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J. F. McCANTS
PURIFICATION OF METHANOL BY
AZEOTROPIC DISTILLATION

2,476,206

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2 Sheets-Sheet 1

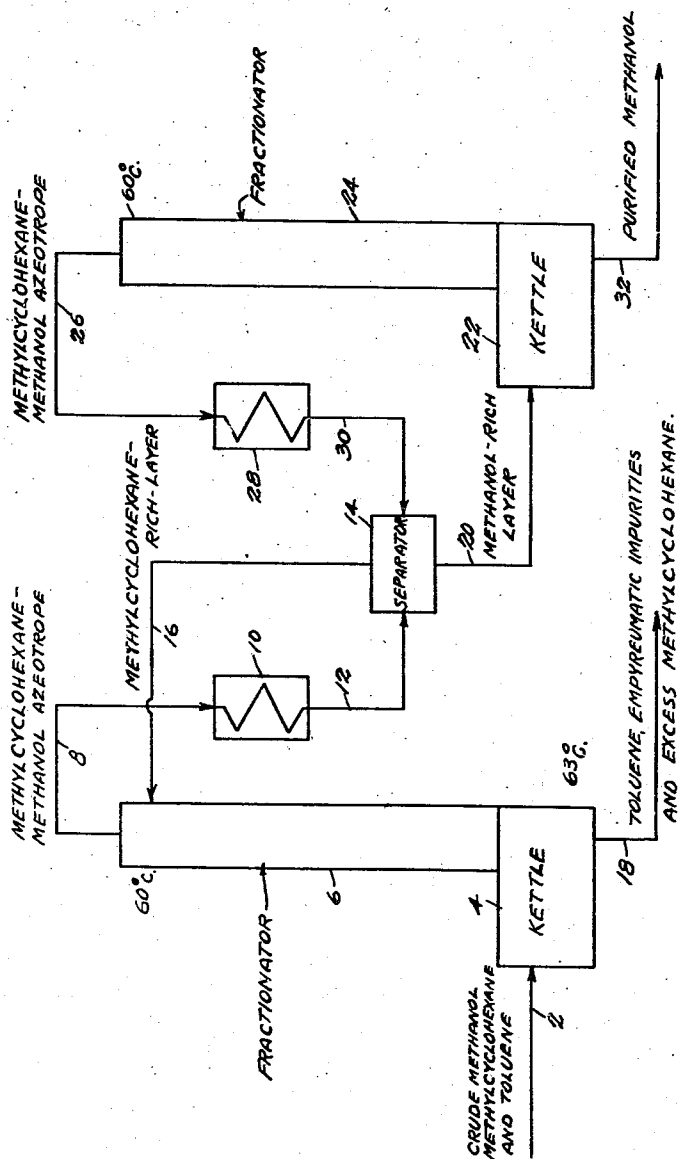


Fig. 1.

