Sept. 9, 1958 J. D. GARBER ET AL 2,851,499

EXTRACTION OF LIQUID HYDROCARBONS WITH 2,5-DIHYDROXYMETHYL TETRAHYDRO FURAN

Filed June 19, 1957 2 Sheets-Sheet 1

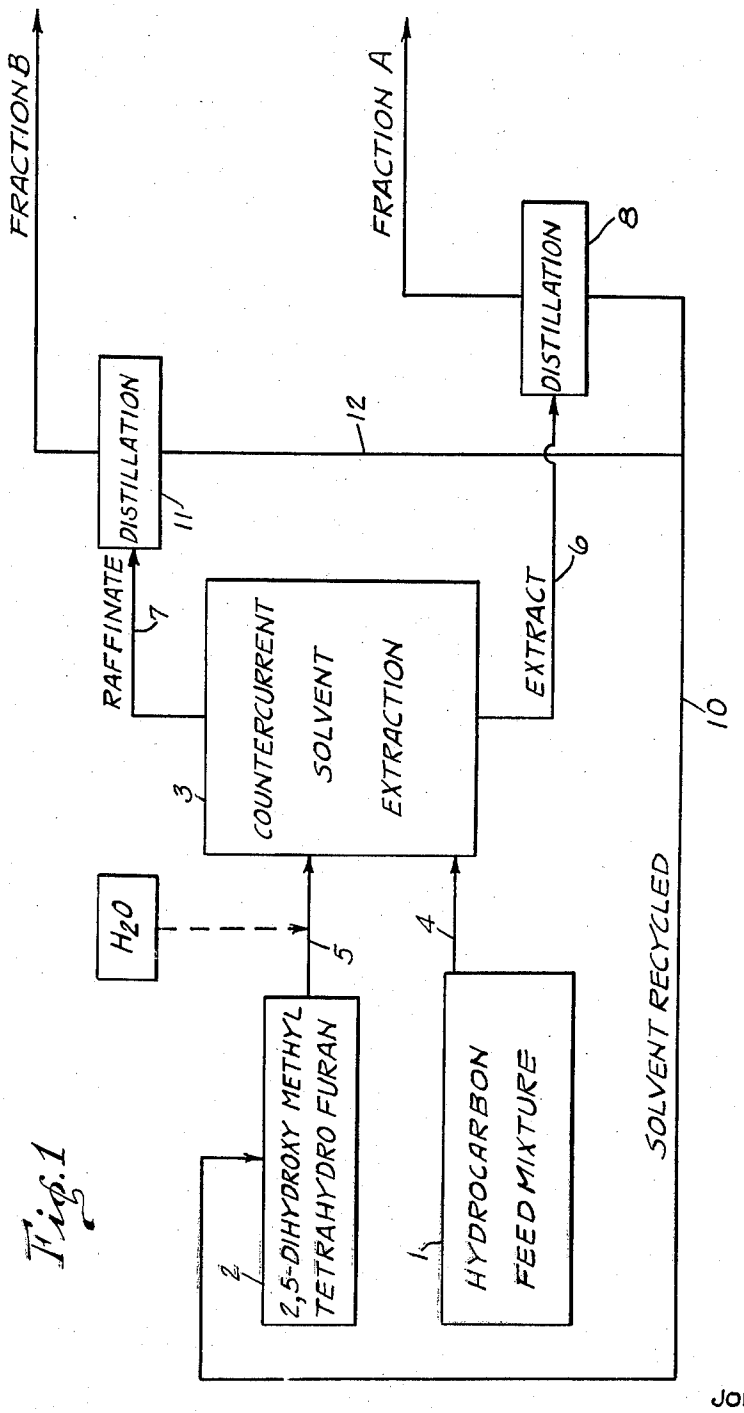


Fig. 1

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Fig. 2

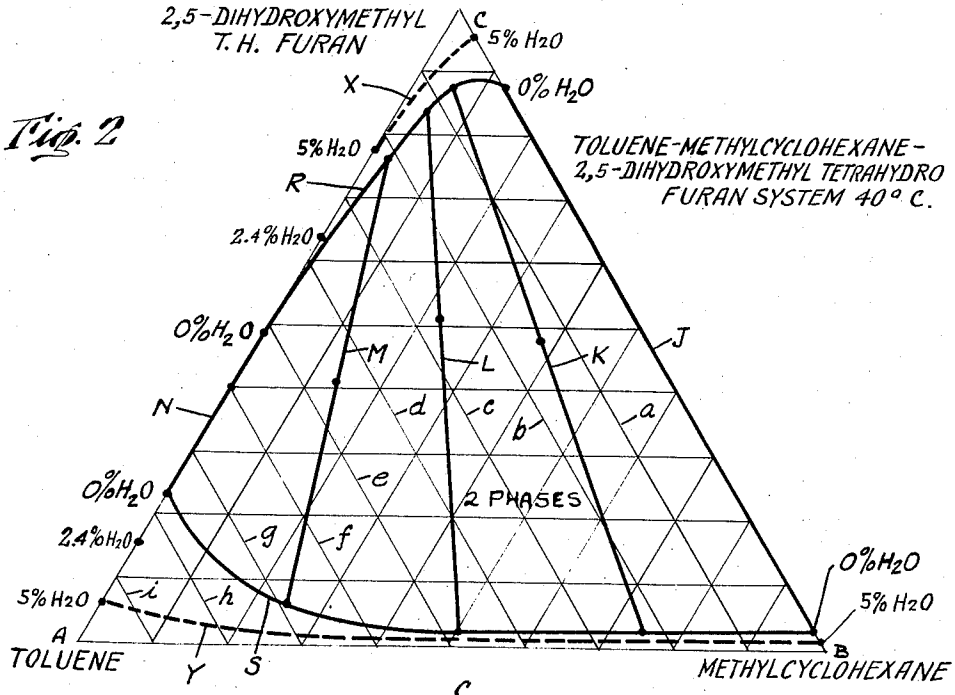
