

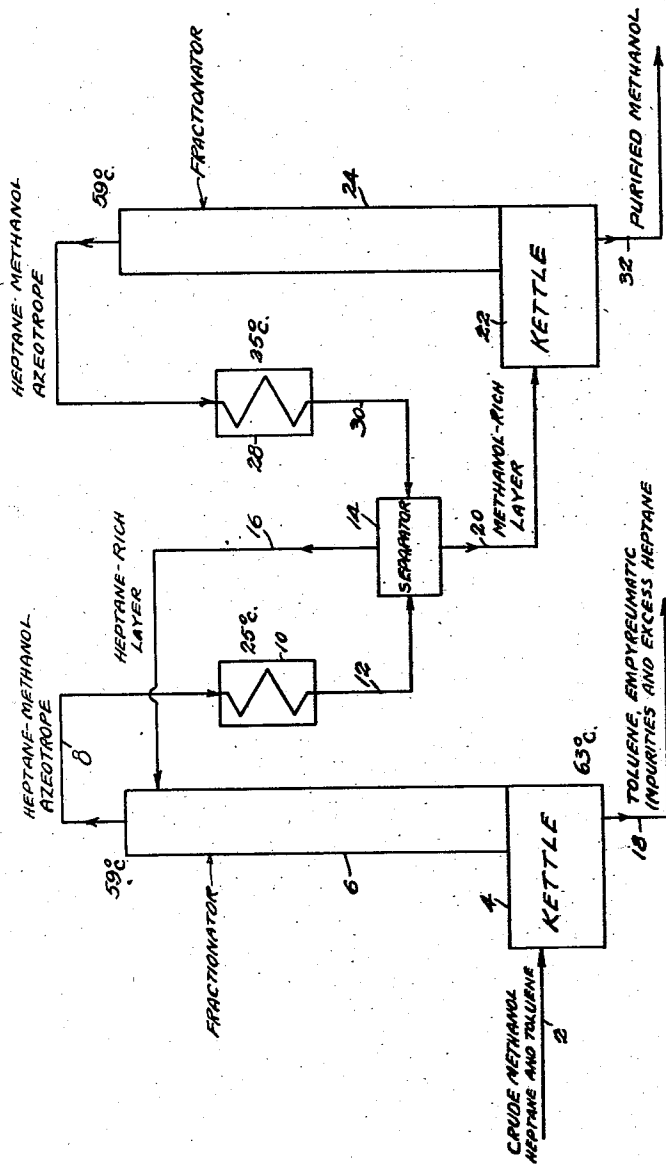
July 12, 1949.

