

LIQUID-PHASE ADSORPTION PROCESS FOR REMOVING AND CONCENTRATING HETEROATOM COMPOUNDS IN HYDROCARBONS

TECHNICAL FIELD

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The present invention relates, in general, to a method of treating hydrocarbons. More particularly, the present invention pertains to a liquid-phase adsorption process, which removes heteroatom compounds such as phenols, naphthenic acids, pyridines, pyrroles, thiophenes, quinolines or carbazoles from a liquid
10 hydrocarbon stream, and concentrates them to heteroatom compound products.

BACKGROUND ART

Hydrocarbons include compounds that contain heteroatoms such as nitrogen,
15 sulfur and/or oxygen. Such heteroatom compounds in hydrocarbons are exemplified by phenols, naphthenic acids, pyridines, pyrroles, thiophenes, quinolines and carbazoles, of which polarities are higher than those of hydrocarbons. For convenience sake, heteroatom compounds in hydrocarbons are abbreviated to HCH, hereinafter.

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As a distillation cut point of petroleum crude increases, HCH contents also increase within the distillate. Physical properties and compositions of HCH vary with different petroleum crudes, however, HCH are generally considered as

undesirable constituents: naphthenic acids corrode metals and poison catalysts; phenols from a FCC (Fluid Catalytic Cracking) process degrade fuel quality; and basic organic nitrogen compounds are known to interfere with hydrodesulfurization reactions.

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Adsorption has long been used to remove or concentrate such polar compounds as HCH. In commercialization of an adsorption process, however, development of an effective regeneration method is essential since an adsorbent has a finite adsorption capacity. In general, regeneration can be carried out by means of thermal energy, chemical reaction, inert gas or solvents. The present invention uses a polar solvent, and such an oxygen containing polar solvent as an alcohol, a ketone, or an ether, can be used to regenerate the adsorbent. Applied to the adsorbent after adsorption is completed, the polar solvent purges adsorbate and returns regeneration effluent, which is an adsorbate-polar solvent mix. Adsorbate is readily separable from the regeneration effluent subject to distillation, however, the problem is that the adsorbate includes not only HCH, but also hydrocarbons: in fact, hydrocarbon portion is much larger than that of HCH in adsorbate, and this is referred to as coadsorption phenomenon: HCH quantities in adsorbate are merely 10 % or less while hydrocarbons take up the rest when kerosene or LGO (Light Gas Oil) are adsorption-treated. Under coadsorption conditions, therefore, process yield, i.e. hydrocarbon yield, is reduced. To resolve this problem, a special step, which selectively displaces coadsorbed hydrocarbons from adsorbate prior to regeneration, is introduced, and this is referred to as "copurging".

Typical copurging methods, which are dependent upon hydrocarbons, are as follows:

In case feedstock has a low boiling point such as naphtha

- 5 Naphtha with a boiling point range of 80 to 130 °C is fed to an adsorber in liquid phase in an upward direction, and an adsorption effluent, i.e., a naphtha-solvent mix, is returned. The adsorption effluent is then separated from solvent in a fractionator. Copurging is carried out by injecting a vaporized naphtha stream in a downward direction to displace coadsorbed naphtha from the adsorber. Finally,
- 10 solvent flushes the adsorber in the downward direction, purging HCH. Regeneration effluent, an HCH-solvent mix, is separated in the other fractionator while copurging effluent is adsorbed again in the beginning of subsequent adsorption.

- 15 In case feedstock has a high boiling point such as LGO

- LGO requires a lot of energy to be fully evaporated, thereby copurging is conducted with non-polar solvent as depicted in Figure 1. LGO, of which the boiling points range 225°C~365°C, is fed to an adsorber in an upward direction.
- 20 After adsorption is completed, copurging is carried out by applying a non-polar solvent such as hexane to the adsorber, in a downward direction, to selectively desorb coadsorbed LGO. Finally, in the downward direction, a polar solvent such as MTBE (Methyl-Tertiary-Butyl-Ether) is injected to the adsorber to purge

remaining adsorbate. This process returns a small amount of a highly concentrated HCH product, but nevertheless, requires 4 fractionators to recover the two different solvents. Operating costs are also high because separation of the two solvents is costly, and copurging effluent is adsorbed again due to its high
5 HCH content.

