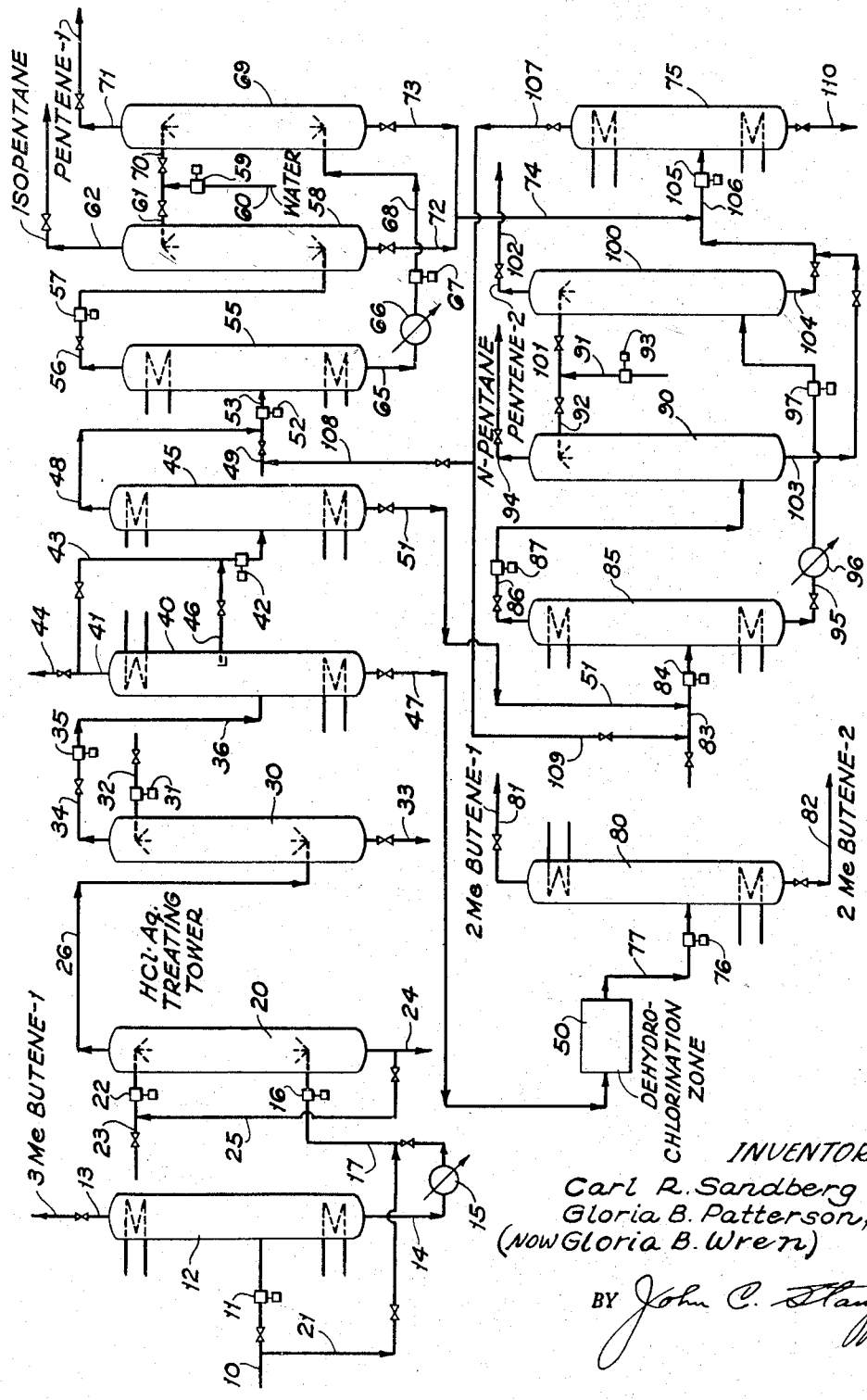
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AZEOTROPIC SEPARATION OF AMYLENES