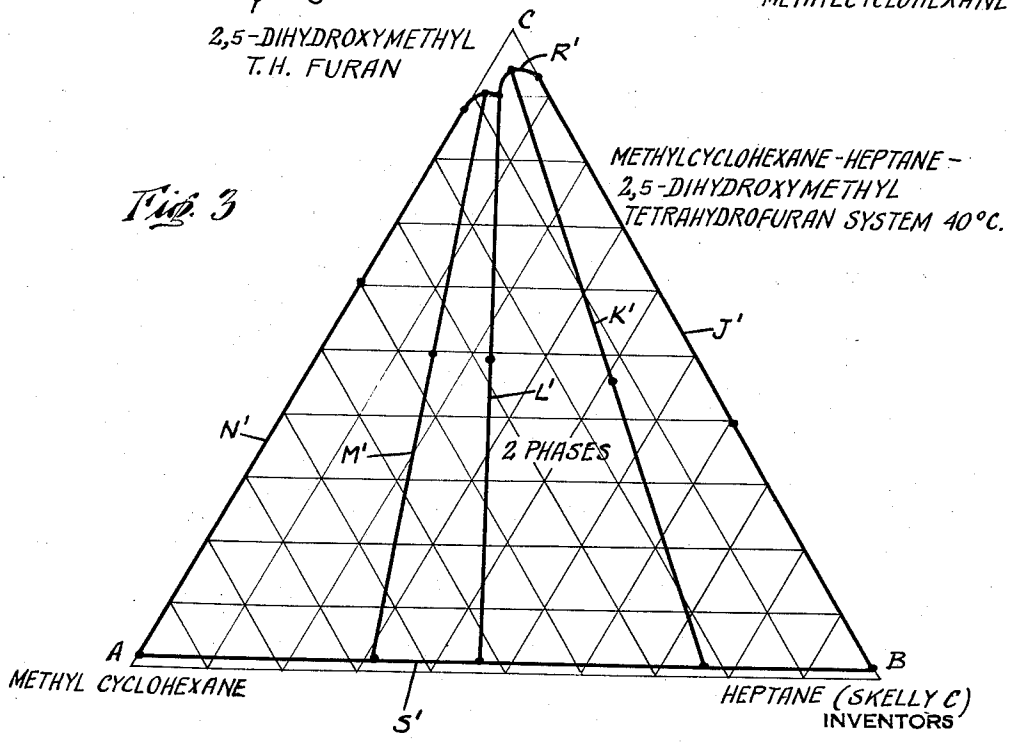


Fig. 3



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EXTRACTION OF LIQUID HYDROCARBONS WITH 2,5-DIHYDROXYMETHYL TETRAHYDRO FURAN

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8 Claims. (Cl. 260—666)

This invention relates to the solvent treatment of liquid mixtures of hydrocarbon products.