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REFINING OF CRUDE METHANOL
BY AZEOTROPIC DISTILLATION

2,476,205

Filed Aug. 4, 1945

2 Sheets-Sheet 1



Inventor:
James F. McCants
By: *Thim, Chan & Mack-Lou Long*
Attys

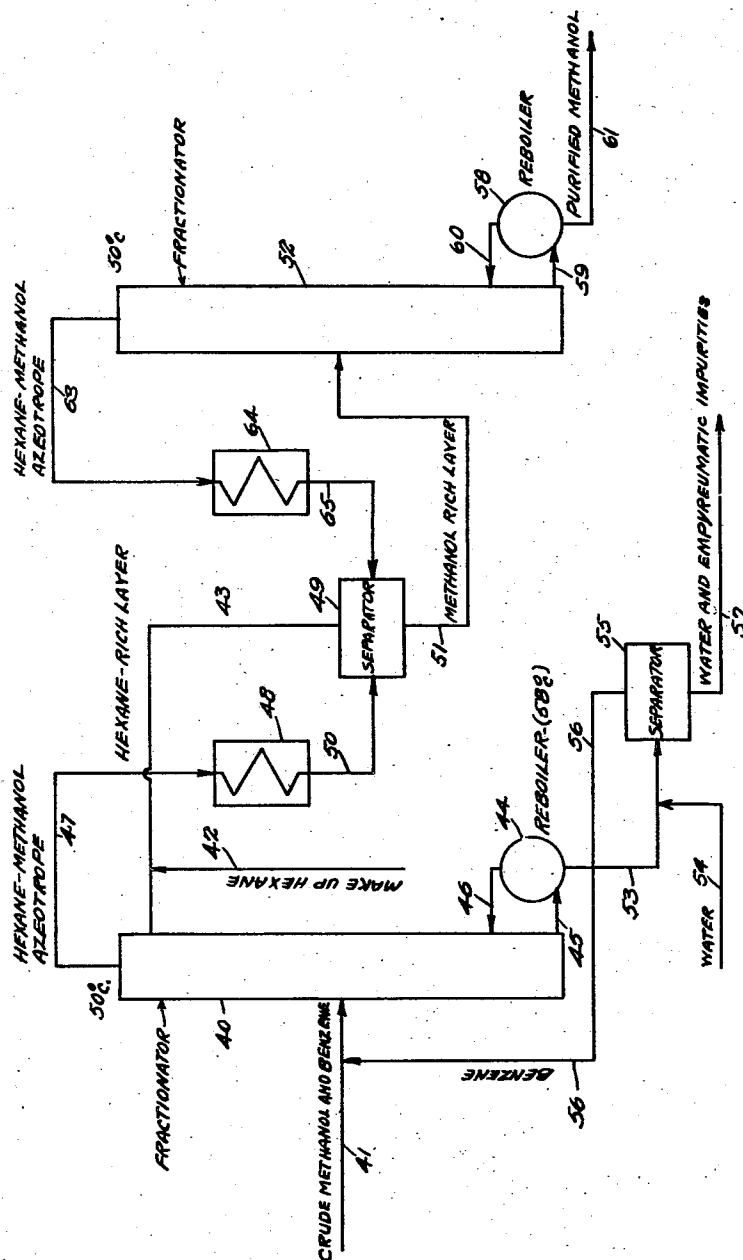
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Inventor:
James F. McCants
By: *Wm. Alan McKelvey*
Attys.

UNITED STATES PATENT OFFICE

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REFINING OF CRUDE METHANOL BY
AZEOTROPIC DISTILLATIONJames F. McCants, Pawhuska, Okla., assignor to
Skelly Oil Company, Tulsa, Okla., a corporation
of Delaware

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10 Claims. (Cl. 202-42)

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The present invention relates to the refining of crude methanol containing small amounts of empyreumatic materials that cannot be completely separated from the methanol by ordinary fractional distillation.

Crude methanol produced by any of numerous prior art methods usually contains impurities, some of which impart an offensive odor to the product. The impurities which are responsible for imparting the offensive odor are present in very low concentration and are very difficult structurally to identify. The generic term "empyreumatic impurities" will be used herein to refer to these odor imparting materials.

A primary object of this invention is to provide a new and useful process for treating crude methanol to produce a product essentially free from such empyreumatic materials as are originally contained therein.

A further object is to provide a method for refining and purifying the methanol fractions of the crude liquid product produced by certain methods, such as the vapor phase partial oxidation of gaseous hydrocarbons.

One feature of the process comprises fractionally distilling crude methanol containing empyreumatic materials in the presence of a normally liquid non-aromatic hydrocarbon which forms a minimum boiling azeotropic mixture with methanol which passes out of the distillation zone as an overhead product that, upon cooling, condenses and forms two phases. In accordance with this invention, this process is applicable to crude methanol fractions having relatively wide boiling ranges. The preferred method for carrying out this process involves fractional distillation of crude methanol in the presence of two different types of liquids, one a normally liquid aromatic hydrocarbon and the other a normally liquid aliphatic or alicyclic hydrocarbon.

In carrying out the preferred method of this process, it is essential that the aromatic hydrocarbon-methanol azeotrope boil somewhat above the boiling point of the normally liquid aliphatic

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or alicyclic hydrocarbon-methanol azeotrope, and furthermore that the aromatic hydrocarbon be charged in excess of that amount necessary for aromatic hydrocarbon-methanol azeotrope formation. The reason for this boiling temperature differential and use of excess aromatic hydrocarbon will become more evident upon further reading of the herein described process.

I have further discovered that certain derivatives of hydrocarbons, such as the halogenated hydrocarbons, may be substituted for the normally liquid aromatic hydrocarbons in the manner herein described. Examples of such halogenated hydrocarbons are amyl chloride, 1,2-dichloro-normal-butane, chloroform, and carbon tetrachloride.