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INVENTORS
Carl R. Sandberg
Gloria B. Patterson,
(Now Gloria B. Wren)

BY John C. Haupfear

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AZEOTROPIC SEPARATION OF AMYLENES

Carl R. Sandberg and Gloria B. Patterson, Dallas, Tex.; said Gloria B. Patterson now by marriage Gloria B. Wren; assignors, by mesne assignments, to Socony-Vacuum Oil Company, Incorporated, New York, N. Y., a corporation of New York

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This invention relates to the fractionation of a C_5 hydrocarbon cut of petroleum naphtha containing pentanes and pentenes. More particularly, this invention is concerned with the separation of relatively pure separate streams of 3-methyl butene-1, isopentane, pentene-1, 2-methyl butene-1, n-pentane, pentene-2, and 2-methyl butene-2 by means of distillative fractionation, using methylal as an azeotropic agent.

The conversion of a light paraffinic virgin naphtha by thermal cracking or catalytic cracking results in the production of a C_5 hydrocarbon fraction consisting of a mixture of paraffinic and mono-olefinic components which are extremely difficult to separate in reasonably pure form by ordinary distillative fractionation means. An efficient method for the separation of the above components in pure form is highly desirable. Thus, relatively pure pentene-1 and/or pentene-2 are desirable for the production of certain polymers. Relatively pure pentene-2 can be pyrolyzed to give high yields of butadiene. 2-methyl butene-1 and 2-methyl butene-2 are desirable feed stocks to alkylation processes for the production of high antiknock alkylates of low volatility. Isopentane is valuable as a blending stock for the production of aviation gasoline, and relatively pure n-pentane is desirable as a feed to catalytic isomerization processes. In general, the amylenes, if recoverable in pure form, are valuable as intermediates in the production of chemicals.

It is an object of this invention to obtain in relatively pure form separate streams of the paraffinic and mono-olefinic components of the C_5 fraction of cracked petroleum naphtha. Another object of this invention is to obtain separate streams of the various amylenes of the C_5 fraction of cracked petroleum naphtha. Another object of the invention is to obtain separate streams of n-pentane and isopentane which are substantially free of mono-olefinic hydrocarbons. Still another object is to separate isopentane from pentene-1. A further object is to separate n-pentane from pentene-2. Other objects will appear hereinafter.

As indicated above, the principal components of the C_5 hydrocarbon fraction consist of two paraffinic components and five mono-olefinic components. The boiling points of these components at normal atmospheric pressure lie within the range of from 20° C. to 40° C. The boiling points of the individual components are indicated below in Table I.

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Table I

Component	Boiling Point, ° C.
3-methyl butene-1	20.2
isopentane	27.9
pentene-1	30.1
2-methyl butene-1	31.1
n-pentane	36.08
pentene-2	36.5
2-methyl butene-2	38.5

It is obvious to one skilled in the art that the successful separation of a mixture containing the above components is impossible by simple distillative fractionation means. We have found, however, that these components can be separated by combining known methods with the use of methylal azeotropic agent for the separation of isopentane from pentene-1 and for the separation of n-pentane from pentene-2.

We have found that methylal forms an azeotrope with isopentane having the approximate composition of 70 volume per cent isopentane and 30 volume per cent methylal. The boiling point of this azeotrope at atmospheric pressure is 24.1° C. We have found that methylal forms an azeotrope with pentene-1 having the approximate composition of 74 volume per cent pentene-1 and 26 volume per cent methylal. The boiling point of this azeotrope is 29.8° C. Thus, the difference in boiling points of these azeotropes is about 5.7° C. By forming the azeotropes of these components we increase the differential boiling point from 2.2° C. to 5.7° C., thereby making possible the separation of the components by distillative fractionation.

