[Second Edition.]

PATENT SPECIFICATION

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2593

COMPLETE SPECIFICATION.

Method and Means for Synthesizing and Separating Higher Alcohols.

I, Georges Patart, 50, rue Spontini, Paris, France, a citizen of the French Republic, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

In the synthetic manufacture of higher alcohols by the catalytic reduction of carbon monoxide by means of hydrogen, at high temperature and pressure, a substantial amount of carbon dioxide and water are produced together with the higher alcohols.

While the synthetic manufacture of methanol may be performed with a gaseous mixture containing a material proportion of carbon dioxide, it is advantageous in the manufacture of higher alcohols in a closed circuit, to eliminate in a continuous manner, from the gaseous mixture issuing from the catalysis chamber, the carbon dioxide which is produced during the reaction and which, added to the small amount of carbon dioxide which may be present in the initial gas mixture, would rapidly attain a proportion of 15—16%.

In a process of manufacture of easily liquefiable hydrocarbons and oxygen compounds of hydrocarbons by the catalytic treatment at high temperature and pressure of gas mixtures containing hydrogen and carbon monoxide, it has already been proposed to remove the carbon dioxide from the gaseous mixture of carbon monoxide and hydrogen issuing from the catalyzer before subjecting the same to a further catalytic treatment. In this process, fractionated cooling without release of pressure is used for the condensation of the reaction products; however, the degree of cooling employed does not appear to be or is not stated to be sufficient to eliminate the carbon dioxide by this means.

The process according to the invention, which has for its object to remove in a periodic manner the carbon dioxide from the gaseous mixture which has been subjected to the reaction, consists in cooling, without releasing the pressure, the gaseous mixture produced in the synthesizing operation in order to condense the alcohols and water produced, in further cooling the non-condensed gas, still under pressure, in order to remove by condensation the carbon dioxide and in subjecting the gaseous mixture freed from carbon dioxide to a further synthesizing operation.

Preferably, the cold produced by the evaporation of the liquid carbon dioxide and the cold vapours of carbon dioxide are utilized for the cooling of said non-condensed gas

The invention also relates to an installation for carrying out the above process, said installation comprising two condensers connected in series and each of which is divided into four sections, the sections of the first condenser being used for heating respectively the gases to be treated in the catalyzing chamber, the collected alcohols to be rectified, a cooling liquid and the gases issuing from the second condenser and to be subsequently sent back to the catalyzing chamber, while the sections of the second condenser are successively cooled by the cold gases discharged at the outlet of said condenser, by the evaporated carbon dioxide, by a cooling liquid and by the evaporation of the liquid carbon dioxide collecting at the bottom of said condenser.

The installation may further comprise expanding apparatus in which the pressure of the liquid mixture of alcohols and water collected in said condensers is partially released, said expanding apparatus being provided with a cooling liquid circulation, with means for supplying and discharging a sodium chloride solution and for discharging the separated alcohols and the gases produced by the said partial expansion.

In carrying the invention into prac-

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tice, I use special catalyzers whose action is such that the almost exclusive product obtained is a mixture of higher alcohols, wholly deprived of hydrocarbons or derivatives thereof, without the formation of methyl alcohol being preponderent, and with a large rate of flow of the reaction mixture. Such catalyzer consists of one or more alkali or earth alkali salts of metal oxides of an acid nature, for instance the chromates, manganates, molybdates, tungstates, uranates, vanadates, and like salts of sodium, potassium, barium, rubidium and like metals; said salts being very intimately mixed with one or more methanol-forming metal oxides, the number of atoms of the alkali metal contained in said salts being at least equal to one-half the total number of atoms of the metals contained in the catalyzer (the proportion of atoms of the earth alkali metal contained in the corresponding salts being one-half the above proportion).

I may obtain a good catalyzing mass by intimately mixing 830 grams of zinc oxide with 2 kgs. of neutral potassium chromate, or by mixing 105 grams of manganese bioxide with 2 kgs. of neutral tungstate of barium. Said substances should be intimately mixed, optionally with dextrine or gum tragacanth, so as to obtain a thick paste which is dried and broken up into grains which are as regular as possible; said grains are then dried and all dust eliminated before use.

The grains may also be obtained by means of the processes employed in the manufacture of gunpowder from saltpeter, sulphur and charcoal, or by analogous processes.

The gas mixture will preferably consist of industrial water gas which contains substantially 50 volumes of hydrogen and 40 volumes of carbon monoxide, which composition corresponds almost exactly to the theoretical amount indicated by the equation of the reaction giving the higher alcohols. The composition of the gas mixture may however depart from the above data, provided the mixture contains hydrogen (or hydrocarbons which, as is well known, are the equivalents for hydrogen in the processes herein described) and carbon monoxide. As the gas mixture used is generally not chemically pure, it contains sometimes small amounts of carbon dioxide, but the proportion should always be less than 2 to 3%. When gaseous products having sulphur or iron as a base, are contained in the reacting gas mixture, the purification may be obtained to a sufficient extent by the methods in use in the manufacture of illuminating gas.