The empyreumatic impurities in low molecular weight crude alcohols are more soluble in the normally liquid aromatic or halogenated hydrocarbons than they are in the normally liquid aliphatic or alicyclic hydrocarbons. With this fact in mind, my discovery utilizes the fact that the aromatic or halogenated hydrocarbons exercise a selective solvent action upon the empyreumatic impurities, thus leading to the greatly improved process of separating these from the methanol, which process is the subject of the present invention.

A novel feature of my invention consists in adding an aromatic hydrocarbon to an aliphatic or alicyclic hydrocarbon and crude methanol and distilling the resulting mixture in a fractionating column. By virtue of the respective boiling points, the aliphatic or alicyclic hydrocarbon-methanol azeotrope formed is taken off as the overhead product, while the aromatic hydrocarbon-methanol azeotrope is retained in the column, and the excess aromatic hydrocarbon and empyreumatic impurities are withdrawn as the kettle product. The aromatic hydrocarbon may be separated from the empyreumatic impurities and sufficiently purified for further use by agitating and extracting with water, since the empyreumatic impurities, being quite soluble in water,

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are easily washed from the aromatic hydrocarbon.

Although the mechanism of the observed improvement in the purification process by the addition of the aromatic hydrocarbon is not known, it is believed that such an improvement is due to two factors:

(1) The selective solvent action of the excess aromatic hydrocarbon for the empyreumatic impurities, and

(2) The formation of a methanol-aromatic hydrocarbon azeotrope which, by virtue of its higher boiling point, is continually refluxed back down the column, carrying with it the empyreumatic impurities.

Another feature in my present invention resides in condensing and cooling the overhead distillate from the fractionating column to a sufficient temperature, and without adding water or diluting it in any other way, to obtain phase separation. That is, in this process, I separate and distill directly, and without intermediate aqueous dilution, the alcohol-rich lower layer from the reflux separator, this being done in a second distillation column. One aspect of the invention, therefore, consists in providing an improved process of separating, purifying, and refining crude methanol, which is more particularly described hereinafter.

A crude oxidation product, produced by the vapor phase partial oxidation of gaseous aliphatic hydrocarbons, comprises an aqueous solution of a large number of compounds including acetaldehyde, acetone, acetals, methanol, ethanol, isopropyl and propyl alcohols, formaldehyde, organic acids, etc. By ordinary fractionation this crude liquid oxidation product can be separated into a fraction containing acetaldehyde, a second fraction containing methyl acetone, a third fraction comprising chiefly methyl alcohol, a fourth fraction comprising chiefly higher alcohols, and a residual fraction of crude aqueous formaldehyde.

The third fraction comprising chiefly crude methanol is preferably purified of certain aldehyde impurities by polymerizing with caustic soda, which step is accomplished by heating the crude methanol in a batch still with sufficient caustic soda to polymerize any aldehyde impurities present, and to drive off as overhead vapors partially purified methanol, leaving as a still residue the waste caustic and aldehyde polymers. It may be advantageous to combine this purification treatment with the fractional distillation step used in isolating a crude methanol fraction from the remainder of the oxidation mixture.

Irrespective of the care with which the aforementioned caustic treatment and fractionation is carried out, this type of partial purification does not remove all of the empyreumatic impurities which impart an offensive and pungent odor to the methanol. For testing purposes, it is convenient to determine the total amount of said empyreumatic impurities, expressing the amount of said impurities in terms of "apparent" dimethyl acetal concentration. This method involves treating a sample of methanol containing said impurities with an equal volume of concentrated sulfuric acid and matching the color produced with methanol solutions of dimethyl acetal of known concentration when treated in like manner with concentrated sulfuric acid.

Fig. 1 is a flow sheet illustrating the procedure and arrangement of equipment for a semi-con-

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tinuous or batch azeotropic distillation according to the process of the present invention;

Fig. 2 is a flow sheet illustrating the procedure and arrangement of equipment for continuous azeotropic distillation employing the method of the present invention.

In the diagrams and in the descriptions of the following operations, no attempt has been made to indicate the position of auxiliary apparatus such as heat exchangers, heating sources, condensers, pumps and other pertinent equipment, as the proper placement of these will at once be apparent to those skilled in the art.