DISCLOSURE OF INVENTION

It is an object of the present invention to provide a process for removing and
10 concentrating heteroatom compounds from a liquid hydrocarbon stream, in which adsorption, copurging and regeneration are conducted in an adsorber that is charged with silica gel and maintained in fully wetted conditions, comprising the following steps:

- i) feeding the liquid hydrocarbon stream to the adsorber, and returning a first
15 effluent, which is a polar solvent-rich mix, to a second fractionator before sending a second effluent, which is a polar solvent and adsorption treated hydrocarbon mix, to a first fractionator;
- ii) injecting a fraction of heteroatom compounds that are extracted in the previous operation to the adsorber, and returning a third effluent, which is a polar solvent
20 and adsorption treated hydrocarbon mix, to a first fractionator before sending a fourth effluent, which is an adsorption treated hydrocarbon and heteroatom compounds mix, to a feed drum for re-adsorption; and
- iii) applying the polar solvent to the adsorber, and returning a fifth effluent, which

is a heteroatom compound rich mix, to a heteroatom compound drum before sending a sixth effluent, which is a heteroatom compounds and polar solvent mix, to the second fractionator.

In the present invention, the liquid hydrocarbon is middle distillates with a boiling
5 range of 100 to 400°C and heteroatom compounds are nitrogen atom containing compounds and oxygen atom containing compounds. The first fractionator separates adsorption treated hydrocarbons from the polar solvent, which are reused in regeneration. The second fractionator separates heteroatom compounds, of which a fraction is taken out as a HCH product and the residue is used in
10 copurging, from the polar solvent, which is reused in regeneration.

As mentioned above, to remove and concentrate HCH, a liquid phase adsorption process has been developed, which comprises steps of adsorption, copurging and regeneration. In an effort to attain commercial feasibility, an adsorbent, a polar
15 solvent, and a copurging method are carefully selected. Silica gel is identified as a suitable adsorbent for its regenerability as well as ability to maintain its adsorption effectiveness; MTBE (Methyl-Tertiary-Butyl-Ether), ETBE (Ethyl-Tertiary-Butyl-Ether) or TAME (Tertiary-Amyl-Methyl-Ether) is selected for its low latent heat and compatibility with the adsorbent; and the copurging method is
20 developed to effectively displace coadsorbed hydrocarbons.

The operation sequence of the process is illustrated in Figure 3 and Figure 4: in "Step 1", a predetermined amount of hydrocarbon is fed to an adsorber, which is

maintained in the vicinity of 50°C, in an upward or downward direction; in "Step 2", copurging is carried out by injecting HCH, which have been extracted and set aside from the previous regeneration, to the adsorber, displacing coadsorbed hydrocarbons from adsorbate, in an upward or downward direction; in "Step 3", a
5 polar solvent such as MTBE is applied to the adsorber, purging remaining adsorbate; and in "Step 4", a fraction of HCH, which is obtained in "Step 3", is taken out as an HCH product while the rest is reserved for the next copurging.

A continuous adsorption unit, shown as Figure 6, is built for the feasibility of the
10 present invention, on which the process repeats aforementioned steps until the process reaches an equilibrium. As a result, the present invention is feasible. As expected, 60% or more of HCH are removed from the hydrocarbon feedstock while as little as 2.0 % of an HCH product is generated.

15 BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic diagram illustrating a conventional process using a non-polar solvent for copurging;

Figure 2 is a schematic diagram illustrating a conventional process without
20 copurging;

Figure 3 is a schematic diagram illustrating an embodiment of the present invention, in which HCH are used for copurging;

Figure 4 is a schematic diagram illustrating another embodiment of the present

invention, in which HCH are used for copurging;

Figure 5 is a drawing illustrating copurging of the present invention, in progress;

Figure 6 is a PFD (Process Flow Diagram) of the present invention; and

Figure 7 is a graph showing a nitrogen removal ratio of the present invention.