Methylal also forms azeotropes with n-pentane and pentene-2. The n-pentane-methylal azeotrope contains about 72 volume per cent n-pentane and 28 volume per cent methylal, which azeotrope boils at about 31.5° C. at atmospheric pressure. The pentene-2-methylal azeotrope contains about 71 volume per cent pentene-2 and 29 volume per cent methylal, and this azeotrope boils at about 34.9° C. at atmospheric pressure. Hence, it can be seen that by utilizing the methylal azeotropes of these components, the differential boiling point is increased from about 0.4° C. to 3.4° C., thus making possible the separation of these two components by distillative fractionation means. In order to obtain complete separation of the components of the C_5 hydrocarbon stream containing the above seven components, it is only necessary to first separate 3-methyl butene-1, 2-methyl butene-1, and 2-methyl butene-2 from the mix-

ture and then obtain by simple fractionation means separate streams containing isopentane and pentene-1 in one stream and n-pentane with pentene-2 in the second stream to completely separate the C_5 hydrocarbon cut into its components.

The first step of our combination process, which is represented diagrammatically in the drawing, consists of separating 3-methyl butene-1, 2-methyl butene-1, and 2-methyl butene-2 from the mixture of C_5 hydrocarbons. The 2-methyl butene-1 and 2-methyl butene-2 are removed by treating the mixture with a concentrated solution of hydrochloric acid containing from about 30 to 37 per cent hydrogen chloride by weight. The acid treatment may be carried out at a temperature of from about 0° C. to about 20° C. in the liquid phase. The mixture of olefin chlorides and unreacted C_5 hydrocarbons is then fractionated to separate the olefin chlorides which may be dehydrohalogenated and fractionated to obtain relatively pure streams of 2-methyl butene 1 and 2-methyl butene-2. The unreacted C_5 hydrocarbon fraction is fractionated to obtain separate cuts containing (1) relatively pure 3-methyl butene-1, (2) a mixture consisting substantially of isopentane and pentene-1, and (3) a mixture consisting substantially of n-pentane and pentene-2. If desired, the 3-methyl butene-1 may be separated in relatively pure form by a preliminary fractionation of the C_5 hydrocarbons which is carried out before the treatment with hydrochloric acid. The separate streams containing respectively n-pentane and isopentane are treated with methylal to form the azeotropes of the paraffins and olefins associated therewith. These streams are separately fractionated to separate the azeotropes. The azeotropic fractions are scrubbed with a solvent selective for the removal of methylal therefrom to separate the methylal which is recycled to the azeotrope-forming steps. Water is an excellent solvent for the removal of the methylal from the azeotropic mixtures.

Referring now to the drawing, the C_5 hydrocarbon stream in line **10** having a boiling range of from about 20° C. to about 40° C. is passed by means of pump **11** to fractionator **12** wherein relatively pure 3-methyl butene-1 is separated and withdrawn as overhead product in line **13**. The mixture of higher boiling C_5 hydrocarbons is withdrawn from fractionator **12** as bottom product through line **14**. This bottom product is cooled by means of cooler **15** to a temperature within the range of from about 0° C. to about 20° C., and is then introduced by means of pump **16** in line **17** to hydrochloric acid-treating tower **20**. If desired, the C_5 hydrocarbon stream in line **10** may be sent directly to tower **20** through line **21** which connects with line **17**. This is particularly advantageous if the content of 3-methyl butene-1 in the hydrocarbon stream is relatively small. The action of concentrated hydrochloric acid on this component is only slight when contact is made with the acid in the above temperature range, but the 3-methyl butene-1 can be obtained as a relatively pure product stream in a subsequent fractionation as described hereinbelow.

