfur compounds contaminate the activated carbon, while naphthalene and other higher hydrocarbons lead to clogging or blocking of said activated carbon, thereby rendering the same unsuitable for further use as an absorption medium.

One of the underlying principles of the present invention is, therefore, the combination of absorption by means of a fluid medium and by means of activated carbon in such a manner that the advantages inherent in both absorption procedures become available.

It is further known that ethane or mixtures of ethane with C_3 - and C_4 -hydrocarbons can be processed in a tube furnace and split or cracked to produce a substantial yield of ethylene. If a suitably lined or otherwise appropriately equipped cracking furnace is charged with ethane, it has been found that the latter may be cracked to produce as much as an 80% yield of ethylene. Because of these high yields ethylene is preferably mass-produced from light hydrocarbons, since the yield of ethylene obtained by splitting or cracking heavier oils is generally fairly small.

In coke oven gas, ethylene usually comprises about 33% of the crude ethylene, the latter term, as indicated above, being employed only to designate a mixture of ethylene, ethane and C_3 - and C_4 -hydrocarbons. It is, therefore, advantageous to join the ethylene recovery from coke oven gas with the coking procedure. This is especially so with respect to the above-described absorption procedures, since the ethylene absorption may be easily carried out together with the usually effected extraction of benzene, naphthalene and other products not desired.

Assuming, for example, that in a modern large scale coke plant there is produced a gas yield of about one million normal cubic meters per day (1,000,000 Nm.³/24 hr.), then a 60% to 80% recovery of ethylene would be tantamount to a recovery of about 15 to 20 tons of ethylene. The maximum recovery to be expected due to addition of oils to be split or cracked, however, would be about 20 to 30 tons of ethylene per day, i.e. an increase of only about 5 to 10 tons per day.

In smaller coke plants, in which the extraction of ethylene is nevertheless of great economic importance, the quantities of ethylene obtained are still smaller, of course. The operation of a tube furnace for splitting ethane into ethylene, especially in the case of small ethylene recovery, thus becomes substantially unprofitable due to the relatively high investment of money required.

The fact still remains, however, that an economical transformation of ethane to ethylene is not only preferable but actually absolutely essential, inasmuch as a part of the prescribed total expenditure which would have to be incurred for this purpose in any event has necessarily already been incurred due to the fact that the ethane has been extracted together with the ethylene from the coke oven gas.

In accordance with known procedures, the ethylene may be isolated from the ethane and other C_3 - and C_4 -hydrocarbons by means of a low temperature fractionation. This is independent of whether or not an absorption step or operation has preceded such fractionation, the only requirement being that the coke oven gas is first freed from undesirable or interfering constituents. This

is similar, for example, to the isolation of hydrogen from coke oven gas for the synthesis of ammonia.

In any event, at the end of such a procedure, and depending on the fractionating arrangement employed, the initial ethylene is obtained with the desired degree of purity, while simultaneously those hydrocarbons having higher boiling points than ethylene can be recovered either individually or in a mixture of C_2 - to C_4 -hydrocarbons. The latter mixture consists mainly of ethane.

It is, therefore, another underlying principle of the present invention to return the ethane, which is a part of the low boiling hydrocarbons obtained during the isolation of ethylene by means of the above mentioned low temperature fractionating procedure, to the coke oven at suitable coking periods of the coal charges in said oven, whereby the ethane is split or cracked into additional quantities of ethylene.

According to a further characteristic of the invention, the other hydrocarbons which are recovered during the low temperature fractionation, besides ethane, are also split into ethylene in the coke oven. To this end, the ethane or the mixture of ethane with other C_3 - and C_4 -hydrocarbons is introduced either into the gas collection space located on the oven side opposite the fuel gas main or into a lower portion of the coke oven, so that a part of the cracking path of these hydrocarbons runs over the glowing coke.

This last-mentioned procedure may best be realized from the following test comparison carried out in a set of coke ovens which were in an advanced coking state. The two hydrocarbon masses which were cracked under similar conditions consisted of an ethane gas mixture and a mass of crude Arabian oil supplied by Aramco (Arabian-American Oil Co.).