The process is carried out in a closed circuit, i.e. the uncombined gases being again circulated under pressure upon the catalytic mass. It has been above stated that it is advantageous to eliminate in a continuous manner the carbon dioxide which is produced during the reaction and which would rapidly attain 15—16 per cent., and would then have a detrimental influence upon the quantity and the uniform composition of the collected products.

According to the invention, I eliminate carbon dioxide by the use of the very high pressure to which the gas mixture is subjected in order to liquefy—by proper cooling—the carbon dioxide contained in the gas mixture discharged from the alcohol condenser, whereby the amount of carbon dioxide will be reduced to 2 or 3 per cent. at the maximum. The condensation of carbon dioxide can be easily obtained by operating at pressures of 500—800 atmospheres and by the use of means which will be further set forth.

By the cooling of the gas mixture under pressure issuing from the catalyzer, I first obtain a condensate which consists of an upper insoluble layer containing the higher alcohols (density 0.885—0.890) and a lower aqueous layer (density 0.925—0.940) which latter represents about two-thirds of the total volume. The upper layer is drawn off, and the lower layer is treated with a saturated aqueous solution of sodium chloride, then cooled to about —20 degrees C. An upper layer is again formed which consists of a further amount of insoluble products representing about one-fourth the volume of the original aqueous layer. This upper layer is drawn off and is added to the portion which was previously withdrawn. This product is treated with potassium carbonate, to remove any water which it may contain. It is then distilled and is rectified firstly under normal pressure, and then in vacuo by the known methods, in order to remove the parts containing practically the whole of the series of monoatomic alcohols derived from the saturated hydrocarbons, from propyl alcohol to the hexyl and heptyl alcohols, and their higher homologues. The heaviest products have an odour which is like that of wood tar. The major part—or about three-fifths—consists of propyl, butyl and amyl alcohols. The salt solution with which the aqueous solution was treated contains a small quantity of ethyl and methyl alcohol which are removed by the known distilling processes.

From the composition of the collected

liquid substances and of the gaseous mixture after the reaction, it appears that the higher alcohols are produced according to the equation.

$$(3n-1)CO+(3n+1)H_2=2C_nH_{2n+2}O+(n)-1)CO_2+(n)-1)H_2O.$$

The resulting alcohols will correspond for the most part to values of n between 3 and 7, or 5 on the average, the corresponding mean composition of the gases entering into the reaction should be 48 parts hydrogen to 42 parts carbon monoxide, by volume, this corresponding almost exactly to the mean composition of industrial water gas.

I find it necessary to remove the whole of the water before the rectifying process, to avoid the formation of azeotropic compounds between certain alcohols and water, as such compounds have a low boiling point and would hinder the separation of the different alcohols by rectification.

By means of the installation which will be described hereunder I am enabled to carry out the said process on a manufacturing scale, this being given solely by way of example and without limiting the scope of the invention, the description being given with reference to the appended drawing which shows diagrammatically the said installation.

The gas mixture, which is compressed to the highest possible operating pressure, enters at 1 in order to supply it to the catalyzing apparatus 2, either directly through the cock 15 or indirectly through the cock 16 and the pipe 17, 18, after recovery of heat at 4. After circulating upon the catalytic mass which is maintained at the operating temperature of 320—400 degrees C., the gases are discharged at 3 and are delivered into the upper part of the set of tubes constituting the condensing apparatus which comprises four sections 4—4—4—4. During their descent to the lower part of said tubes, the gases are successively cooled, 1°, in the upper section, by the gas which is to be sent back to the catalyzing apparatus and which enters at 17 and issues at 18; 2°, in the second section by the alcohols to be evaporated, which enter at 33 and issue at 34; 3°, in the third section by cold water supplied at 65 and discharged at 66; 4°, in the bottom section by the cold gases from the second condensing apparatus 7, which enter at 10 and issue at 11.

Due to this successive cooling, the alcohols and the water, contained in the gases, will be entirely condensed and will collect at 5. The non-condensable gases, including the carbon dioxide formed during the reaction, will issue at 6 and will enter the upper part of the second condensing apparatus having the four sections 7, 7, 7, 7; the gases circulate through these tubes to the bottom, and are successively cooled as follows:

1° in the upper section by the gases sent back to the first condenser which are supplied at 9 and discharged at 10; 2°, in the second section by the gaseous carbon dioxide discharged from the bottom section, which enters at 48 and issues at 49 at which point a pressure regulating cock is placed; 3°, in the third section, by means of an artificially cooled brine which enters at 50 at a temperature between −20 and—35 degrees C. and which issues at 51; 4°, in the bottom section, by the evaporation of the liquid carbon dioxide which enters at 46 and is discharged in the gaseous state at 47, and whereof the evaporation pressure, and consequently the temperature, is regulated by the cock disposed at 49.