Preferably tower **20** is packed with an inert material in order to increase contact of the hydrocarbon with hydrochloric acid which is introduced at a point near the top of the tower by means of pump **22** in line **23**. The hydrochloric acid is introduced as a fine spray, and as it passes downward over the surface of the packing, it

reacts with the 2-methyl butene-1 and 2-methyl butene-2 components to form the corresponding hydrocarbon chlorides. The acid is withdrawn from tower **20** through line **24** and at least a part of the acid is recycled to line **23** through line **25**. The mixture of unreacted hydrocarbons and hydrocarbon chlorides passes overhead through line **26** to scrubbing tower **30** wherein the ascending stream is scrubbed with water to remove residual acid from the mixture. The water is introduced to tower **30** by means of pump **31** in line **32**. Tower **30** may likewise be packed with inert packing material. The wash water is withdrawn from tower **30** through bottom drawoff line **33**. The liquid stream containing hydrocarbons and hydrocarbon chlorides passes overhead from tower **30** through line **34** and is introduced by means of pump **35** in line **36** to fractionator **40** at a pressure within the range of from about atmospheric to 5 atmospheres, preferably about 3 atmospheres.

Fractionator **40** which may be operated in one of two ways serves to separate the relatively high boiling hydrocarbon chlorides from the unreacted hydrocarbons of the C_5 fraction. If the 3-methyl butene-1 has been separated from the hydrocarbon mixture in fractionator **12** and recovered through line **13**, the remainder of the mixture of C_5 hydrocarbons passes overhead through line **41**, whence it is passed by means of pump **42** in line **43** to fractionator **45**. On the other hand, if the virgin C_5 hydrocarbon stream is not given a preliminary fractionation before treatment with hydrochloric acid, 3-methyl butene-1 is taken overhead from tower **40** through lines **41** and **44**, and the higher boiling hydrocarbons are withdrawn from tower **40** as a trapout stream through line **46**, which connects with line **43** leading to fractionator **45**. The mixture of hydrocarbon chlorides passes from tower **40** through line **47** to dehydrochlorination zone **50** described hereinbelow.

Fractionating tower **45** serves as a separation zone wherein the mixture of isopentane and pentene-1 is separated from the mixture of n-pentane and pentene-2. Tower **45** is operated at a pressure of from about atmospheric to about 5 atmospheres. The mixture of isopentane and pentene-1 is taken overhead through line **48** which connects with line **49** wherein the C_5 hydrocarbons are mixed with methylal azeotropic agent. The mixture of n-pentane with pentene-2 is withdrawn as bottom product through line **51**.

The amount of methylal introduced to line **49** depends on the composition of the C_5 hydrocarbon stream in line **48**. For every 70 parts of isopentane in the mixture there is introduced 30 parts of methylal, and for every 74 parts of pentene-1 in the mixture there is introduced to line **49** about 36 parts of methylal. The mixture of methylal, isopentane, and pentene-1 is passed by means of pump **52** in line **53** to fractionator **55**, which is operated at a pressure within the range of about 1 to 3 atmospheres. The methylal-isopentane azeotrope is taken overhead through line **56** and is passed by means of pump **57** to a point near the bottom of scrubbing tower **58**. Water is introduced to tower **58** by means of pump **59** in line **60** which joins line **61**. Tower **58** is packed with an inert packing material in order to obtain better distribution of the water and better contact of the same with the ascending hydrocarbon stream. Relatively pure isopentane which is free of methylal is taken overhead through line **62**.

The bottom product from fractionator **55** which consists of the methylal azeotrope of pentene-1 is withdrawn via line **65** and passes through cooler

66. From cooler 66 the azeotrope is passed by means of pump 67 in line 68 to the bottom of scrubbing tower 69 which is also packed with inert packing material. Water from line 60 is passed to line 70 and introduced into scrubbing tower 69 at a point near the top thereof. Pentene-1 substantially free of methylal is withdrawn from the top of tower 69 through line 71. Water solutions of methylal are withdrawn from the bottoms of towers 58 and 69 through lines 72 and 73 respectively, and the solutions are passed through line 74 to methylal recovery tower 75 as described hereinbelow.