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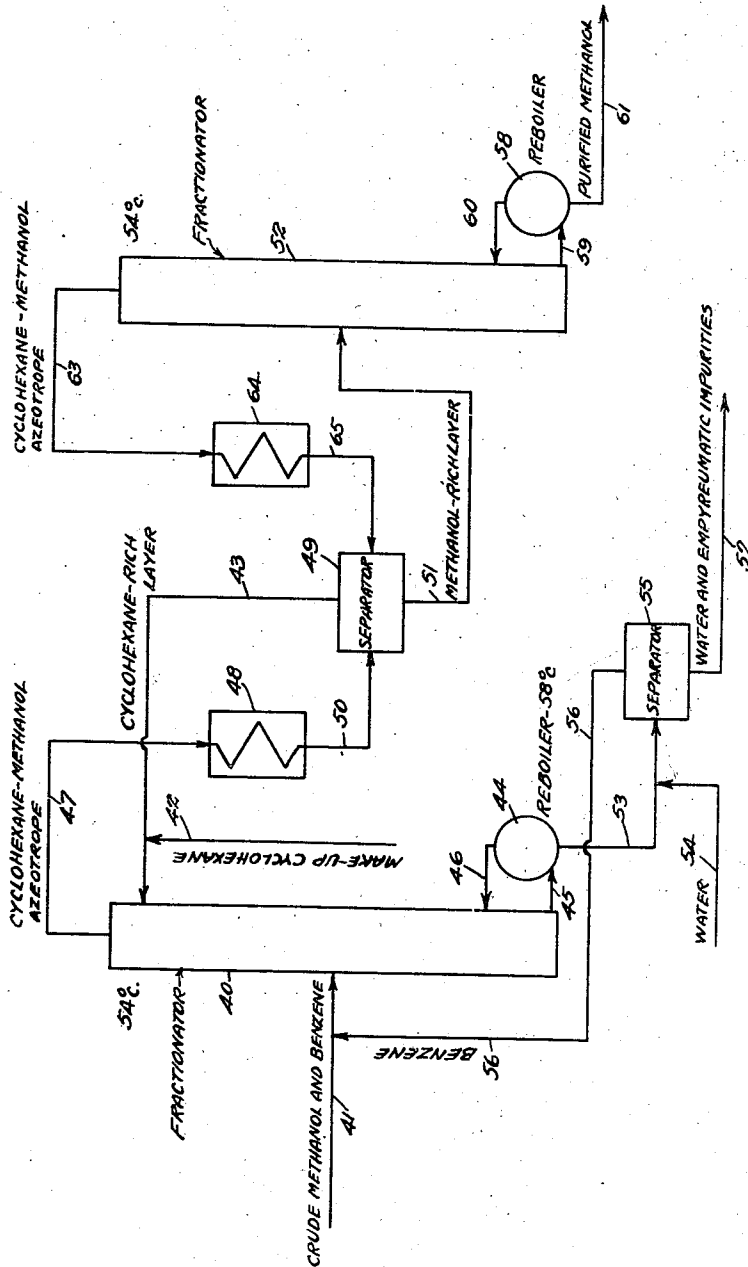


Fig. 2.

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UNITED STATES PATENT OFFICE

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PURIFICATION OF METHANOL BY
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14 Claims. (Cl. 202-42)

1

The present invention relates to the refining of and purification of crude methanol containing small amount 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 the present invention is to provide a new and useful process for treating crude methanol to produce a product essentially free from such empyreumatic materials 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 methods, such as the vapor phase partial oxidation of gaseous hydrocarbons.

An important feature of the process consists of fractionally distilling crude methanol containing empyreumatic materials in the presence of a normally liquid alicyclic hydrocarbon which forms a minimum boiling azeotropic mixture with methanol whereupon said azeotropic mixture upon cooling forms two phases. The empyreumatic materials remain as the kettle product of the fractionating column.

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 hydrocarbon azeotropic agents, one a normally liquid aromatic hydrocarbon and the other a normally liquid 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 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.

The empyreumatic impurities in low molecular weight crude alcohols are more soluble in the normally liquid aromatic hydrocarbons than they are in the normally liquid alicyclic hydrocarbons. With this fact in mind, my discovery utilizes the fact that aromatic hydrocarbons exercise selective

2

solvent action upon the empyreumatic impurities in a process for the purification of methanol.

A novel feature of my invention consists in adding an aromatic hydrocarbon to alicyclic hydrocarbon and crude methanol and distilling the resulting mixture in a fractionating column. By virtue of the respective boiling points, the 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, 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 elective 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 novel feature of my invention resides in condensing and cooling the overhead distillate from the fractionating column to a sufficient temperature, and without adding water or diluting 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.