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BEST MODE FOR CARRYING OUT THE INVENTION

The objective of the present invention is to develop a liquid phase adsorption process that removes and concentrates HCH in an economical and efficient way.

- 10 In an effort to realize the aforementioned objectives, the adsorption process is developed pursuing three technical goals: identification of a semi-permanent adsorbent that lasts for an extended period of time after a series of adsorption and regeneration while maintaining its adsorption effectiveness; selection of a polar solvent that regenerates the adsorbent effectively and is recovered economically;
- 15 and development of an effective copurging method that minimizes an HCH product amount and concentrates HCH therein.

Identification of a Semi-permanent Adsorbent

- 20 A nitrogen removal ratio is measured to quantify adsorption effectiveness of an adsorbent; a nitrogen content in hydrocarbon serves as a barometer of HCH presence therein, and the nitrogen removal ratio is monitored to compare adsorption effectiveness of each adsorbent. Although alumina and bauxite are

superior in their initial adsorption effectiveness, nitrogen removal ratios of successive adsorptions decrease sharply. On the other hand, silica gel seems to be less effective in the initial test, however, maintains adsorption effectiveness for an extended period of time. Consequently, the present invention selects silica gel
5 to be used in the process. Furthermore, silica gel with a pore size of 40~100 Å and a pore volume ratio to bulk volume of 0.40 or higher is found to be desirable.

Selection of Polar Solvent

10 Polar solvents including methanol, MTBE, and acetone are tested to determine the most suitable solvent for the process. In case of methanol, an additional thermal gas purging step is required to recover the solvent. Regeneration effluent, an adsorbate-methanol mix, also demands a large amount of energy for separation due to methanol's high latent heat. On the contrary, MTBE needs a small amount
15 of energy for separation due to its low latent heat, which is a quarter and one third compared to methanol and acetone, respectively. Also, MTBE turns out to be compatible with silica gel, not degrading the adsorbent's performance. Consequently, the present invention selects MTBE to be used in the adsorption process. Physical properties of acetone, methanol and MTBE are given in Table

20 1.

[TABLE 1]

	Mol. Formula	Specific Gravity	Boiling Point (°C)	Latent Heat (Btu/gal)	Solubility with LGO	Solubility in Water(cc/100cc)
Acetone	C ₃ H ₆ O	0.791	56.0	2,580	Fully Miscible	Fully Miscible
Methanol	CH ₄ O	0.791	64.7	3,340	Phase Separated	Fully Miscible
MTBE	C ₅ H ₁₂ O	0.740	55.3	863	Fully Miscible	1.4

Development of an Economically Feasible Copurging

5 Effective copurging is then sought to minimize HCH product generation and to increase HCH concentrations therein. As illustrated in Figure 1, an adsorption process using a non-polar solvent for copurging is proven to be greatly disadvantageous in investment expenses and operation costs. On the other hand, as given in Figure 2, an adsorption process without copurging generates 15% of

10 the HCH product, making the process economically unfeasible. To overcome such shortcomings, as illustrated in Figure 3 and Figure 4, copurging is carried out by reapplying a fraction of HCH, which is obtained from the previous operation, to the adsorber. As HCH are preferably adsorbed onto the adsorber in place of coadsorbed hydrocarbon, coadsorbed hydrocarbons are displaced, turning into

15 copurging effluent of very low HCH contents. Copurging effluent is then combined with adsorption effluent before being sent to the first fractionator, where the polar solvent and HCH-removed hydrocarbon are separated. Given below in

Table 2 are representative properties of LGO feedstock and HCH product.