Under the action of this successive and systematic cooling, the carbon dioxide in the gas mixture condenses and collects at 8, at the lower part of the second condenser 7. The uncondensable gases are discharged at 9, circulate in the upper section of the device 7, issue at 10, enter the lower section of the condenser 4, issue at 11, and are taken up by the circulation pump 12 and are circulated through 13 to the gas inlet piping into which they enter at 14, and are again circulated into the catalyzing apparatus 2.

The mixture of the alcohols and water which collects at the lower part 5 of the apparatus 4, flows out through 19 and 20 and the cocks 21 and 22 and enters one of the two water-removing apparatus 23 or 24 which are put into alternate use and may be externally cooled by a cooling mixture which respectively enters at 35—36 or 35—37 and issues at 37^1—35^1 or at 36^1—35^1. Since the total amount of the liquid is about one-half the capacity of the recipient in use, the pressure of the liquid is first partially released by opening cocks 27 or 28 so as to discharge the dissolved gases through the pipe 29 which leads them to the compressor, the pressure being thus reduced to one or two atmospheres, this being necessary for the circulation movement of the liquids. The gases which are disengaged may be scrubbed in the brine used to supply the recipients, as will be further mentioned. When the liquid has thus been allowed to expand, I supply at 44—42 or 44—43 a suitable amount of a saturated common salt solution, compressed to the proper degree. The water of the salt solution serves for the dissolution and subsequent separation of the soluble alcohols, while the salt lowers the freezing point of the water and prevents the latter from freezing within the apparatus 23, 24 when the cooling brine is subsequently circulated around said apparatus. The device for the cooling of the refrigerating liquid is then operated. The alcoholic liquid in the presence of the internal salt solution separates into two layers, whereof the bottom layer contains only the very soluble alcohols (methyl and ethyl alcohols) which are present in very small quantities. This bottom layer is evacuated according to the indications of the external level gauges, and the operation is performed a second time. The insoluble alcohols remaining in the apparatus are then circulated through 38 under the control of cocks 31, 32 into the second section of the condenser 4, in which they will be heated and will be wholly or partially volatilised, and will proceed thence through 34, after a total dehydration upon potassium carbonate, into the first column 52 of the rectifying plant. The salt solution is discharged at 43 or 42 into tube 44 and is separately distilled to remove the soluble alcohols contained therein, and said salt solution may be again employed, after concentration. Tube 41 and cocks 39, 40 serve for emptying the apparatus when it is desired to discharge the cooling brine.

As concerns the carbon dioxide which is liquefied at 8, this is discharged at 45—46 and sent into the lower section of the condenser 7 in which it is volatilised, issuing thence at 47; it is heated in the second section of the condenser 7 into which it enters at 48, issuing at 49, at which point its expansion is regulated by a suitable cock.

The different alcohols are separated in the columns 52, 53, 56, 57, 60 and 61 which form part of the rectifying plant. The pure alcohols are collected in the recipients 54, 58 and 62 and the last-distilled products are collected at 64. 63 is a manometric tube. The rectifying operation may be completed in vacuum.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1. Method for synthesizing higher alcohols by the catalytic treatment of gas mixtures containing hydrogen and carbon monoxide at high temperature and pressure with the catalysts herein specified, which consists in cooling without releasing the pressure the gaseous mixture produced in the synthesizing operation in order to condense the alcohols and water produced, in further cooling the non-condensed gas still under pressure, in order to remove by condensation the carbon dioxide, and in subjecting the gaseous mixture freed from carbon dioxide to a further synthesizing operation.

2. Method according to Claim 1, wherein the cold produced by the evaporation of the liquid carbon dioxide and the cold vapours of carbon dioxide are utilized for the cooling of said non-condensed gas.

3. Method according to Claim 1 or 2, in which the pressure of the mixture of liquid alcohols and water under pressure obtained in the first cooling step is partially released, the gases thus generated being again subjected to the synthesizing operation, while the alcohols which separate by gravity, and those dissolved in water which are separated by means of a sodium chloride solution, are successively dehydrated, distilled and rectified.

4. Installation for carrying out the method according to Claims 1 to 2, comprising two condensers connected in series and each of which is divided into four sections, the sections of the first condenser being used for heating respectively the gases to be treated in the catalyzing chamber, the collected alcohols to be rectified, a cooling liquid and the gases issuing from the second condenser and to be subsequently sent back to the catalyzing chamber, while the sections of the second condenser are successively cooled by the cold gases discharged at the outlet of said condenser, by the evaporated carbon dioxide, by a cooling liquid and by the evaporation of the liquid carbon dioxide collecting at the bottom of said condenser.

