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SEPARATION AND RECOVERY OF NAPHTHENIC HYDROCARBONS FROM MIXTURES THEREOF

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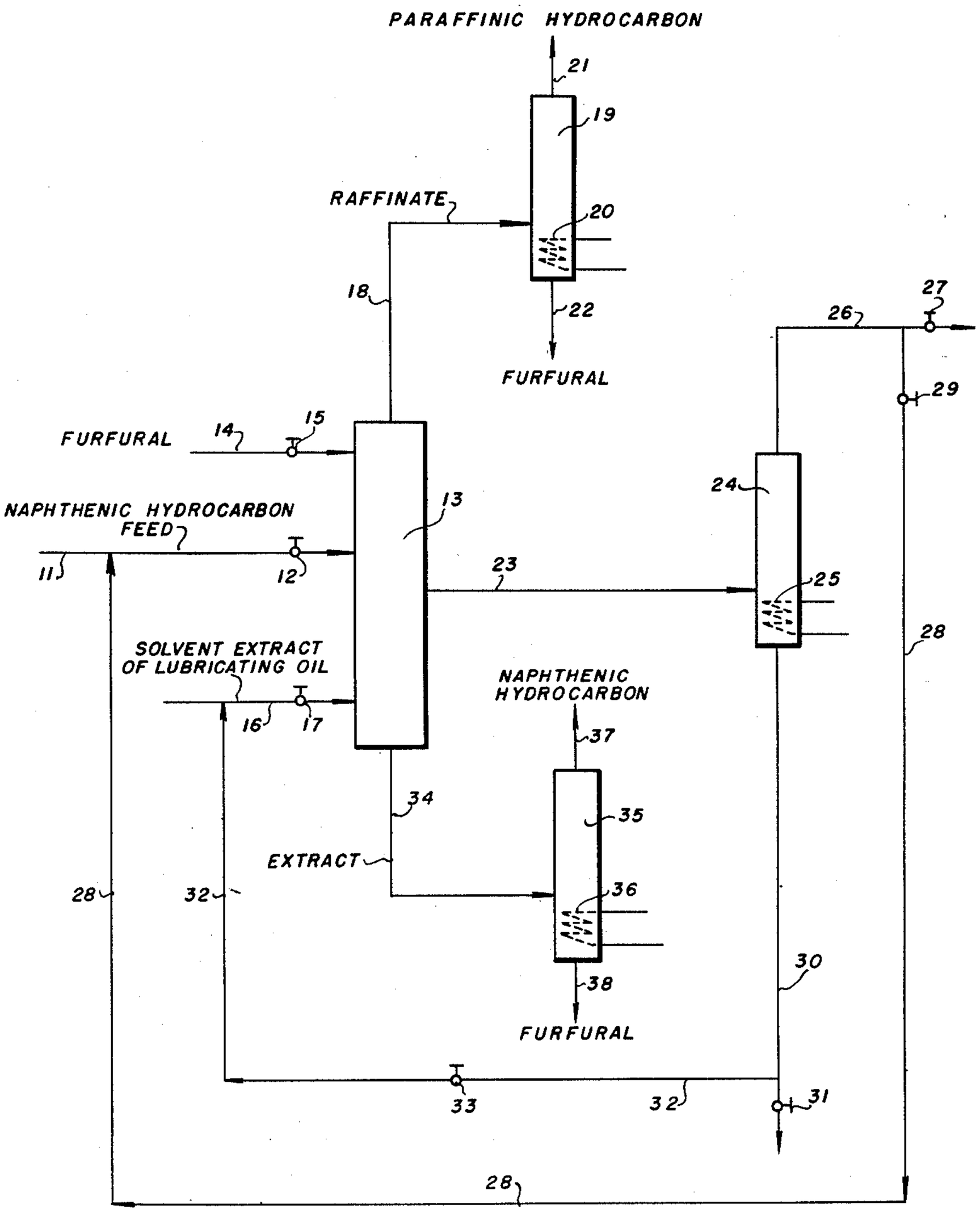

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SEPARATION AND RECOVERY OF NAPHTHENIC HYDROCARBONS FROM MIXTURES THEREOF

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6 Claims. (Cl. 260—666)

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The present invention is directed to the preparation and recovery of naphthenic hydrocarbons from a mixture consisting essentially of naphthenic and paraffinic hydrocarbons. The invention has to do particularly with the separation and recovery of cyclohexane from naphthenic hydrocarbon fractions containing it.