The invention is applicable to increase, readily and simply, the proportion of one of the constituents of the mixture in relation to the other constituent or constituents. It is particularly useful (i) to increase the aromatic hydrocarbon content of natural and straight run gasolines, (ii) to obtain aromatic hydrocarbons of high purity in high yield and (iii) to strip gasolines and kerosenes of aromatic hydrocarbons.

In accordance with the present invention, aromatic constituents are separated from liquid hydrocarbon products by contacting said liquid hydrocarbon products with 2,5-dihydroxymethyl tetrahydro furan. This is a hygroscopic, odorless, colorless and viscous liquid boiling at 265° C. at 760 mm. pressure and at 120° C. at 0.1 mm. pressure.

The invention is illustrated in the accompanying drawings in which:

Fig. 1 is a flow sheet used to explain the process of this invention;

Fig. 2 is a solubility diagram, at 40° C., of the ternary system consisting of (A) toluene, (B) methylcyclohexane, and (C) 2,5-dihydroxymethyl tetrahydro furan, based on the data set forth in Table I (Example 1), Table III (Example 3) and Table IV (Example 4); and

Fig. 3 is a solubility diagram, at 40° C., of the ternary system consisting of (A) methylcyclohexane, (B) heptane, and (C) 2,5-dihydroxymethyl tetrahydro furan, based on the data set forth in Table II (Example 2).

Referring to Figure 1, **1** is a source of supply, such as a tank, of a mixture of liquid hydrocarbons in a boiling range of gasoline or kerosene.

2 is a source of supply, such as a tank, of 2,5-dihydroxymethyl tetrahydro furan, which, according to this invention, is employed as a solvent to separate the hydrocarbon mixture into various components.

3 is a treating tower for solvent extraction which is operated in a counter-current manner. The mixture of liquid hydrocarbons flows from its supply **1** through line

4 into tower **3** near its bottom. The solvent 2,5-dihydroxymethyl tetrahydro furan flows from its supply **2** through line **5** into the top portion of tower **3**. In the tower **3** the feed mixture of liquid hydrocarbons and the solvent 2,5-dihydroxymethyl tetrahydro furan, flow in counter-current relation.

The extract is withdrawn from the bottom of tower **3** through line **6**, while the raffinate is withdrawn from the top of the tower through line **7**.

The extract is introduced into still **8**, wherein the fraction A extracted from the hydrocarbon feed mixture is separated from the 2,5-dihydroxymethyl tetrahydro furan by distillation, the distillate being condensed when the fraction A is desired in liquid form. The 2,5-dihydroxymethyl tetrahydro furan remaining in the still **8** is returned to the supply tank **2** through lines **9** and **10**.

The raffinate is introduced into still **11**, wherein the fraction B (consisting of the balance of the hydrocarbon feed mixture after the removal of fraction A therefrom) is separated by distillation from the relatively small quantity of 2,5-dihydroxymethyl tetrahydro furan contained in the raffinate, the distillate being condensed when the fraction B is desired in liquid form. The 2,5-dihydroxymethyl tetrahydro furan remaining in still **11** is returned to the supply tank **2** through lines **12** and **10**. Alternatively, the 2,5-dihydroxymethyl tetrahydro furan may be separated from fraction B by water washing.

The selective solvent action of 2,5-dihydroxymethyl tetrahydro furan is illustrated by the following table of various situations in which it may be used in the process shown schematically in Figure 1.

TABLE A

Situation	Hydrocarbon Feed Mixture	Fraction A	Fraction B
1	Aromatics and Naphthenics	Aromatics	Naphthenics.
2	Toluene (a single aromatic) and Methylcyclohexane (a single naphthenic)	Toluene	Methylcyclohexane.
3	Naphthenics and Aliphatics	Naphthenics	Aliphatics.
4	Methylcyclohexane (a single naphthenic) and Heptane (a single aliphatic)	Methylcyclohexane.	Heptane.
5	Aromatics and Aliphatics	Aromatics	Aliphatics.
6	Aromatics and Naphthenics and Aliphatics	Aromatics	Naphthenics and Aliphatics.