(a) The ethane gas mixture included the following constituents:

	Percent by volume
Ethylene	8.6
Ethane	78.5
Propene	5.8
Propane	4.8
C_4 and higher boiling hydrocarbons	2.3

Upon analysis of the gases leaving the coke oven subsequent to the cracking operation it was found that 52% of the introduced ethane gas mixture was cracked and transformed into ethylene.

(b) In the case of the crude oil it was found that only 17% of the introduced charge of oil was cracked and transformed into ethylene.

Although the above-described test comparison was not carried out under optimum conditions for forming ethylene by cracking of relatively higher hydrocarbons, it will be readily seen that the process according to the present invention is considerably more efficacious than the heretofore known procedures.

The complete and integrated ethylene recovery process according to the present invention is carried out substantially as follows:

As set forth in the above-mentioned copending application Ser. No. 554,814, the coke oven gas is initially subjected to a superatmospheric pressure, which may be as low as 8 to 10 atm. or as high as approximately 20 atm., and mingled with a fluid absorption medium such as crude benzene at a temperature of about 20° to 25° C. The benzene absorbs not only the desired hydrocarbons, i.e., ethylene, ethane, etc., but also methane and a number of undesired ballast substances such as hydrogen sulfide, organic sulfur compounds and higher hydrocarbons.

The charged benzene is then repeatedly expanded, i.e., subjected to a series of successive pressure reductions carried out in a plurality of subordinate pressure drop stages, whereby the crude ethylene is substantially liberated from said benzene while the ballast substances, es-

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pecially hydrogen sulfide and naphthalene, which are harmful to activated carbon, are retained by the benzene.

By way of example, the benzene and gases absorbed thereby are expanded to a pressure of about 3 atm. in a first expansion stage and then expanded in three subsequent expansion stages to pressures of about 1 to 1.2 atm., 0.25 to 0.4 atm., and 0.1 to 0.2 atm., respectively. At each expansion stage, an additional amount of the remaining benzene is separated from the crude ethylene, such separated benzene being then recirculated for further use.

The gases liberated in the first two expansion or pressure reduction stages generally contain only small amounts of the desired hydrocarbons, such as ethylene, and consist mostly of methane since the latter is present in great amounts in the mixture of gases, such as coke oven gas and producer gas, from which the ethylene is to be extracted.

Heretofore it has been customary to return the gases obtained in the first expansion stage to the initial or crude gas mixture for reabsorption by additional benzene, whereas gases from the second stage were added to the crude ethylene still to be treated. In this manner, the methane content of said crude ethylene was always increased.

According to the invention, the gases liberated from the benzene or like fluid absorption medium, e.g. toluene, in at least the first and second expansion stages are conducted to an activated carbon absorption system. As will be readily understood, the gases from any further expansion stages need not be led through the activated carbon system since these last-mentioned gases include substantially only the desired constituents.

The activated carbon retains the desired hydrocarbons, i.e., ethylene and slightly higher hydrocarbons and especially unsaturated hydrocarbons, while methane and other gaseous constituents such as hydrogen, carbon monoxide, etc., pass through the system and are added at a suitable location to a mass of such undesired gases. The quantities of gas liberated thereafter and in predetermined time intervals from the activated carbon by means of steam thus contain the desired hydrocarbons, and especially ethylene, in high concentrations.

According to a modification of the invention, however, provision may be made for passing the gases from all of the expansion stages through the activated carbon system, in which case the number of expansion stages can actually be reduced. Since sulfur compounds and high boiling hydrocarbons, which, due to their harmful characteristics with respect to activated carbon, are removed by means of benzene in the preliminary fluid absorption stage of the process and are no longer permitted to contact said activated carbon, the useful life of the latter is substantially increased.

Inasmuch as the quantity of gases liberated from the benzene or other fluid absorption medium and transmitted to the activated carbon is relatively small with respect to the total quantity of said medium, it is possible, when proceeding in accordance with the present invention, to employ only a minimum amount of activated carbon which amount is not at all comparable to, i.e. not nearly as large as, the quantity of activated carbon that must be employed when the absorption of the gases consisting only of about 1% to 3% ethylene is effected solely by means of activated carbon.