The present invention may be described briefly as comprising a method for separating a naphthenic hydrocarbon fraction from a hydrocarbon fraction in the gasoline boiling range consisting essentially of naphthenic and paraffinic hydrocarbons. This hydrocarbon fraction is extracted with furfural at a temperature in the range between 40° and 300° F. in the presence of a solvent extract of a naphthenic lubricating oil fraction boiling in the range between 570 and 850° F. and containing a major amount of aromatics and naphthenes and a minor amount of paraffins with the naphthenes in excess of the aromatics to form at least an extract phase and a raffinate phase. The two phases are separated and naphthenic hydrocarbon is separated from the extract phase by removing solvent therefrom.

In practicing the present invention it is essential that a substantially aromatic free hydrocarbon fraction be employed boiling in the gasoline boiling range which contains naphthenic hydrocarbons and paraffinic hydrocarbons. If aromatic hydrocarbons are present the naphthenic hydrocarbons will be contaminated with the aromatic hydrocarbons. It is, therefore, contemplated that the hydrocarbon fraction forming a feed stock in the practice of the present invention will be substantially free of aromatic hydrocarbons and this may be accomplished by a suitable pretreatment. For example, the feed stock may be suitably treated with concentrated sulfuric acid or with a halosulfonic acid under sulfonation conditions to sulfonate preferentially the aromatic hydrocarbons and cause their removal.

The feed stock for the present invention will ordinarily have a boiling range from about 80° to about 300° F. although narrower boiling fractions may suitably be employed. For example, when it is desired to separate cyclohexane from mixtures of it with other naphthenic hydrocarbons and paraffins, a feed stock boiling in the range from 80° to 200° F. should be used.

The solvent extract employed in the practice of the present invention is a solvent extract of naphthenic lubricating oil fraction; solvent extracts such as furfural extracts, phenol extracts and nitrobenzene extracts and the like may be used in the practice of the present invention. It is preferred to employ a phenol extract of a naphthenic lubricating oil fraction. For example, a phenol extract of a Coastal lubricating oil distillate boiling in the range from 570° to 850° F. may be used satisfactorily. It is preferred,

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however, to use a phenol extract of a Coastal lubricating oil distillate boiling at a temperature between the range of 570° and 750° F. which contains approximately 30% aromatics, approximately 40% naphthenes and approximately 30% paraffins. As a general statement, it may be said that the solvent extract employed in the practice of the present invention should contain a major amount of aromatics and naphthenes and a minor amount of paraffins with the naphthenes in excess of the aromatics.

The temperature employed in the present invention may range from about 40° to about 300° F. Ordinarily the temperature employed in the solvent extraction should not exceed the boiling point of the feed stock. When cyclohexane is separated and recovered the extraction temperature may suitably be in the range from 40° to 200° F.

In order to obtain satisfactory separation of naphthenic hydrocarbons in the present invention a furfural to feed hydrocarbon ratio in the range from 10:1 to about 30:1 should be employed; in separating cyclohexane from a mixture containing it a ratio of approximately 20:1 should be employed to obtain efficient separation.

The solvent extract of a naphthenic lubricating oil fraction which is employed in the present invention should be used in a ratio of solvent extract to feed hydrocarbon in the range from about 2:1 to about 10:1. Best results are obtained at a ratio of about 5:1 to 7:1.

In conducting the solvent extraction operation it is desirable to employ a vertical solvent extraction tower such as well known in the art. A solvent extraction tower having from about 5 to 20 extraction stages may suitably be used in conducting the present invention. The furfural solvent would be introduced into the top of the vertical extraction tower and the feed hydrocarbon introduced at about the center thereof. An extract phase which would contain the desirable naphthenic hydrocarbon would be recovered from the bottom of the tower while the solvent extract of the lubricating oil fraction would be introduced at the bottom of the tower to exert a washing action on the extract phase and this would be removed as a secondary raffinate phase at a point just below the point where the feed hydrocarbon is introduced into the tower.

This raffinate phase would be separated by distillation into a naphtha fraction which would be admixed with the fresh feed and returned to the extraction tower, and a lubricating oil fraction which would be recycled with the solvent extract to the bottom of the extraction tower or discarded as desired. The primary raffinate phase would be separated and recovered out of the top of the extraction tower.

The invention will be further illustrated by reference to the drawing in which the single figure illustrates a mode of practicing the invention.