In the following descriptions the process is described and claimed as if carried out at atmospheric pressure, which at the place where the process was carried out is approximately 740 millimeters. It will be understood, however, that subatmospheric pressures or superatmospheric pressures may be used without departing from the spirit and scope of the invention.

The following examples and table illustrate the principles underlying my process for refining and purifying crude methanol as applied in actual operation:

EXAMPLE I

Reference is made to Fig. 1. This shows a semi-continuous or batch operation, using as a charging stock 300 ml. of caustic-treated methanol, containing 1.25 per cent of "apparent" dimethyl acetal as an impurity. This was charged through pipe 2 to kettle 4 of fractionating column 6. To this fractionator, through pipe 2, was also charged 200 ml. of commercial grade heptane along with 100 ml. of toluene. Heat was applied to the kettle 4 at the base of the column. When the temperature at the top of the column reached about 59° C., distillate vapors composed of heptane and methanol in azeotropic proportions were withdrawn from the fractionating column through the overhead pipe 8, leaving the toluene, excess heptane, methanol, and empyreumatic impurities in the column and kettle. The overhead vapors were condensed and cooled to about 25° C. in the condenser 10. On cooling to this temperature the condensate formed a methanol-rich phase and a heptane-rich phase, and the mixture of phases being passed to separator 14 at the approximate vertical center thereof through pipe 12, where the methanol-rich phase settled to form a lower layer and the heptane-rich phase rose to form an upper layer. The heptane-rich upper layer was withdrawn through pipe 16 and returned to the upper portion of fractionator 6 as reflux. The methanol-rich lower layer was withdrawn through pipe 20 and introduced into a kettle 22 at the base of fractionating column 24 constituting a second distillation zone for other treatment, as hereinafter described. The material remaining in fractionating column 6 and kettle 4 formed a second azeotropic mixture comprising methanol and toluene, having a boiling point of about 63° C. The empyreumatic impurities contained in the crude methanol, being more soluble in toluene than in heptane, were concentrated in kettle 4 and in the lower plates of column 6 and were withdrawn as a part of the residual fraction of toluene and excess heptane from kettle 4 through pipe 18.

Heat was supplied to kettle 22 to which the methanol-rich layer from reflux separator 14 was discharged. The mixture of the methanol-rich layer consisted predominantly of methanol and a small amount of heptane. When the temperature at the top of fractionating column 24

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reached about 59° C., distillate vapors composed of heptane and methanol in azeotropic proportions were withdrawn through overhead vapor pipe 26, leaving as a kettle product substantially pure methanol, which was withdrawn from kettle 22 through pipe 32. The overhead vapors were condensed and cooled to about 25° C. in condenser 28. On cooling to this temperature the condensate formed a methanol-rich phase and a heptane-rich phase, which mixture of phases was passed through pipe 30 to separator 14 at the vertical center thereof where the methanol-rich phase settled to form a lower layer and the heptane-rich phase rose to form an upper layer. These layers self-evidently blended with similar layers already present.

The "apparent" dimethyl acetal impurity content of the methanol treated in the method described above was reduced from 1.25 per cent to 0.075 per cent. A second portion of the same crude methanol charging stock, having a dimethyl acetal impurity of 1.25 per cent was processed in this batch distillation without employing the second azeotropic agent, i. e., the toluene. The "apparent" dimethyl acetal impurity content of the methanol thus treated without the azeotropic agent toluene was reduced from 1.25 per cent to 0.20 per cent, thus showing the beneficial effects of the added aromatic azeotropic agent in purifying methanol-containing empyreumatic impurities.