The effectiveness of this solvent in readily separating a mixture of toluene and methylcyclohexane (situation No. 2 of the above Table A), and which is illustrative of its effectiveness in separating aromatic hydrocarbons from a mixture of aromatic and naphthenic hydrocarbons (situation No. 1 of the above Table A), where these components of the feed mixture are not readily separable by distillation, is derivable from the solubility diagram shown in Fig. 2.

This Figure 2 is a graphic representation of the ternary (3-variable) system involved, using the apexes (A, B and C) of an equilateral triangle to represent each pure component, and using the distance along a straight line extending from a given apex perpendicularly to the opposite side to represent the magnitude of the corresponding component, in percent of the total mixture, the magnitude being 100 percent at the apex, and zero percent at the opposite side, of the triangle. Consequently, the

fine line "a" of Figure 2 parallel to the side of the triangle B—C is a scale line representing the mathematical condition in which the toluene (represented by apex A) is 10 percent of the total mixture, scale line "b" similarly represents the mathematical condition where toluene is 20 percent of the total mixture, and so on until scale line "i" similarly represents the mathematical condition where toluene is 90 percent of the total mixture. The other fine lines, parallel to the other sides of the triangle, similarly are scale lines representative of the various mathematical conditions for the other components of the ternary system.

Each of the heavy, solid straight lines J, K, L, M and N, termed tie-lines, of Figure 2 represents a test made to determine the composition of the components after an initial mixture has been separated into two phases (i. e., (i) a heavy phase, or extract portion, and (ii) a light phase, or raffinate portion). The heavy, solid curved line R joining the top ends of the tie-lines, and the heavy, solid curved line S joining the bottom ends of the tie-lines, together portray the solubility characteristics of this ternary system. Further, in a multiple-stage extraction system, such as schematically indicated by the treating tower 3, in Figure 1, the curve R of Figure 2 is the loci of the composition of the extract of any original composition lying between curves R and S (the loci progressing from right to left on curve R as the extract approaches the bottom outlet of the tower), while curve S of Figure 2 is the loci of the composition of the raffinate of such original composition (the loci progressing from left to right on curve S as the raffinate approaches the top outlet of the tower).

The effectiveness of this solvent in readily separating a mixture of methylclohexane and heptane (situation No. 4 of the above Table A), and which is illustrative of its effectiveness in separating naphthenics from a mixture of naphthenics and aliphatics (situation No. 3 of the above Table A), where these components of the feed mixture are not readily separable by distillation, is derivable from the solubility diagram shown in Fig. 3. This is a graphic representation based on the same principles described in connection with Figure 2. The heavy, solid straight lines J^1, K^1, L^1, M^1 and N^1 are the tie-lines, and the heavy, solid curve line R^1 joining the top ends of the tie-lines, and the heavy, solid curved line S^1 joining the bottom ends of the tie-lines, together portray the solubility characteristics of this ternary system. (The line S^1 is in fact curved, but in the scale employed in Figure 3 it is difficult to show the curvature involved, and the line appears as a straight line.) Further, in a multiple-stage extraction system such as schematically indicated by the treating tower 3 in Figure 1, the curve R^1 of Figure 3 is the loci of the composition of the extract of any original composition lying between the curves R^1 and S^1 (the loci progressing from right to left on curve R^1 as the extract approaches the bottom outlet of the tower), while curve S^1 of Figure 3 is the loci of the composition of the raffinate of such original composition (the loci progressing from left to right on curve S^1 as the raffinate approaches the top outlet of the tower).

In accordance with a further embodiment of this invention, water may be added to the 2,5-dihydroxymethyl tetrahydro furan and this aqueous mixture employed as the solvent for separating the constituents of an original mixture. When water is added to the 2,5-dihydroxymethyl tetrahydro furan, the solvency and selectivity of the aqueous mixture for the hydrocarbons toluene and methylcyclohexane is indicated by the solubility diagram shown in Figure 2. In this figure the heavy dotted curved lines X and Y together portray the solubility characteristics of this ternary system when 2,5-dihydroxymethyl tetrahydro furan and water mixture consists of 95 parts of 2,5-dihydroxymethyl tetrahydro furan and 5 parts of water, this ratio being indicated as "5% H_2O."