[TABLE 2]

	LGO	HCH product of LGO
Specific Gravity	0.85-0.86	0.90-0.95
Color	Yellow	Dark Brown
N content	160ppm	5,000-10,000ppm

5 Upon completion of copurging, the polar solvent is applied to the adsorber,
purging remaining adsorbate. Regeneration effluent, which is now an HCH-rich
adsorbate-polar solvent mix, is sent to the second fractionator where the polar
solvent and HCH are separated. As most of the HCH obtained in the second
fractionator are reserved for the next copurging, a fraction of them are taken out as
10 the HCH product. Repetitions of the aforementioned procedures concentrate
HCH in the HCH product, and consequently, the nitrogen content and density
thereof increase until the process reaches an equilibrium in approximately 40-80
operations. The present invention is applicable to treatment of middle distillates
such as LGO and kerosene, of which the evaporation is economically impractical
15 because of high boiling points.

Figure 5 illustrates copurging in progress. Since HCH have higher polarities and
specific gravities compared to those of hydrocarbon, they can effectively displace
coadsorbed hydrocarbons. As copurging progresses, coadsorbed hydrocarbons in

adsorbate and applied HCH form a distinct interface where mixing between the two fluids occurs. A small amount of such an HCH-coadsorbed hydrocarbon mix needs to be adsorbed again in the next adsorption. Copurging can be more effective when silica gel is fully wetted. When silica gel is completely immersed
5 with a liquid, flow characteristics inside the adsorber resemble ideal plug flow, as long as a space velocity is not too fast. Once this condition is disrupted, mixing at the interface intensifies, resulting in HCH-rich copurging effluent.

Upon completion of copurging, the bed is now fully filled with HCH. An amount
10 of the polar solvent necessary for regeneration, however, remains unchanged from the case without copurging, as given in Figure 2. Copurging reduces HCH product generation to a tenth while increasing HCH concentrations thereof to ten-fold. Still, such HCH product generation is approximately 1.5 times larger than the case with hexane copurging, as given in Figure 1. The present invention,
15 however, is advantageous in saving investment expenses for additional fractionators, reducing operation costs for recovering the two solvents, and minimizing the amount of copurging effluent that requires repetitive adsorption.

ILLUSTRATIVE EXAMPLES

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A better understanding of the present invention may be obtained in light of the following examples that are set forth to illustrate, but are not to limit the present invention. In the following examples, LGO, of which the boiling point, nitrogen,

and sulfur content are 225°C to 365°C, 160 wppm and 14,000 wppm, respectively, is exclusively used, and represented hereinafter as "A". Concentric glass columns are maintained in the vicinity of 50 °C by constantly circulating water in the annulus of the columns while the inner column is charged with 40 cc of silica gel, of which the diameter is between 0.2 and 0.5mm.

EXAMPLE I: Nitrogen Removal Effectiveness of Silica gel

HCH are removed from "A" using alumina, silica gel, bauxite, and acidic kaolin. Among these adsorbents, when regenerated by a polar solvent, only silica gel turns out to constantly maintain nitrogen removal ratio after repetitive adsorption and regeneration. In order to examine adsorption effectiveness, i.e. a nitrogen removal ratio, of silica gel over the extended period of time, a series of experiments are conducted as described below, and the corresponding results are given in Figure 7.

- 1) 200 cc of "A" is fed to the inner column at 400 cc/hr in the upward direction;
- 2) adsorption effluent, which is collected at the top of the inner column, is kept in a container, labeled as "B";
- 3) 80 cc of MTBE is flowed through the inner column in the downward direction at 400 cc/hr;
- 4) regeneration effluent, which is collected at the bottom of the inner column, is discarded;

- 5) procedures from steps 1) to 4) are repeated 10 times, and ten samples of "B" are poured into a single container and well shaken.
- 6) a small amount of "B mix" is then sampled, labeled as "C";
- 7) after MTBE is evaporated from "C" with use of a vacuum rotary evaporator,
- 5 nitrogen content of "C" is measured; and
- 8) procedures from steps 1) to 7) are repeated 45 times.

EXAMPLE II: Identification of Optimal Physical Properties of Silica gel

- 10 Experiments are conducted to identify optimal physical properties of silica gel, and it is found that silica gel with a pore size of $40 \sim 100 \text{ \AA}$ and a pore volume ratio to bulk volume of 0.40 or greater are desirable. A series of experiments are conducted with 8 different silica gels as described below, and the corresponding results are given in Table 3.