3

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 thereto an offensive and pungent odor. 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-continuous 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 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 methyl cyclohexane along with 100 ml. of toluene. Heat was applied to kettle 4 at the base of the column. When the temperature at the top of the column reached about 60° C., distillate vapors composed of methyl cyclohexane and methanol in azeotropic proportions were withdrawn from the fractionating column through the overhead pipe 8, leaving in the column and kettle toluene, excess methyl cyclohexane, methanol and empyreu-

4

matic impurities. The overhead vapors were condensed and cooled to about 25° C. in condenser 10. On cooling to this temperature, the condensate formed a methanol-rich phase and a methyl cyclohexane-rich phase, and the mixture of phases was 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 methyl cyclohexane-rich phase rose to form an upper layer. The methyl cyclohexane-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 herein-after 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 methyl cyclohexane, were concentrated in kettle 4 and lower plates of column 6 and were withdrawn as a part of the residual fraction of toluene and excess methyl cyclohexane 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 methyl cyclohexane. When the temperature at the top of fractionating column 24 reached about 60° C., distillate vapors composed of methyl cyclohexane 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 methyl cyclohexane-rich phase, and the 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 methyl cyclohexane-rich phase rose to form an upper layer.

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 charge stock, having a dimethyl acetal impurity of 1.25 per cent was processed in this batch distillation without employing the second azeotropic agent 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 0.25 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 40 through pipe 41. An alicyclic hydrocarbon, in this instance cyclohexane (boiling range 78-81° C.), was charged to fractionating column 40 through pipes 42 and 43, in sufficient quantity to start the system in operation. Heat for column

40 was provided by a heater or reboiler 44 at its base into which benzene and empyreumatic impurities from the base of the column were withdrawn through pipe 45 to be heated and returned as vapors through pipe 46 to the column. In fractionating column 40 there were formed two azeotropes; one was cyclohexane-methanol azeotrope (boiling point about 54° C.); and the other was benzene-methanol azeotrope (boiling point about 58° C.). When the temperature at the top of the column reached approximately 54° C., distillate vapors composed of cyclohexane and methanol were continuously withdrawn from the 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 cyclohexane-rich phase and a methanol-rich phase. The mixture of phases was passed to reflux separator 49 at the approximate vertical center thereof, through pipe 50, where the methanol-rich phase settled to form a lower layer and the cyclohexane-rich phase rose to form an upper layer. The cyclohexane-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 51 and introduced at an intermediate level into a second fractionating column 52, constituting a second distillation zone for other treatment, as hereinafter described. The residual product of benzene and empyreumatic impurities not 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 separator 55 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.

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 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 cyclohexane and methanol and a residual product of substantially pure methanol, which was continuously withdrawn from the reboiler through the product discharge pipe 61.

5 The cyclohexane-methanol azeotropic vapors left the top of the fractionating column 52 at a temperature of about 54° 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 15 from the reflux separator might be returned with the alicyclic hydrocarbon layer to the fractionating column 40 as reflux.

While the present invention has been described, so far as these specific examples of methods of 20 semi-continuous and continuous operations are concerned, it is to be understood that alicyclic hydrocarbons other than cyclohexane and methyl cyclohexane may also be used. Methyl cyclopentane, for example, forms with methanol a 25 binary azeotrope boiling at about 51° C., which is very effective for purifying methanol. The percentage of methanol in the methanol-methyl cyclopentane azeotropic mixture is relatively low when compared with that of a methanol-methyl cyclohexane azeotropic mixture. Aromatic hydrocarbons, other than benzene, and toluene, such as the xylenes, may be used as aromatic azeotropic agents to remove a substantial amount 30 of the impurities from the low molecular weight crude alcohols; and alicyclic hydrocarbons other than methyl cyclohexane, cyclohexane, and methyl cyclopentane, may also be used as the alicyclic azeotrope forming agents, such as, for example, cyclopentane, the dimethyl cyclopentanes, and ethyl cyclopentane.