Referring to the drawing, numeral 11 designates a charge line through which a naphthenic hydrocarbon feed containing paraffins and boiling in the range between 80° and about 300° F. is introduced into the system from a source not shown. Naphthenic hydrocarbon feed flows through line 11 controlled by valve 12 into a solvent extraction tower 13. Solvent extraction tower 13 is of a type well known in the art and is understood to include all auxiliary equipment usually associated with solvent extraction towers. Such auxiliary equipment may include means for inducing reflux and internal contacting means whereby intimate contact between the hydrocarbon feed and the solvent is achieved.

Leading into the top of solvent extraction tower 13 is line 14 controlled by valve 15 by way of which furfural is introduced into the system from a source not shown. At a point adjacent the bottom of solvent extraction tower 13 a solvent extract of a lubricating oil such as a phenol extract boiling in the range between 570° and 850° F. is introduced by line 16 controlled by valve 17. This solvent extract is comprised essentially of aromatics and naphthenes with a minor amount of paraffins.

The naphthenic hydrocarbon feed contacts the furfural countercurrently and results in the formation of a raffinate phase containing furfural and paraffinic hydrocarbons. This raffinate phase is removed from the top of extraction tower 13 by line 18 and is discharged thereby into a solvent stripping zone 19 which is shown as a distillation tower. Distillation tower 19 is provided with a heating means such as coil 20 which allows adjustment of temperature and pressure conditions to allow obtaining of an overhead fraction of paraffinic hydrocarbons by line 21 while the furfural is recovered by line 22 and may be recycled to line 14. By virtue of introducing a solvent extract of a lubricating oil fraction into the tower 13, a secondary raffinate is formed by the washing action of the lubricating oil fraction on the extract phase formed by countercurrent contact of the feed hydrocarbon with the furfural. This secondary raffinate phase is withdrawn from extraction tower 13 at a point just below the point where the feed hydrocarbon is introduced by line 11. This second raffinate phase is withdrawn by line 23 into a stripping zone illustrated by distillation tower 24 which is provided with a heating means illustrated by a coil 25. Conditions of temperature and pressure are adjusted in zone 24 to allow separation of naphthenic and paraffinic hydrocarbons which have been washed out of the extract phase by the solvent extract of the lubricating oil fraction. This mixture is withdrawn from zone 24 by line 26 and may be discharged from the system by opening valve 27, but preferably is recycled to line 11 by branch line 28 controlled by valve 29. Likewise, there is withdrawn from zone 24 the recovered solvent extract of the lubricating oil fraction by line 30 which may be discharged from the system by valve 31, but preferably is recycled to line 16 by branch line 32 containing valve 33 which connects line 16 with line 30.

The extract phase is withdrawn from the bottom of solvent extraction zone 13 by line 34. This extract phase contains naphthenic hydrocarbon and furfural which are separated from each other in stripping zone 35 illustrated as a distillation tower and which is provided with a heating means illustrated by coil 36. Conditions of temperature and pressure are adjusted in zone 35 to allow withdrawal as an overhead fraction of the naphthenic hydrocarbon in a purified form by line 37 while the furfural is recovered from zone 35 by line 38 for recycling to line 14 as may be desired.

In the description of the stripping zones 19, 24, and 35, it is assumed that these stripping zones are distillation towers, and this term is meant to embrace all auxiliary equipment usually associated with such distillation towers, such as means for providing reflux and internal contacting means to insure intimate contact between liquid and vapors.

In order to illustrate the invention further, a naphthenic hydrocarbon fraction boiling in the range from 80° to 200° F. which contained cyclohexane and which was substantially free of aromatics was charged into a 20 stage vertical extraction tower with furfural being introduced into the top of the tower. The feed hydrocarbon was introduced near the center and it was extracted with the solvent in the presence of a phenol extract of a light coastal lubricating oil distillate which was introduced at the bottom. A primary raffinate was obtained out of the top of the tower. An extract phase containing cyclohexane was recovered from the bottom of the tower while a secondary raffinate phase containing the phenol extract was recovered from the tower at a point just below the point where the feed was introduced thereto.

Runs were made in accordance with the foregoing description at temperatures of about 70 to 90° F. In these runs the temperature of the feed was around 86 to 87° F., the temperature of the solvent was in the neighborhood of 72° F. and the temperature of the extract phase containing cyclohexane was about 90° F. The phenol extract was introduced at a temperature of about 87° F.