EXAMPLE II

Reference is made to Fig. 2. This shows a continuous operation, using as a charging stock a fraction of crude methanol in admixture with an aromatic hydrocarbon, in this example benzene, which was charged to fractionating column 10 through pipe 41. An aliphatic hydrocarbon, in this instance, hexane (boiling range 67°-71° C.), was charged to fractionating column 10 through pipes 42 and 43, in sufficient quantity to start the system in operation. Heat for this column was provided by a heater or reboiler 44 at its base, into which excess benzene and empyreumatic impurities from the base of the column were withdrawn through pipe 45 to be heated and returned as vapors to the column through pipe 46. In fractionating column 40 there were formed two azeotropes; one was a hexane-methanol azeotrope (boiling point about 50° C.); and the other was a benzene-methanol azeotrope (boiling point about 58° C.). When the temperature at the top of the column 40 reached approximately 50° C., distillate vapors, composed of hexane and methanol, were continuously withdrawn from said column through overhead pipe 47, and were condensed and cooled to approximately 25° C. in condenser 48. On cooling to this temperature, the condensate formed a hexane-rich phase and a methanol-rich phase. The mixture of phases was passed to reflux separator 9 at the approximate vertical center thereof, through pipe 50, where the methanol-rich phase settled to form a lower layer and the hexane-rich phase rose to form an upper layer. The hexane-rich upper layer was continuously withdrawn through pipe 43, and returned to the upper portion of column 40. The methanol-rich lower layer was continuously withdrawn through pipe 41, and introduced at an intermediate level into second fractionating column 52, constituting second distillation zone for other treatment, as hereinafter described. The residual product of benzene and empyreumatic impurities, not

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vaporized and returned from reboiler 44 to column 40 through pipe 46, was continuously withdrawn through pipe 53 and mixed with water introduced through pipe 54, and then passed to separator 55, in which two phases formed. The lower phase comprised water and empyreumatic impurities and the upper phase comprised substantially pure benzene. The purified benzene was continuously returned through pipes 56 and 41 for reuse in column 40, while the water and empyreumatic impurities were continuously withdrawn as a residue from the separator 55 through pipe 57.

The second fractionating column 52 to which the methanol-rich layer from reflux separator 49 was discharged, was supplied with heat from a reboiler 58 to which substantially pure methanol from the base of fractionator 52 was introduced by pipe 59. Methanol vapors generated in reboiler 58 were returned to column 52 through pipe 60. In column 52, the introduced methanol-rich layer partially volatilized to form vapors comprising an azeotropic mixture of hexane and methanol and a residual product of substantially pure methanol, which was continuously withdrawn from the reboiler through the product discharge pipe 61. The hexane-methanol azeotropic vapors left the top of the fractionating column 52 at a temperature of about 50° C. through pipe 63 and were condensed and cooled in condenser 64 to approximately 25° C., and then passed to reflux separator 49 through pipe 65 at the approximate vertical center thereof where phase separation occurred as above described.

In a modified form of either of the examples given, some portion of the methanol-rich layer from the reflux separator might be returned with the aliphatic hydrocarbon layer to the fractionating columns 6 or 40 as reflux.

While the present invention has been described, so far as these specific examples of methods of semi-continuous and continuous operations are concerned, it is to be understood that aliphatic hydrocarbons other than heptane and hexane may also be used. Pentane, for example, forms with methanol a binary azeotrope boiling at about 31° C., which is very effective for purifying methanol. The percentage of methanol in the methanol-hexane azeotropic mixture (Example II) is about 51 mole per cent, while that of methanol in a pentane-methanol azeotropic mixture is about 13 mole per cent. Aromatic hydrocarbons, other than benzene and toluene, such as the xylenes, may be used as aromatic azeotropic agents to remove a substantial amount of the impurities from the methanol; and aliphatic hydrocarbons other than heptane, hexane, and pentane, may also be used as the aliphatic azeotrope-forming agents, such as for example the octanes, and the dimethyl pentanes. The use of halogenated hydrocarbons in place of the aromatic hydrocarbons has already been mentioned.

To illustrate the efficient results obtained by the practice of this process, actual data recorded on several runs are found in the table. Commercial grade hydrocarbons were used as the azeotropic agents in compiling the data comprising this table. The effectiveness of the added aromatic hydrocarbon is made more apparent when the temperature differential between the boiling points of the aliphatic hydrocarbon-methanol azeotrope and the methanol itself is relatively small. Through the use of the added aromatic hydrocarbon, it is possible to use a higher boiling aliphatic azeotropic agent and still produce highly purified methanol.