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 alicyclic hydrocarbon-methanol azeotrope and the methanol itself is relatively 35 small. Through the use of the added aromatic hydrocarbon, it is possible to use a higher boiling alicyclic 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	Alicyclic Hydrocarbon Azeo. Agent	Aromatic or Hydrocarbon Azeo. Agent	Vol. of Alicyclic Azeo. Agt. in ml.	Vol. of Aromatic Azeo. Agent in ml.	Vol. of Methanol Charged in ml.	Per Cent Impurities in Recovered Methanol
1.25	cyclopentane	benzene	100	25	200	none
1.25	methyl cyclopentane	do	100	25	200	none
1.25	do	none	100	0	200	trace
1.25	cyclohexane	xylene	100	25	200	none
2.9	do	toluene	100	25	200	none
2.9	do	benzene	100	25	200	none
1.25	do	none	100	0	200	0.05
2.9	methyl cyclohexane	toluene	200	50	300	0.15
2.9	do	none	200	0	300	0.25
1.25	do	toluene	200	50	300	0.075
1.25	do	xylene	200	50	300	0.10
1.25	do	none	200	0	300	0.20
1.25	ethylcyclohexane	do	100	0	200	0.35
1.25	do	xylene	100	25	200	0.10

NOTE.—All runs were made using a 10 plate column and a reflux ratio of 10:1.

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 2.9% "apparent" dimethyl acetal, was purified by the process heretofore described using benzene and cyclohexane as the purifying agents. The final product contained no detectable empyreumatic impurities. From the same narrow boiling fraction of crude methanol containing 2.9% "apparent" dimethyl acetal, when subjected to purification using toluene and methyl cyclohexane as the purifying agents, a product of purified methanol containing 0.15% dimethyl acetal was produced. Even when using the alicyclic hydrocarbon as the sole azeotrope-former, good purification of the methanol resulted, as shown by the above table.

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 alicyclic azeotropic agent than could be used if the aromatic compound were not present.

The presently described process may also be used for separating and concentrating other oxidation products, such as the aldehydes and ketones normally present in the crude methanol. The process may likewise be used to purify such higher-boiling alcohols as ethanol and propanol.

While the principle of the present separation, refining, and purification process for low molecular weight alcohols and practical methods of operation have been described such as the examples given, it is to be understood that the illustrations are merely to clarify the general mode of operation, and that this invention is not intended to be limited to the specific alicyclic and aromatic hydrocarbon azeotropic agents used, the specific temperatures, volume ratios, or specific apparatus except as defined in the appended claims.

I claim:

1. Process of producing purified methanol from crude methanol containing empyreumatic impurities which comprises azeotropically distilling said crude methanol while in admixture with a sufficient amount of a saturated alicyclic hydrocarbon having from five to eight carbon atoms per molecule to form an azeotropically boiling mixture with said methanol and with an amount of an aromatic hydrocarbon in excess of that required to form a second azeotropically boiling mixture with said methanol, said aromatic hydrocarbon being selected from the group consisting of benzene, toluene and xylene, whereby an overhead distillate consisting of an azeotrope of said alicyclic hydrocarbon and purified methanol is formed, leaving as a kettle product said aromatic hydrocarbon containing the empyreumatic impurities.

2. The process of claim 1 in which the aromatic hydrocarbon is benzene.

3. The process of claim 1 in which the aromatic hydrocarbon is toluene.

4. The process of claim 1 in which the aromatic hydrocarbon is xylene.

5. Process of producing purified methanol from crude methanol containing empyreumatic impurities which comprises conjointly distilling said crude methanol through a fractionating system with a sufficient amount of a saturated alicyclic 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, whereby two azeotropically boiling mixtures result, that of methanol and said alicyclic hydrocarbon having the lower-boiling point, and that of methanol and aromatic hydrocarbon having the higher-boiling point; separating said lower-boiling azeotropic mixture as an overhead distillate, and withdrawing the excess aromatic hydrocarbon containing empyreumatic impurities from the system.