The yield data, the composition of the feed, primary raffinate after removal of solvent, and extract after removal of solvent the phenol extract, as well as the volume of feed, phenol extract and furfural employed are presented in the following table:

	Charge	Run 1		Run 2	
		Raffinate	Extract	Raffinate	Extract
Yield, Vol. Percent	----------	49.0	51.0	60.0	40.0
Composition, Vol. Percent:					
Aromatics	2.2	0.0	1.8	0.0	6.9
Naphthenes	48.3	26.3	71.7	32.1	74.5
Paraffin	49.5	73.7	26.5	67.9	18.6
Cyclohexane	23.6	3.8	46.8	8.8	54.7
Input, Volumes/hr.:					
Feed	----------	0.77	----------	0.77	----------
Phenol extract	----------	3.40	----------	4.50	----------
Furfural	----------	15.60	----------	15.60	----------
Total	----------	19.77	----------	20.87	----------

It will be seen from the data in the above table that the feed stock was substantially free of aromatics containing only 2.2 volume per cent. It will be further seen that the naphthenes were concentrated in both runs in the extract and that the cyclohexane was also concentrated in the extract to a greater extent than that of other naphthenes in the feed stock.

It is understood that a greater concentration of naphthenes may be obtained by adjusting the ratio of furfural to feed to employ furfural feed ratios in the upper portion of the range and that further concentration may also be obtained by using additional solvent extraction stages as is well known to the art.

While it has been stated that the feed stock of the present invention should be substantially aromatic free it is considered that the aromatics should not exceed 10% by volume of the feed stock and preferably should be substantially absent from the feed stock.

In the foregoing description it is understood that the furfural will be removed from the raffinate and extract by techniques well known to the art. It is also understood that the secondary raffinate which includes portions of the phenol extract may be reused in the process.

The nature and objects of the present invention having been completely described and illustrated, what I wish to claim as new and useful and to secure by Letters Patent is:

1. A method for separating a naphthenic hydrocarbon from a hydrocarbon fraction boiling in the range between 30° and 300° F. comprising essentially of naphthenic and paraffinic hydrocarbons which comprises extracting said hydrocarbon fraction with furfural employing a ratio of furfural to hydrocarbon fraction in the range between 10:1 and 30:1 at a temperature in the range between 40° and 300° F. in the presence of a phenol extract of a naphthenic lubricating oil fraction, boiling in the range between 570° and 850° F. and containing a major amount of aromatics and naphthenes and a minor amount of paraffins with the naphthenes in excess of the aromatics, to form at least an extract phase and a raffinate phase, and recovering naphthenic hydrocarbon from said extract phase.

2. A method for separating cyclohexane from a hydrocarbon fraction containing it boiling in the range between 50° and 200° F. comprising essentially of naphthenic and paraffinic hydrocarbons which comprises extracting said hydrocarbon fraction with furfural employing a ratio of furfural to hydrocarbon fraction in the range of 10:1 to 30:1 at a temperature in the range between 40° and 200° F. in the presence of a phenol extract of a naphthenic lubricating oil fraction, boiling in the range between 570° and 750° F. and

containing approximately 30% aromatics, approximately 40% naphthenes, and approximately 30% paraffins, to form a first raffinate phase, second raffinate phase and an extract phase, said extract phase containing cyclohexane and said second raffinate phase containing said phenol extract, and recovering cyclohexane from said extract phase.

3. A method in accordance with claim 2 in which the hydrocarbon fraction is extracted with furfural at a temperature in the range between 70° and 90° F. with a ratio of furfural to hydrocarbon fraction of approximately 20:1.

4. A method in accordance with claim 2 in which the phenol extract and hydrocarbon fraction are employed in a ratio in the range from 2:1 to 10:1.

5. A method for separating cyclohexane from a hydrocarbon fraction boiling in the range between 80° and 200° F. comprising essentially of naphthenic and paraffinic hydrocarbons which comprises extracting said hydrocarbon fraction with furfural employing a ratio of furfural to hydrocarbon fraction in the range of 10:1 to 30:1 at a temperature in the range between 40° and 200° F. in the presence of a sufficient amount of a phenol extract of a naphthenic lubricating oil fraction, boiling in the range between 570° and 750° F. and containing approximately 30% aromatics, approximately 40% naphthenes, and approximately 30% paraffins, to provide a ratio of phenol extract to hydrocarbon fraction in the range between 2:1 to 10:1 to form a first and second raffinate phase and an extract phase, said extract phase containing cyclohexane and said second raffinate phase containing said phenol extract, and recovering cyclohexane from said extract phase.

6. A method in accordance with claim 2 in which the hydrocarbon fraction is extracted with furfural at a temperature in the range between 70° and 90° with a ratio of furfural to hydrocarbon fraction of approximately 20:1 and with a ratio of phenol extract to hydrocarbon fraction of approximately 6:1.

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