Returning to the recovery of 2-methyl butene-1 and 2-methyl butene-2 from the corresponding chlorides in zone 50, the chlorides may be dehydrochlorinated thermally at temperatures within the range of from about 800° C. to 900° C. However, we prefer to obtain a mixture of these C_5 hydrocarbons by first hydrolyzing the chlorides with sulfuric acid of from 60 to 70 per cent strength, and then dehydrating the alcohols with 100 per cent sulfuric acid. The mixture of C_5 hydrocarbons recovered in zone 50 is passed by means of pump 76 in line 77 to fractionator 80. Substantially pure 2-methyl butene-1 is recovered overhead through line 81, and 2-methyl butene-2 is recovered as bottoms from tower 80 through line 82.

The mixture of n-pentane and pentene-2 in line 51 passes to line 83 wherein it is mixed with methylal in the ratio of about 28 or 29 parts of methylal per 71 or 72 parts of hydrocarbon to form the methylal azeotropes of these hydrocarbons. The azeotropic mixture is passed by means of pump 84 to fractionator 85 which is operated at a pressure of from about atmospheric to about 3 atmospheres gage. The n-pentane-methylal azeotrope is taken overhead from tower 85 through line 86 and is introduced at a point near the bottom of scrubbing tower 90 by means of pump 87. In tower 90, which may suitably be packed with inert material, the azeotrope is scrubbed with water introduced to tower 90 through lines 91 and 92 by means of pump 93. Relatively pure n-pentane passes overhead through line 94. The bottom product from tower 85 which consists of the methylal azeotrope of pentene-2 is passed through line 95 and cooler 96 by means of pump 97 and introduced to scrubbing tower 100 at a point near the bottom of the tower. Water is introduced at a point near the top of tower 100 from line 101. The descending stream of water removes the methylal from the azeotrope, and relatively pure pentene-2 is recovered as overhead through line 102. The water solution of methylal from towers 90 and 100 are withdrawn through lines 103 and 104. These water solutions together with the water solution of methylal in line 74 are passed to methylal recovery tower 75 by means of pump 105 in line 106. Methylal is taken overhead from recovery tower 75 through line 107 and is recycled to line 49 through line 108, and to line 83 through line 109. Water is withdrawn from tower 75 through bottom drawoff line 110.

The following examples illustrate the effectiveness of methylal as an azeotropic agent for the separation of isopentane from pentene-1, and the separation of n-pentane from pentene-2.

Example 1

Equal volumes of technical grade isopentane and technical grade pentene-1 were mixed. An attempt was made to fractionate a part of the mixture in a wire gauze-packed fractionator tower. No separation of these C_5 hydrocarbons was effected; that is, it was impossible to obtain cuts which even approximated pure isopentane and pure pentene-1. In a second experiment 70 milliliters of the above mixture and 70 milliliters of methylal were mixed and distilled in the same column under the same conditions relative to reflux ratio, throughput, and pressure. Azeotropes were formed with both isopentane and pentene-1. The methylal-isopentane azeotropic fraction which distilled at 24.1° C., was collected, and washed with water to remove the methylal. Hydrocarbon residue of this azeotropic fraction consisted of 28 milliliters of isopentane having an index of refraction of $N_D^{20}1.3539$ (theoretical, $N_D^{20}1.3537$). The methylal-pentene-1 azeotrope was collected at 29.8° C. 24 milliliters of pentene-1 was recovered from this fraction by washing the methylal from the fraction with water. The pentene-1 had a refractive index of $N_D^{20}1.3712$ (theoretical, $N_D^{20}1.3710$).