6. The process of claim 5 in which the alicyclic hydrocarbon is cyclohexane and the aromatic hydrocarbon is benzene.

7. The process of claim 5 in which the alicyclic hydrocarbon is methyl cyclohexane and the aromatic hydrocarbon is toluene.

8. The process of claim 5 in which the alicyclic hydrocarbon is ethylcyclohexane and the aromatic hydrocarbon is xylene.

9. Process of purifying methanol containing empyreumatic impurities which comprises mixing it with substantial volumes each of cyclohexane and benzene and heating the resulting mixture in an initial distillation zone to a temperature of about 58° C. (at substantially atmospheric pressure) whereby a methanol-cyclohexane azeotrope having a boiling point of about 54° C. and a methanol-benzene azeotrope having a boiling point above 58° C. are formed; distilling off the first azeotrope, separating it by cooling into liquid cyclohexane-rich and liquid methanol-rich phases, returning the cyclohexane-rich phase to the initial distillation zone, redistilling the methanol-rich phase in a second distillation zone, and forming a purified liquid methanol and a cyclohexane-methanol azeotrope, cooling the latter to form a liquid methanol-rich and a liquid cyclohexane-rich phase, and returning the latter to the initial distillation zone; and withdrawing benzene carrying said impurities from the initial distillation zone.

10. Process of purifying methanol which comprises conjointly distilling it through a fractionating system with more than sufficient amounts of both a saturated alicyclic hydrocarbon having from five to eight carbon atoms per molecule and an aromatic hydrocarbon selected from the group consisting of benzene, toluene and xylene, to form whereby two azeotropically boiling mixtures separating the lower boiling methanol-alicyclic hydrocarbon azeotropic mixture as an overhead distillate from the higher-boiling methanol-aromatic hydrocarbon azeotropic mixture, cooling and condensing the former into liquid saturated aliphatic hydrocarbon-rich and methanol-rich phases, and returning the saturated alicyclic hydrocarbon-rich phase to the initial distillation zone; withdrawing as a kettle product that portion of the aromatic hydrocarbon which has not formed an azeotrope and which

hence contains the empyreumatic impurities, adding water thereto to effect the separation of said impurities therefrom, and recirculating said aromatic hydrocarbon to the initial distillation zone; redistilling the methanol-rich phase in a second distillation zone, to form purified liquid methanol, and a methanol-alicyclic hydrocarbon azeotrope, withdrawing the purified methanol as a kettle product and separating the methanol-alicyclic hydrocarbon azeotrope as an overhead distillate, cooling the said azeotrope to form a liquid methanol-rich and a liquid alicyclic hydrocarbon-rich phase, and returning the latter to the initial distillation zone.

11. The process of claim 10 in which the alicyclic hydrocarbon is cyclohexane and the aromatic hydrocarbon is benzene.

12. The process of claim 10 in which the alicyclic hydrocarbon is methyl cyclohexane and the aromatic hydrocarbon is toluene.

13. The process of claim 10 in which the alicyclic hydrocarbon is ethylcyclohexane and the aromatic hydrocarbon is xylene.

14. Process of removing empyreumatic water-soluble impurities from methanol which comprises distilling a given volume thereof with from about one-half to about one-third of its volume of an alicyclic hydrocarbon having from about 5 to 8 carbon atoms and with from about one-sixth to one-eighth of its volume of an aromatic hydrocarbon from the group consisting of benzene, toluene and xylene, thereby forming a first azeotropically boiling mixture having a boiling

point of about 54° C. at atmospheric pressure and a second azeotropically boiling mixture having a boiling point of about 58° C. at atmospheric pressure; distilling off the first azeotropically boiling mixture while the second mixture remains as a kettle product, the said impurities being concentrated therein and in that portion of the aromatic hydrocarbon that has not formed an azeotropically boiling mixture, withdrawing said aromatic hydrocarbon from the system, washing it with water to transfer the empyreumatic impurities to the same and returning the thus purified aromatic hydrocarbon to the process.

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