The following examples are given primarily by way of illustration and not of limitation.

EXAMPLE 1

Initial mixtures containing various proportions of toluene, methyl cyclohexane and 2,5-dihydroxymethyl tetrahydro furan were prepared. Each initial mixture was stirred in a vessel immersed in an oil bath maintained at a constant temperature of 40° C. After one-half hour the stirrer was stopped and the mixture allowed to stand. The lower solvent or extract layer separated rapidly, the upper raffinate layer was decanted and the composition of each layer determined by distillation of the hydrocarbons away from the solvent and by the refractive index of the mixed hydrocarbons. The compositions of the extract layer and of the raffinate layer for each initial composition are given below in Table I, and graphically represented in Figure 2.

TABLE I

Composition of layers in ternary system toluene, methyl cyclohexane and 2,5-dihydroxymethyl tetrahydro furan at 40° C.

Data represented in Fig. 2 by tie-line	Percent by weight				
	J	K	L	M	N
Original Mixture:					
Toluene		14.3	25.5	46.2	59.8
Methyl Cyclohexane	39.7	37.9	22.6	13.1	
2,5-Dihydroxymethyl tetrahydro furan	60.3	47.8	51.9	40.7	40.2
Extract Layer:					
Toluene		6.4	12 2	20.2	50.6
Methyl Cyclohexane	12.7	6.5	5.0	3.3	
2,5-Dihydroxymethyl tetrahydro furan	78.4	87.1	82.8	76.5	49.4
Raffinate Layer:					
Toluene		23.2	47.3	69.4	76.7
Methyl Cyclohexane	98.4	75.4	50.6	24.3	
2,5-Dihydroxymethyl tetrahydro furan	1.6	1.4	2.1	6.3	23.3

EXAMPLE 2

Initial mixtures containing various proportions of heptane, methyl cyclohexane and 2,5-dihydroxymethyl tetrahydro furan were prepared. Each initial mixture was stirred in a vessel immersed in an oil bath maintained at a constant temperature of 40° C. After one-half hour the stirrer was stopped and the mixture allowed to stand. The lower solvent or extract layer separated rapidly, the upper raffinate layer was decanted and the composition of each layer determined by distillation of the hydrocarbons away from the solvent and by the refractive index of the mixed hydrocarbons. The compositions of the extract layer and of the raffinate layer for each initial composition are given below in Table II, and graphically represented in Figure 3.

TABLE II

Composition of layers in ternary system heptane, methyl cyclohexane and 2,5-dihydroxymethyl tetrahydro furan at 40° C.

Data represented in Fig. 3 by tie-line	Percent by weight				
	J^1	K^1	L^1	M^1	N^1
Original Mixture:					
Heptane	50.2	41.1	23.1	15.0	
Methyl Cyclohexane		13.2	28.2	35.3	39.7
2,5-Dihydroxymethyl tetrahydro furan	49.8	45.7	48.7	49.7	60.3
Extract Layer:					
Heptane	6.7	3.3	3.3	0.9	
Methyl Cyclohexane		2.9	6.7	8.1	12.7
2,5-Dihydroxymethyl tetrahydro furan	93.3	93.8	90.0	91.0	87.3
Raffinate layer:					
Heptane	99.4	76.3	46.1	31.0	
Methyl Cyclohexane		22.8	52.8	66.9	98.4
2,5-Dihydroxymethyl tetrahydro furan	0.6	0.9	1.1	2.1	1.6

EXAMPLE 3

Initial mixtures containing various proportions of toluene, 2,5-dihydroxymethyl tetrahydro furan and water were prepared. Each initial mixture was stirred in a vessel immersed in an oil bath maintained at a constant temperature of 40° C. After one-half hour the stirrer was stopped and the mixture allowed to stand. The lower solvent or extract layer separated rapidly, the upper raffinate layer was decanted and the composition of each layer determined by distillation of the hydrocarbons away from the solvent. The compositions of the extract layer and of the raffinate layer for each initial composition are given below in Table III, and are graphically represented along the side A—C of the triangle shown in Figure 2.

TABLE III

Effect of water on the miscibility of toluene and 2,5-dihydroxymethyl tetrahydro furan, at 40° C.