Thereafter, the recovered gases are subjected to a low temperature fractionation to substantially separate the ethylene already on hand from the ethane, propene, propane and C_4 = or higher hydrocarbons. The mixture of these hydrocarbons, which may or may not still include some ethylene, or the ethane alone is then fed back into all or some of the coke ovens from which the original coke oven gas was taken, the particular ovens employed being those in which the coking condition of the coal is

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such as not to interfere with the flow of the ethane or ethane gas mixture. As stated above, large amounts of ethylene are thus formed by cracking of the ethane and the other hydrocarbons being processed. The resulting ethylene is then finally isolated from all other remaining gaseous constituents, preparatory to be used in the desired syntheses.

The following is a specific example of the manner of practicing the present invention.

15,000 Nm.³/hr. of coke oven gas are washed with crude benzene under a pressure of approximately 10 atm. During stepwise expansion of the absorption medium, masses of gas having a composition substantially as set forth below in Table I are liberated in the individual expansion stages, the amounts of the various constituents being given in mol./hr.

Table I

Substance	Expansion stages and lowest pressure			
	1 3 atm.	2 1.05 atm.	3 0.25 atm.	4 0.1 atm.
H ₂ -----	4.1	0.52	0.02	0.00
CO-N ₂ -O ₂ -----	2.9	0.75	0.026	0.00
CO ₂ -----	1.14	2.75	4.78	1.36
CH ₄ -----	14.1	17.70	11.60	1.48
C ₂ H ₄ -----	1.74	4.53	9.20	3.80
C ₂ H ₆ -----	0.45	1.19	2.92	1.50
C ₃ H ₈ -----	0.06	0.12	0.325	0.18
C ₃ H ₆ -----	0.06	0.15	0.56	0.49
C ₄ H ₁₀ -----	0.03	0.03	0.15	0.12
C ₄ -----	0.00	0.00	0.03	0.03
C ₆ H ₆ -----	0.385	1.22	7.70	6.50
Total-----	24.965	28.96	37.311	15.46
Corresp. amt. in Nm. ³ /hr.-----	580	650	835	345

The gases obtained from the first and second expansion stages are mixed with one another, whereby a gas mixture having a composition as set forth below in column 1 of Table II is obtained. This gas mixture is led to the activated carbon system. After a predetermined lapse of time the gases are liberated from the activated carbon by means of steam, and the resulting gas mixture has a composition as set forth in column 2 of Table II.

Table II

Substance	1 Mol./hr.	2 Mol./hr.
H ₂ -----	4.62	0.3
CO-N ₂ -O ₂ -----	3.65	0.2
CO ₂ -----	3.89	1.4
CH ₄ -----	31.80	5.4
C ₂ H ₄ -----	6.27	5.8
C ₂ H ₆ -----	1.64	1.47
C ₃ H ₈ -----	0.18	0.17
C ₃ H ₆ -----	0.21	0.20
C ₄ H ₁₀ -----	0.06	0.05
C ₄ -----	0.0	0.0
C ₆ H ₆ -----	1.605	1.80
Total-----	53.925	16.59
Corresp. amt. in Nm. ³ /hr.-----	1,210	365

From Table II it will be seen that from an initial quantity of 1,210 Nm.³/hr. of a mixture of crude ethylene and other gases there are obtained 365 Nm.³/hr. of a final mixture of crude ethylene and other gases. Thus, a subsequent low temperature fractionation for processing the crude ethylene so as to isolate some ethylene in its pure state as well as the other hydrocarbons constituting said crude ethylene is carried out on a quantity much less than the quantity which would have had to be processed in accordance with heretofore known procedures.

It was, moreover, found that in accordance with the invention as embodied in the above set forth example, the

losses of ethylene and higher hydrocarbons incurred amounted to only 0.67 mol/hr. which is equivalent to about 15 Nm³/hr.

After the low temperature fractionation is completed, as indicated hereinabove, the ethane or mixture of ethane with, say, C₃- and C₄-hydrocarbons is returned to one or more properly conditioned coking ovens in the coke plant or installation from which the initial coke oven gas was obtained for further cracking of the ethane and the other appropriate hydrocarbons into additional ethylene.

The advantages attendant the process according to the present invention, in contradistinction to the procedures employing either only a fluid absorption medium or only activated carbon, are the following:

(1) The crude ethylene is obtained in concentrated form, whereby further processing of the crude ethylene to its pure state becomes simpler and less expensive.