TABLE

Comparison of results of runs using two azeotropic agents with results of runs using one azeotropic agent

Per Cent Impurities Contained in Crude Methanol	First Azeotropic Agent	Second Aromatic or Halogenated Hydrocarbon Liquid	Vol. of First Azeo. Agent in ml.	Vol. of Second Liquid in ml.	Vol. of Methanol Charged in ml.	Per Cent Impurities in Recovered Methanol
1.25	pentane.....	benzene.....	100	25	200	none
1.25	do.....	xylene.....	100	25	200	none
1.25	hexane.....	benzene.....	100	25	200	none
2.9	do.....	xylene.....	100	25	200	none
2.9	do.....	none.....	100	0	200	trace
2.9	heptane.....	toluene.....	300	100	300	0.10
2.9	do.....	do.....	200	50	300	0.12
1.25	do.....	do.....	200	100	300	0.075
1.25	do.....	xylene.....	200	100	300	0.075
1.25	do.....	none.....	100	0	200	0.20
2.9	do.....	do.....	100	0	200	0.20
1.25	do.....	1,2-dichloro-normal-butane.....	100	25	100	0.15
1.25	do.....	amyl chloride.....	100	25	100	0.15
1.25	octane.....	none.....	100	0	200	0.30
1.25	do.....	xylene.....	100	25	200	0.10
1.25	pentane.....	chloroform.....	100	25	100	none
1.25	cyclopentane.....	do.....	100	25	100	none
1.25	methylcyclopentane.....	carbontetrachloride.....	100	25	100	none
1.25	hexane.....	do.....	100	25	100	none
1.25	heptane.....	1,2-dichloro-normal-butane.....	100	25	100	0.15
1.25	do.....	amyl chloride.....	100	25	100	0.15

Illustrative of the degree of purification which it is possible to secure by this new and improved process, a narrow boiling range fraction of methanol, containing 1.25% of "apparent" dimethyl acetal, was purified by one of the processes heretofore described, using benzene and hexane as the purifying agents. The final product contained no detectable empyreumatic impurities. From the same narrow boiling fraction of crude methanol containing 2.9% of "apparent" dimethyl acetal, when subjected to purification using toluene and commercial heptane as the purifying agents, a product of purified methanol containing less than 0.12% dimethyl acetal was produced.

As the boiling point of the methanol-azeotropic agent mixture which is collected as the overhead product from columns 40 and 52, as shown in the illustrative Example II, approaches the boiling point of methanol, the tendency for the empyreumatic impurities to be carried over with the azeotropic mixture increases, thus reducing the effectiveness of the purification process. However, the higher boiling azeotropic mixtures are more economical to use because a higher percentage of methanol is contained in the overhead product. It is in this critical range that the added effectiveness of the second purifying agent, namely an aromatic hydrocarbon, is of greatest value. In other words, it then becomes possible to use a higher boiling more efficient normally liquid aliphatic azeotropic agent than could be used if the aromatic compound were not present.

The process of the present invention is particularly directed to the purification of crude methanol; however, it may also be used for separating and concentrating other oxidation products, such as the aldehydes and ketones normally present in oxidation products. The process may likewise be used to purify such higher boiling alcohols as ethanol and propanol.

While the general principles of the improved purification methods have been hereinabove described in some detail, it is to be understood that the invention is by no means limited to the exact examples given, as these are given merely by means of illustration. The essential feature is the use of the second liquid which, while capable

of forming a second, higher-boiling azeotrope with the methanol or other alcohol being purified, is capable of carrying out of the system, in substantially unvolatilized form, the empyreumatic impurities contained in the alcohol that is being subjected to this method of purification.

The use of alicyclic hydrocarbons as the "non-aromatic hydrocarbons" in the process described above is claimed in my application Serial No. 608,971, filed August 4, 1945.

Accordingly, I claim:

1. In a process for the elimination of empyreumatic impurities from methanol by azeotropic distillation with a normally liquid non-aromatic hydrocarbon having from five to eight carbon atoms per molecule and in which process the methanol forms an azeotropically boiling mixture with said hydrocarbon that forms an overhead product of said distillation, the improvement which comprises carrying out said process in the presence of an amount of a second liquid in excess of that required to form a second azeotropically boiling mixture with said methanol, said second liquid being selected from the group consisting of the aromatic hydrocarbons benzene, toluene and xylene, and of halogenated hydrocarbons selected from the group consisting of amyl chloride, 1,2-dichloro-n-butane, chloroform and carbon tetrachloride, which second liquid enables the more adequate and complete separation of the empyreumatic impurities from the methanol in the form of a non-volatilized material capable of being withdrawn as such from the distillation zone in association with said second-named liquid.