5. Installation according to Claim 4 which further comprises expanding apparatus in which the pressure of the liquid mixture of alcohols and water collected in said condensers is partially released, said expanding apparatus being provided with a cooling liquid circulation, with means for supplying and discharging a sodium chloride solution and for discharging the separated alcohols and the gases produced by the said partial expansion.

6. Method for synthesizing higher alcohols substantially as described.

7. Installation for synthesizing higher alcohols substantially as described and as shown in the accompanying drawing.

Dated this 29th day of March, 1926.

MARKS & CLERK.

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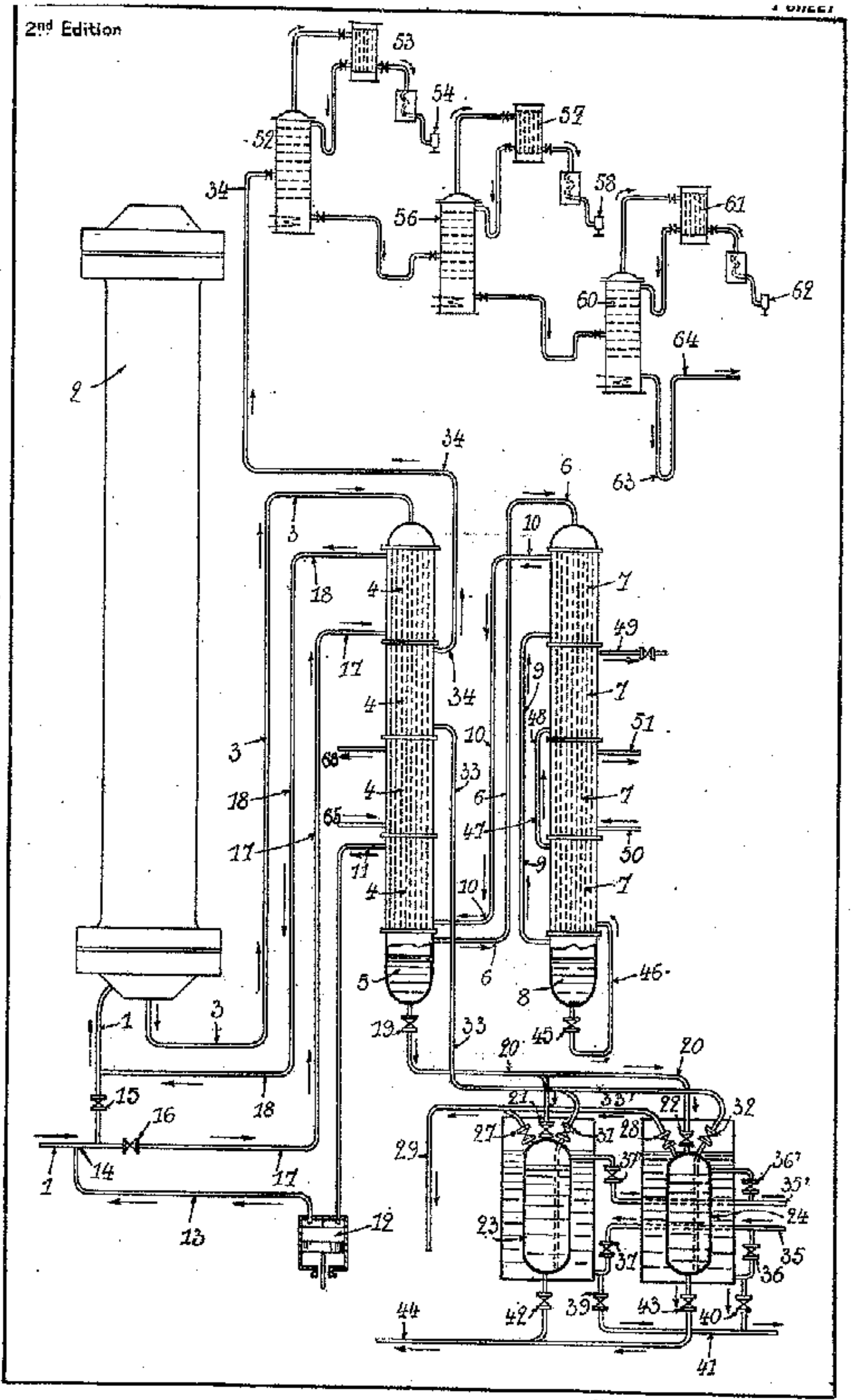
2nd Edition

1 SHEET

[This Drawing is a reproduction of the Original on a reduced scale]



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