Example 2

A 70-milliliter sample of C_5 hydrocarbons consisting of 35 milliliters of technical grade pentene-2 and 35 milliliters of technical grade n-pentane was mixed with 70 milliliters of methylal, and the mixture was distilled in the wire gauze-packed fractionating column. 24 milliliters of n-pentane having a refractive index of $N_D^{20}1.3571$ (theoretical, $N_D^{20}1.3575$) was recovered from the n-pentane-methylal azeotropic fraction which also contained about 9⅓ milliliters of methylal. The methylal-n-pentane azeotropic fraction was recovered at a boiling point of about 31.5° C. The methylal azeotrope of pentene-2 consisting of 23 milliliters of pentene-2 and 9.4 milliliters of methylal was recovered at a temperature of 34.9° C. The methylal was removed from the fraction by scrubbing with water, and the pentene-2 recovered had a refractive index of $N_D^{20}1.3803$. The index of refraction of an equilibrium mixture of pentene-2(cis) and pentene-2(trans) is $N_D^{20}1.3800$. The index of refraction of pure pentene-2(cis) is $N_D^{20}1.3820$, and the index fraction of pure pentene-2(trans) is $N_D^{20}1.3795$.

The above examples indicate that it is possible and economically feasible to separate isopentane-pentene-1 and n-pentane-pentene-2 mixtures by fractionating these mixtures in the presence of methylal. Methylal is easily recoverable by washing the azeotropic fractions with water.

We claim:

1. The process for obtaining relatively pure streams consisting substantially of n-pentane, isopentane, pentene-1, and pentene-2 from a C_5 hydrocarbon stream containing the same which comprises adding to said C_5 hydrocarbon stream sufficient methylal to convert said n-pentane, isopentane, pentene-1, and pentene-2 to the methylal azeotropes of these C_5 hydrocarbons, fractionally distilling the mixture containing methylal, n-pentane, isopentane, pentene-1, and pentene-2 to produce separate streams consisting substantially of methylal-n-pentane azeotrope, methylal-isopentane azeotrope, methylal-pentene-1 azeotrope, and methylal-pentene-2 azeotrope, treating the separate streams containing the methylal azeotropes with a solvent selective for the removal of methylal from said azeotropes, and recovering separate streams of n-pentane, isopentane, pentene-1, and pentene-2 substantially free of methylal.

2. The process for separating a mixture of C_5

hydrocarbons containing normal pentane, isopentane, pentene-1, and pentene-2 into streams containing substantially only one C_5 hydrocarbon component which comprises the steps of (1) fractionating said mixture to obtain at least two fractions consisting of (*a*) a mixture of isopentane with pentene-1 and (*b*) a mixture of normal pentane with pentene-2, (2) adding methylal to fractions *a* and *b* of step 1, (3) fractionating in separate fractionating zones the mixtures of methylal with said fractions of step 2 to obtain separate azeotropic mixtures consisting of methylal with isopentane, methylal with pentene-1, methylal with normal pentane and methylal with pentene-2, (4) scrubbing the azeotropic mixtures of step 3 in separate scrubbing zones with a solvent to remove methylal from said azeotropic mixtures, and (5) recovering separate streams consisting substantially of normal pentane, isopentane, pentene-1, and pentene-2 from step 4 of the process.

3. The process for obtaining relatively pure streams of pentene-1 and pentene-2 from a C_5 hydrocarbon fraction of cracked naphtha which comprises the steps of (1) fractionating said C_5 hydrocarbon fraction to obtain fractions consisting substantially of (*a*) a mixture of isopentane with pentene-1 and (*b*) a mixture of normal pentane with pentene-2, (2) adding methylal to mixtures *a* and *b* of step 1 to form methylal-C_5 hydrocarbon mixtures, (3) fractionally distilling in separate fractionating zones the methylal-C_5 hydrocarbon mixtures of step 2 to produce overhead products consisting of methylal-paraffinic C_5 hydrocarbon azeotropic mixtures and to produce separate higher boiling fractions consisting of methylal-pentene-2 and methylal-pentene-1 azeotropic mixtures as bottom-drawoff products, (4) scrubbing the bottom drawoff products of step 3 with a solvent selective for the removal of methylal therefrom, and (5) recovering said relatively pure streams of pentene-1 and pentene-2 from step 4 of the process.