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- 1) 400 cc of "A" is fed to the inner column at 400 cc/hr in the upward direction;
- 2) adsorption effluent, which is collected at the top of the inner column, is kept in a container, labeled as "D";
- 3) 80 cc of MTBE is flowed through the inner column in the downward
- 20 direction at 400 cc/hr;
- 4) regeneration effluent, which is collected at the bottom of the inner column, is discarded;
- 5) procedures from steps 1) to 4) are repeated 3 times, and three samples of "D"

- are poured into a single container and well shaken;
- 6) a small amount of "D mix" is then sampled, labeled as "E";
- 7) after MTBE is evaporated from "E" with use of a vacuum rotary evaporator, nitrogen content of "E" is measured; and
- 5 8) procedures from steps 1) to 7) are repeated with each of 8 different silica gels.

【TABLE 3】

Pore Volume Ratio to Bulk Volume (cc/bulk cc)	Pore Size (Å)	Surface Area to Bulk Volume (m ² /bulk cc)	Nitrogen Removal Ratio(%)
0.2625	184.8	56.9	44.4
0.4292	164.4	104.9	47.0
0.3555	25.9	504.2	21.6
0.3848	48.6	316.1	52.5
0.3002	20.2	579.2	6.6
0.4408	234.4	75.3	49.7
0.4280	104.4	164.4	53.1
0.4725	69.0	273.6	61.2

EXAMPLE III: Nitrogen Removal Effectiveness with Respect to VFA

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For convenience sake, a feedstock amount is quantified in a dimensionless form of

VFA (Volumetric ratio of Feedstock to Adsorber): it is defined as a volumetric ratio of feedstock treated to adsorbent charged. The present invention discovered that the nitrogen removal ratio tends to be inversely proportional to the logarithm of VFA: in other words, as more LGO is adsorbed onto silica gel, less effective becomes the adsorbent logarithmically. To verify the point, a series of experiments are conducted with VFA of 3, 5, and 10 as described below. The corresponding results are given in Table 4.

- 1) 120 cc (VFA of 3) of "A" is fed to the inner column at 400 cc/hr in the upward direction;
- 2) adsorption effluent, which is collected at the top of the inner column, is kept in a container, labeled as "F";
- 3) 80 cc of MTBE is injected into the inner column in the downward direction at 400 cc/hr;
- 4) regeneration effluent, which is collected at the bottom of the inner column, is kept in a container, and labeled as "G";
- 5) after MTBE is evaporated from "F" and "G" with use of a vacuum rotary evaporator, their volumes and nitrogen contents are measured, respectively; and
- 6) procedures from steps 1) to 5) are repeated with 200cc (VFA of 5) and 400cc (VFA of 10) of "A".

【TABLE 4】

VFA	Adsorption Effluent (F)	HCH Product Volume (G)	Nitrogen Removal Ratio (F)
3	90cc	30cc(25%)	81%
5	170cc	30cc(15%)	75%
10	370cc	30cc(7.5%)	63%

In order to achieve a nitrogen removal ratio of 80% or higher, VFA needs to be no more than 5. Under such a VFA requirement without proper copurging, 15% to 25% of the feedstock could turn into an HCH product as shown in Table 4.

EXAMPLE IV: Copurging with HCH

To clearly illustrate advantages of the present invention, a series of experiments are conducted, using HCH for copurging, as depicted in Figure 3. The corresponding results are given in Table 5.