	Percent by weight of added water		
	0	2.4	5.0
Original Mixture:			
Toluene	59.8	46.9	57.3
2,5-Dihydroxymethyl tetrahydro furan and water	40.2	53.1	46.3
Extract Layer:			
Toluene	50.6	35.8	21.6
2,5-Dihydroxymethyl tetrahydro furan and water	49.4	64.2	78.4
Raffinate layer:			
Toluene	76.7	83.5	93.3
2,5-Dihydroxymethyl tetrahydro furan and water	23.3	16.6	6.7

EXAMPLE 4

Initial mixtures containing various proportions of methyl cyclohexane, 2,5-dihydroxymethyl tetrahydro furan and water were prepared. Each initial composition was stirred in a vessel immersed in an oil bath maintained at a constant temperature of 40° C. After one-half hour the stirrer was stopped and the mixture allowed to stand. The lower solvent or extract layer separated rapidly, the upper raffinate layer was decanted and the composition of each layer determined by distillation of the hydrocarbons away from the solvent. The compositions of the extract layer and of the raffinate layer for each initial composition are given below in Table IV, and are graphically represented along the side B—C of the triangle shown in Figure 2.

TABLE IV

Effect of water on the miscibility of methyl cyclohexane and 2,5-dihydroxymethyl tetrahydro furan, at 40° C.

	Percent by weight of added water	
	0	5
Original Mixture:		
Methyl Cyclohexane	39.7	49.5
2,5-Dihydroxymethyl tetrahydro furan and water	60.3	50.5
Extract Layer:		
Methyl Cyclohexane	12.7	3.7
2,5-Dihydroxymethyl tetrahydro furan and water	78.4	96.3
Reffinate Layer:		
Methyl Cyclohexane	98.4	99.6
2,5-Dihydroxymethyl tetrahydro furan and water	1.6	0.4

EXAMPLE 5

The use of 2,5-dihydroxymethyl tetrahydro furan for the production of more highly aromatic gasoline from poorly aromatic gasoline was demonstrated in the following manner:

A petroleum fraction boiling in the gasoline range and containing 48.6% aromatic hydrocarbons (51% toluene and 49% xylene) with the balance being mixed naphthenic and aliphatic hydrocarbons, was found to have a light absorption of 13.9 at a wavelength of 268 mu. Of this absorption, 13.0 was due to aromatic hydrocarbons and 0.9 was due to aliphatic and naphthenic hydrocarbons.

This mixture was successively extracted four times with 2,5-dihydroxymethyl tetrahydro furan, the amount by weight of this solvent employed for each extraction being nearly equal to the weight of the hydrocarbon mixture being extracted. The combined extracts were distilled to recover the hydrocarbons. The distillate had an absorption of 19.3 at 268 mu, corresponding to 68.7% aromatic hydrocarbons. Thus, the aromatic hydrocarbon content of the gasoline was increased from 48.6% in the initial or feed material to 68.7% in the extracted material.

In the same manner the final raffinate was distilled to recover the naphthenic and aliphatic hydrocarbons. The distillate had an absorption of 11.4 at 268 mu, corresponding to 39.7% aromatic hydrocarbons in the raffinate. Thus, the aromatic hydrocarbon content of the gasoline was decreased from 48.6% in the initial or feed material to 39.7% in the raffinate. By the use of an extraction tower providing many more extraction stages than the four used herein, the aromatic hydrocarbon content of the extracted gasoline (i. e. fraction A) can be readily increased to a still higher level. If enough extraction stages are employed, the final product (i. e. fraction A) contains substantially nothing except the aromatic hydrocarbon, or aromatic hydrocarbons, present in the initial feed material.

EXAMPLE 6

This example is similar to Example 5, the initial material being straight run gasoline which, upon analysis, was found to contain 5.9% benzene, by comparison of the ultraviolet light absorption at 268 mu with absorption of pure benzene at the same wavelength. On extraction with 2,5-dihydroxymethyl tetrahydro furan and recovery of the hydrocarbons from the extract by distillation, the extracted hydrocarbons contained 27.3% benzene, determined in the same fashion. A second extraction, performed on the raffinate of the first extraction, yielded hydrocarbons containing 20.5% benzene, determined in the same fashion. A third extraction, performed on the raffinate of the second extraction, yielded hydrocarbons containing 14.5% benzene, also determined in the same fashion. Analysis of the raffinate of the third extraction did not indicate any appreciable remaining benzene.