4. The process for separating the C_5 hydrocarbon components of a petroleum naphtha stream consisting substantially of 3-methyl butene-1, isopentane, pentene-1, normal pentane, pentene-2, 2-methyl butene-1, and 2-methyl butene-2 which comprises the steps of (1) passing said naphtha stream in contact with a concentrated aqueous solution of hydrogen chloride to form a mixture consisting of unreacted C_5 hydrocarbons and the hydrocarbon chlorides formed from the 2-methyl butene-1 and 2-methyl butene-2 in said stream, (2) fractionating the mixture obtained in step 1 in at least one fractionating column to obtain separate streams comprising (*a*) a stream of substantially pure 3-methyl butene-1, (*b*) a stream consisting substantially of an intimate mixture of isopentane and pentene-1, (*c*) a stream consisting substantially of a mixture of normal pentane and pentene-2, and (*d*) a stream consisting substantially of said hydrocarbon chlorides, (3) converting the hydrocarbon chlorides of step 2 to a hydrocarbon mixture containing 2-methyl butene-1 and 2-methyl butene-2, (4) fractionating the product of step 3 to obtain separate streams of 2-methyl butene-1 and 2-methyl butene-2, (5) fractionating streams *b* and *c* of step 2 in separate fractionating towers in the presence of methylal azeotropic agent to obtain separate streams consisting of azeotropic mixtures of methylal with isopentane, pentene-1, normal pentane, and pentene-2, (6) removing methylal azeotropic agent from the azeotropic mixtures of step 5, (7) recovering said 3-methyl butene-1 from step 2 and separately recovering 2-methyl butene-1 and 2-methyl butene-2 from step 4, and (8) separately recovering isopentane, pentene-1, normal pentane, and pentene-2 from step 6 of the process.

5. The process for separating a mixture of isopentane and pentene-1 which comprises the steps of (1) adding to said mixture about 30 parts by volume of methylal for each 70 parts by volume of isopentane in said mixture and also adding to said mixture about 26 parts by volume of methylal for each 74 parts by volume of pentene-1 in said mixture, (2) fractionally distilling the resulting mixture containing methylal, isopentane, and pentene-1 to obtain separate streams consisting of methylal azeotropes of isopentane and pentene-1, (3) separately treating said methylal azeotropes with water to remove methylal therefrom, and (4) recovering said isopentane and pentene-1 from step 3 of the process.

6. The process for separating a mixture of normal pentane and pentene-2 which comprises the steps of (1) adding to said mixture about 28 parts by volume of methylal for each 72 parts by volume of normal pentane in said mixture and also adding to said mixture about 29 parts by volume of methylal for each 71 parts by volume of pentane-2 in said mixture, (2) fractionally distilling the resulting mixture containing methylal, normal pentane, and pentene-2 to obtain separate streams consisting of methylal azeotropes of normal pentane and pentene-2, (3) separately treating said methylal azeotropes with water to remove methylal therefrom, and (4) recovering said normal pentane and pentene-2 from step 3 of the process.