- 1) 200 cc (VFA of 5) of "A" is fed to the inner column at 400 cc/hr in the upward direction;
- 2) adsorption effluent, which is obtained at the top of the inner column, is discarded;
- 3) 60 cc of MTBE is flowed through the inner column in the downward direction at 400 cc/hr;

- 4) regeneration effluent, which is collected at the bottom of the inner column, is put in a vacuum rotary evaporator to separate MTBE;
- 5) HCH, which are obtained in the vacuum rotary evaporator, are kept in a container, labeled as "H";
- 5 6) 200 cc (VFA of 5) of "A" is fed to the inner column at 400 cc/hr in the upward direction;
- 7) adsorption effluent, which is collected at the top of the inner column, is kept in a container, labeled as "I";
- 8) 3cc of "H" is set aside labeled as "J", and the rest, 27 cc, is injected into the
10 inner column at 80cc/hr in the upward direction;
- 9) copurging effluent, which is collected at the top of the inner column, is kept in a container, labeled as "K";
- 10) "I" and "K" are poured into a single container, labeled as "L" and MTBE is evaporated from "L" with use of the vacuum rotary evaporator;
- 15 11) volumes and nitrogen contents of "J" and "L" are measured, respectively; and
- 12) procedures from steps 3) to 11) are repeated 40 times.

At VFA of 5, the process is found to maintain nitrogen removal ratio of 70% or
20 higher, which is comparable to the case without copurging. Nitrogen contents of "I" and "K" are 40 and 50 wppm respectively, and nitrogen content of "L", i.e. "I-K mix", is 41 wppm. The results of the experiments are given in Table 5. Although the nitrogen content of "J" is a mere 800 wppm in the initial experiment,

7,000 wppm is attained when the experiment is repeated more than 40 times.

[TABLE 5]

VFA	Nitrogen Removal Ratio of L	Proportion of J, HCH Product (vol. %)
3	80%	1.75
5	74%	1.50
10	62%	1.25

5 EXAMPLE V: Copurging with HCH in the Downward Direction

Adsorption, copurging and regeneration are carried out in the downward direction, to prove that the present invention is effective regardless of flow directions. To maintain an adsorber in fully wetted conditions, back-pressure regulators are
10 attached as depicted in Figure 6. A series of experiments are conducted as depicted in Figure 4. The corresponding results are given in Table 6.

- 1) 120 cc (VFA of 3) of "A" is fed to the inner column at 80 cc/hr in the downward direction;
- 15 2) adsorption effluent, which is obtained at the bottom of the column, is discarded;
- 3) 60 cc of MTBE is flowed through the inner column in the downward direction at 80 cc/hr;

- 4) regeneration effluent, which is collected at the bottom of the inner column, is put in a vacuum rotary evaporator to separate MTBE;
- 5) HCH, which are obtained in the vacuum rotary evaporator, are kept in a container, labeled as "T";
- 5 6) 120 cc (VFA of 3) of "A" is fed to the inner column at 80 cc/hr in the downward direction;
- 7) first 35cc of adsorption effluent, which is collected at the bottom of the inner column, is kept in a container, labeled as "P" while the rest is discarded;
- 8) 3cc of "T" is set aside labeled as "U", and the rest, 36 cc is injected into the
10 inner column at 80cc/hr in the downward direction;
- 9) first 31cc of copurging effluent, which is collected at the bottom of the inner column, is kept in a container, labeled as "R" while the rest is kept in another container, labeled as "S";
- 10 10) 60 cc of MTBE is flowed through the inner column in the downward
15 direction at 80 cc/hr;
- 11) regeneration effluent, which is collected at the bottom of the inner column, is poured into the container "P" and MTBE is evaporated from "P" with use of the vacuum rotary evaporator;
- 12) HCH, which are obtained in the vacuum rotary evaporator, are kept in a
20 container, labeled as "T";
- 13) 120 cc (VFA of 3) of "A-S mix" is fed to the inner column at 80 cc/hr in the downward direction;
- 14) first 35cc of adsorption effluent, which is collected at the bottom of the

inner column, is kept in a container, labeled as "P" while the rest is kept in another container, labeled as "Q";

15) "R" and "Q" are poured into a single container, labeled as "V" and MTBE is evaporated from "V" with use of the vacuum rotary evaporator;

5 16) procedures from the step 8) to 15) are repeated 40 times: and

17) volumes and nitrogen contents of "U" and "V" are measured, respectively.