It is noted that the benzene content of the gasoline was increased from 5.9% in the initial gasoline, to 27.3% in the gasoline from the first extract, to 20.5% in the gasoline from the second extract, and to 14.5% in the gasoline from the third extract. In the process, substantially all of the benzene was stripped from the initial gasoline.

Various changes and modifications may be made in carrying out the present invention without departure from the spirit and scope thereof. Insofar as these changes and modifications are within the purview of the annexed claims they are to be considered as part of this invention.

What is claimed is:

1. A process for treating a liquid mixture of hydrocarbon products selected from the mixture consisting of (i) a mixture of aromatics and naphthenics, (ii) a mixture of a single aromatic and a single naphthenic, (iii) a mixture of naphthenics and aliphatics, (iv) a mixture of a sinfle naphthenic and a single aliphatic, (v) a mixture of aromatics and aliphatics, and (vi) a mixture of aromatics, naphthenics and aliphatics, which comprises (*a*) contacting said liquid mixture with a solvent selected from the group consisting of (i) 2,5-dihydroxymethyl tetrahydro furan, and (ii) 2,5-dihydroxymethyl tetrahydro furan containing 0.5% to 10% by weight of water,

and then allowing the resulting mixture to separate into two phases, (*b*) separating from the lighter phase the heavier phase containing most of the solvent and a mixture of hydrocarbon products in which the first-named component thereof is in higher proportion than is contained in the original material, and (*c*) removing the solvent from the heavier phase and thereby recovering a liquid hydrocarbon mixture in which the first-named component is in higher proportion than is contained in the original material.

2. The process of claim 1 in which the contact of the solvent with the liquid mixture of hydrocarbon products is effected by subjecting the mixture to multiple stage extraction with the solvent.

3. The process of claim 1 in which the contact of the solvent with the liquid mixture of hydrocarbon products is by counter-current solvent extraction, with the final extract distilled at a temperature below the boiling point of the solvent, the distillate being recovered as the final liquid hydrocarbon product.

4. A process for increasing the aromatic hydrocarbon content of gasoline which comprises (*a*) mixing the gasoline with a solvent selected from the group consisting of (i) 2,5-dihydroxymethyl tetrahydro furan and (ii) 2,5-dihydroxymethyl tetrahydro furan containing 0.5% to 10% by weight of water, and allowing the resulting mixture to separate into two phases, (*b*) removing the heavier phase, (*c*) distilling the so-removed heavier phase and (*d*) recovering the distillate as the gasoline with increased aromatic hydrocarbon content.

5. The process for isolating an aromatic hydrocarbon in substantially pure state from a mixture of hydrocarbons consisting of said aromatic hydrocarbon and hydrocarbons selected from the group consisting of aliphatic and naphthenic hydrocarbons, which comprises (*a*) successively extracting the mixture with a solvent selected from the group consisting of (i) 2,5-dihydroxymethyl tetrahydro furan and (ii) 2,5-dihydroxymethyl tetrahydro furan containing 0.5% to 10% by weight of water, the extract of each extraction being contacted with additional solvent until the final extract is a solution of the substantially pure aromatic hydrocarbon in the solvent, (*b*) distilling the final extract to remove the aromatic hydrocarbon from the solvent and (*c*) recovering the distillate.

6. A process for separating toluene and methyl cyclohexane from a mixture thereof which comprises contacting said mixture with 2,5-dihydroxymethyl tetrahydro furan to form extract and raffinate layers and recovering the major portion of the toluene from the extract layer and the major portion of the methyl cyclohexane from the raffinate layer.

7. The process for separating toluene and methyl cyclohexane from a mixture thereof which comprises contacting said mixture with 2,5-dihydroxymethyl tetrahydro furan containing 0.5 to 10% by weight of water to form extract and raffinate layers and recovering the major portion of the toluene from the extract layer and the major portion of the methyl cyclohexane from the raffinate layer.

8. The process of separating heptane and methyl cyclohexane from a mixture thereof which comprises contacting said mixture with 2,5-dihydroxymethyl tetrahydro furan to form extract and raffinate layers and recovering the major portion of the heptane from the raffinate layer and the major portion of the methyl cyclohexane from the extract layer.

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