7. The process for separating a mixture consisting substantially of 3-methyl butene-1, isopentane, pentene-1, n-pentane, pentene-2, 2-methyl butene-1, and 2-methyl butene-2 which comprises the steps of (1) fractionating said mixture to obtain (*a*) an overhead stream consisting substantially of 3-methyl butene-1 and (*b*) a fraction containing isopentane, pentene-1, n-pentane, pentene-2, 2-methyl butene-1, and 2-methyl butene-2, (2) passing fraction *b* of step 1 in contact with an aqueous solution of hydrogen chloride to form a mixture consisting of unreacted C_5 hydrocarbons and hydrocarbon chlorides formed from 2-methyl butene-1 and 2-methyl butene-2 in said fraction *b*, (3) fractionating the mixture of unreacted hydrocarbons and hydrocarbon chlorides obtained in step 2 in at least one fractionating column to obtain separate streams comprising a stream consisting substantially of an intimate mixture of isopentane and pentene-1, a stream consisting substantially of a mixture of n-pentane and pentene-2, and a stream consisting of said hydrocarbon chlorides, (4) converting the hydrocarbon chlorides of step 3 to a hydrocarbon mixture containing 2-methyl butene-1 and 2-methyl butene-2, (5) fractionating the product of step 4 to obtain separate streams of 2-methyl butene-1 and 2-methyl butene-2, (6) fractionating the isopentane-pentene-1 stream and the n-pentane-pentene-2 stream of step 3 in separate fractionating towers in the presence of methylal azeotropic agent to obtain separate streams consisting of azeotropic mixtures of methylal with isopentane, pentene-1, n-pentane, and pentene-2, (7) removing methylal azeotropic agent from the azeotropic mixtures of step 6, (8) recovering said 3-methyl butene-1 from step 1 and separately recovering 2-methyl butene-1 and 2-methyl butene-2 from step 5, and

(9) separately recovering isopentane, pentene-1, n-pentane, and pentene-2 from step 7 of the process.

8. In the process of separating the paraffinic components from the mono-olefinic components of a C_5 hydrocarbon fraction containing n-pentane, pentene-2, isopentane, and pentene-1, the improvement comprising the steps of (1) fractionating said C_5 hydrocarbon fraction to obtain separate streams consisting substantially of n-pentane and pentene-2 in one stream, and isopentane and pentene-2 in a second stream, (2) adding to the streams obtained in step 1 sufficient methylal to form methylal azeotropes of the paraffinic and mono-olefinic components in said streams, (3) separately fractionating the methylal n-pentane azeotrope from the methylal pentene-2 azeotrope, and separately fractionating the methylal isopentane azeotrope from the methylal pentene-1 azeotrope obtained in step 2, (4) scrubbing methylal from the azeotropes obtained in step 3 with a solvent to remove methylal from said azeotropes and (5) separately recovering n-pentane, pentene-2, isopentane, and pentene-1 from step 4 of the process.

9. The process of separating isopentane from a mixture containing paraffinic and mono-olefinic C_5 hydrocarbons which comprises the steps of (1) adding to said mixture sufficient methylal to form a methylal-isopentane azeotrope with the isopentane in said mixture, (2) fractionating the methylal containing C_5 hydrocarbon mixture of step 1 to obtain a low boiling azeotropic fraction consisting of methylal-isopentane azeotrope, and at least one fraction containing at least one C_5 hydrocarbon boiling at a higher temperature than said azeotropic fraction, (3) treating the azeotropic fraction of step 2 with a solvent to separate methylal therefrom, thereby forming two liquid phases consisting of liquid isopentane in one phase and a solution of methylal in said solvent in the other phase, and (4) recovering isopentane from step 3 of the process.

10. The process for separating normal pentane from a C_5 hydrocarbon fraction containing normal pentane and C_5 mono-olefins boiling at a higher temperature than normal pentane which comprises the steps of (1) adding to said fraction sufficient methylal to form a methylal-normal pentane azeotrope with the normal pentane in said fraction, (2) subjecting the methylal containing C_5 hydrocarbon fraction of step 1 to distillative fractionation to obtain a low boiling azeotropic fraction consisting of a methylal-normal pentane azeotrope and to obtain at least one fraction containing at least one C_5 hydrocarbon boiling at a higher temperature than said azeotropic fraction, (3) treating the azeotropic fraction of step 2 with a solvent to separate methylal therefrom and form two liquid phases consisting of liquid normal pentane in one phase and a solution of methylal in said solvent in the other phase, and (4) recovering normal pentane from step 3 of the process.

CARL R. SANDBERG.
GLORIA B. PATTERSON,
Now by marriage Gloria B. Wren.

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