(2) In contradistinction to absorption exclusively by means of activated carbon according to procedures heretofore known, the activated carbon employed in accordance with the present invention cannot be contaminated and may, therefore, be used for longer periods of time.

Another advantage attendant the present invention resides in the fact that the inherently produced ethane or mixture of ethane with C₃- and C₄-hydrocarbons is reconducted to one or more of the coke ovens, whereby these light and low boiling hydrocarbons produced in concentrated form during the low temperature fractionation may be cracked in said oven or ovens (for producing more ethylene) to a considerably better extent than higher boiling hydrocarbons.

A further advantage of the invention stems from the combination of a low temperature fractionation with ethane cracking in a coke oven. In other words, the quantity of ethane or ethane gas mixture produced during the low temperature fractionation is so small that, at the operational speeds required for the cracking, the gases to be cracked need only be fed to a small number of the coke ovens which make up the coke plant employed for producing the total coke oven gas quantity to be subjected to the ethylene extraction procedures.

It is, therefore, possible to employ only such coke ovens for cracking ethane as are found to be in a coking condition or state most suited for this reaction.

A further considerable advantage of carrying out the supplementary cracking procedure in a coke oven, as distinguished from carrying such cracking procedure out in a specially provided tube furnace, is that the expenses relating to setting up a tube furnace and providing the same with fuel are completely eliminated.

As a further refinement of the process according to the present invention and depending on the amount of the benzene or like absorption medium in the gas mass being treated, a certain quantity of said medium is continuously removed as the same is circulated after liberation therefrom of the desired hydrocarbons. In this manner, excessive enriching of the solvent in high boiling hydrocarbons and undesired sulfur compounds is avoided.

It will, of course, be realized that other modifications of the invention, such as, inter alia, the use of different

pressure values in the various expansion stages, of different numbers of such expansion stages, of different temperatures, of different fluid and solid absorption media, and of different procedures for separating the initially recovered ethylene from the other low boiling hydrocarbons prior to cracking of the latter, are all contemplated within the scope of the present invention, which is to be limited only to the extent expressed in the appended claim.

Having thus described the invention, what is claimed as new and desired to be secured by Letters Patent is:

The process of recovering gaseous ethylene from a coke oven gas mixture of relatively low ethylene concentration and further containing other desired gaseous low boiling hydrocarbons, undesired gaseous higher boiling hydrocarbons and other undesired gaseous substances, comprising the steps of bringing said mixture into contact with benzene under a relatively high superatmospheric pressure and at a temperature ranging from 20° C. to 25° C. to effect absorption of all of the constituents of said mixture by said benzene, reducing to a first predetermined superatmospheric value ranging up to three atmospheres the pressure on said benzene and mixture absorbed thereby to effect a partial liberation from said benzene of a relatively small quantity of said ethylene and desired hydrocarbons and a relatively large quantity of said undesired hydrocarbons and other substances, reducing the pressure on the remainder of said benzene and mixture absorbed thereby to a second predetermined value of about 1.05 atmospheres to effect a partial liberation of an additional relatively small quantity of said ethylene and desired hydrocarbons and an additional relatively large quantity of said undesired hydrocarbons and other substances, reducing the pressure of the remainder of said benzene and mixture absorbed thereby successively to a third value of about 0.25 atmosphere and to a fourth value of about .1 atmosphere to effect partial liberation of still further but relatively large quantities of said ethylene and desired hydrocarbons and still further but relatively small quantities of said undesired hydrocarbons and other substances, bringing said quantities of liberated hydrocarbons and other substances into contact with activated carbon to effect absorption only of said desired hydrocarbons, said ethylene and some of said undesired hydrocarbons by said activated carbon, applying steam to said activated carbon to liberate said ethylene and said desired hydrocarbons therefrom, fractionating the latter at low temperatures to separate said ethylene from the remainder of said desired hydrocarbons, and further passing the latter through the coke ovens from which said coke oven gas mixture was obtained to thereby crack and transform said desired hydrocarbons into additional ethylene, whereby the total ethylene yield is considerably enhanced.

References Cited in the file of this patent

UNITED STATES PATENTS

2,014,724	Eastman	Sept. 17, 1935
2,519,343	Berg	Aug. 22, 1950
2,715,947	Alexander	Aug. 23, 1955
2,781,862	Fussman	Feb. 19, 1957