2. The process of claim 1 in which the second liquid is benzene.

3. The process of claim 1 in which the second liquid is toluene.

4. The process of claim 1 in which the second liquid is xylene.

5. Process of purifying methanol which comprises conjointly distilling it through a fractionating system with a sufficient amount of a saturated aliphatic hydrocarbon having from five to eight carbon atoms per molecule to form an azeotropically boiling mixture with said methanol and an amount of an aromatic hydrocarbon selected from the group consisting of benzene

toluene and xylene in excess of that required to form a second azeotropically boiling mixture with said methanol; separating the lower-boiling methanol-aliphatic hydrocarbon azeotropic mixture as an overhead distillate from the higher-boiling methanol-aromatic hydrocarbon azeotropic mixture; withdrawing as a kettle product the excess aromatic hydrocarbon containing empyreumatic impurities, adding water thereto to effect the separation of aromatic hydrocarbon therefrom, and recirculating said aromatic hydrocarbon to the initial distillation zone; cooling and condensing the overhead distillate into liquid saturated aliphatic hydrocarbon-rich and methanol-rich phases, returning the saturated aliphatic hydrocarbon-rich phase to the initial distillation, and redistilling the methanol-rich phase in a second distillation zone, to form a purified liquid methanol and a saturated aliphatic hydrocarbon-methanol azeotrope, cooling the said azeotrope to form a liquid methanol-rich and a liquid saturated aliphatic hydrocarbon-rich phase, and returning the latter to the initial distillation zone, and withdrawing the purified liquid methanol as the kettle product.

6. The process of claim 5 in which the non-aromatic hydrocarbon is hexane and the aromatic hydrocarbon is benzene.

7. The process of claim 5 in which the non-aromatic hydrocarbon is heptane and the aromatic hydrocarbon is toluene.

8. The process of claim 5 in which the non-aromatic hydrocarbon is octane and the aromatic hydrocarbon is xylene.

9. Process of purifying methanol which comprises mixing it with sufficient amounts of heptane and toluene, the former sufficient to form an azeotropically boiling mixture with the methanol and the latter in excess of that required also to form an azeotropically boiling mixture with the methanol and heating the resulting mixture of heptane, toluene and methanol in an initial distillation zone to a temperature of about 63° C. (at substantially atmospheric pressure) whereby a methanol-heptane azeotrope having a boiling point of about 59° C. and a methanol-toluene azeotrope having a boiling point about 63° C. are formed; distilling off the first azeotrope, separating it by cooling into a liquid heptane-rich and a liquid methanol-rich phase, returning the heptane-rich phase to the initial distillation zone, re-

distilling the methanol-rich phase in a second distillation zone to form purified liquid methanol and a vaporous heptane-methanol azeotrope, and cooling the latter to form a liquid methanol-rich and a liquid heptane-rich phase, and returning the latter to the initial distillation zone.

10. Process of purifying methanol which comprises mixing it with an amount of benzene in excess of that required to form an azeotropically boiling mixture with said methanol and introducing the mixture along with a sufficient amount of hexane to form an azeotropically boiling mixture with said methanol into an initial distillation zone, whereby two different boiling azeotropes form: one comprising hexane and methanol having a boiling point of about 50° C. at atmospheric pressure, and one of benzene and methanol having a boiling point above about 58° C. at atmospheric pressure; distilling off the first azeotrope as an overhead product, cooling it to cause its separation into a hexane-rich phase and a methanol-rich phase and returning the hexane-rich phase to the initial distillation zone; withdrawing the excess benzene and empyreumatic impurities from the kettle of the initial distillation zone, adding water thereto to effect the separation of benzene therefrom, and recirculating said benzene to the initial distillation zone; redistilling the aforesaid methanol-rich phase in a second distillation zone to form liquid purified methanol and a vaporous hexane-methanol azeotrope, withdrawing the purified methanol as a kettle product, and cooling the said vaporous azeotrope to form a liquid methanol-rich and a liquid hexane-rich phase and returning the latter to the initial distillation zone.

JAMES F. McCANTS.

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