[TABLE 6]

VFA	Nitrogen Removal Ratio of V	Proportion of U, HCH Product (vol. %)
3	81%	2.50

10 INDUSTRIAL APPLICABILITY

Advantages of the present invention are summarized as follows: the adsorbent, silica gel, is regenerable for an extended period of time; a polar solvent such as MTBE is economically recovered due to its low latent heat and does not degrade
15 the adsorbent; and coadsorbed hydrocarbons are efficiently displaced by the newly developed copurging, resulting in a small amount of an HCH product with high HCH concentrations.

As an alternative to the present invention, a refinery may adjust distillation cut
20 point of LGO to reduce the nitrogen content thereof. In this case, however, a

drastic reduction in LGO yield is inevitable. For instance, in order to reduce the nitrogen content of LGO by 60 %, the cut point should be readjusted to 225 to 335°C. Although the nitrogen content of LGO falls to 60 ~ 70 wppm from 160wppm, an LGO yield is to be cut down by as much as 25%: such a drop in the
5 production yield is intolerable by the refinery from an economic standpoint.

As explained hereinbefore, the present invention contributes to the refining industry in the following aspects: the nitrogen content is to be reduced by more than 60 % without a yield loss; the amount of HCH product is less than 2.0 % of
10 the throughput; and the HCH product is applicable to a blending stock of heating oil and/or a marine fuel. For a reference, a sulfur and a nitrogen content of the HCH product are 1.5 times and tens of times higher than those of LGO, respectively.

15 The present invention has been described in an illustrative manner, and it is to be understood that the terminology used is intended to be in the nature of description rather than of limitation. Many modifications and variations of the present invention are possible in light of the above teachings. Therefore, it is to be understood that within the scope of the appended claims, the present invention
20 may be practiced otherwise than as specifically described.

CLAIMS



1. A process for removing and concentrating heteroatom compounds from a liquid hydrocarbon stream, in which adsorption, copurging and regeneration are conducted in an adsorber that is charged with silica gel and maintained in fully wetted conditions, comprising the following steps:
- 5
- i) feeding the liquid hydrocarbon stream to the adsorber, and returning a first effluent, which is a polar solvent-rich mix, to a second fractionator before sending a second effluent, which is a polar solvent and adsorption treated hydrocarbon mix, to a first fractionator;
- 10
- ii) injecting a fraction of heteroatom compounds that are extracted in the previous operation to the adsorber, and returning a third effluent, which is a polar solvent and adsorption treated hydrocarbon mix, to a first fractionator before sending a fourth effluent, which is an adsorption treated hydrocarbon and heteroatom compounds mix, to a feed drum for re-adsorption;
- 15
- iii) applying the polar solvent to the adsorber, and returning a fifth effluent, which is a heteroatom compound rich mix, to a heteroatom compound drum before sending a sixth effluent, which is a heteroatom compounds and polar solvent mix, to the second fractionator.
- 20

2. The process as set forth in claim 1, wherein said liquid hydrocarbon is middle distillates with a boiling range of 100 to 400 °C.
3. The process as set forth in claim 1, wherein said silica gel has a pore size of
5 40~100 Å and a pore volume ratio to bulk volume of 0.40 or higher.
4. The process as set forth in claim 1, wherein said polar solvent is selected from the group consisting of MTBE (Methyl-Tertiary-Butyl-Ether), ETBE (Ethyl-Tertiary-Butyl-Ether) and TAME (Tertiary-Amyl-Methyl-Ether).
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5. The process as set forth in claim 1, wherein said heteroatom compounds are nitrogen atom containing compounds and oxygen atom containing compounds.
6. The process as set forth in claim 1, wherein said first fractionator separates
15 adsorption treated hydrocarbons from the polar solvent, which are reused in regeneration.
7. The process as set forth in claim 1, wherein said second fractionator separates heteroatom compounds, of which a fraction is taken out as a product and the
20 residue is used in copurging, from the polar solvent, which is reused in regeneration.

