

# UNITED STATES PATENT OFFICE

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## HYDROCARBON SEPARATION PROCESS

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This invention relates to an improved method of separating normal paraffinic hydrocarbons from hydrocarbon mixtures containing these and other hydrocarbons by contacting these mixtures with solid urea pre-wet with a low boiling non-polar liquid in the manner hereinafter described.

It is known that normal paraffinic hydrocarbons containing at least six carbon atoms per molecule can be separated from hydrocarbon mixtures containing these and other hydrocarbons by contacting the mixtures with a concentrated solution of urea in methanol or with a urea-methanol slurry. As a result of this contact, a solid composite consisting essentially of normal paraffinic hydrocarbons and urea is formed and may be separated by filtration from the unreacted portion of the hydrocarbon mixture. The normal paraffinic hydrocarbons may then be separated from the composite by heating or by adding water to the composite. The alcohol employed in this method appears, for the most part, in the filtrate obtained, but minor quantities of the alcohol are retained on the composite and appear in the normal paraffinic hydrocarbons which are separated therefrom.

When it is attempted to employ this method on a large scale to separate hydrocarbons for use as fuels or as charging stocks to processes such as cracking, isomerization, and the like, serious process difficulties are encountered. The alcohol is an excellent solvent for urea, and that portion of the alcohol which passes through the filter carries with it considerable quantities of dissolved urea. Both the urea and the alcohol must be removed from the filtrate to render it suitable for use as fuel or as a process charge stock. Similarly, the normal paraffinic hydrocarbons separated from the solid composite must be treated for the removal of alcohol and dissolved urea prior to their use or further processing.

The difficulties attending the use of a solvent for urea, such as methanol, in the process have previously been recognized, and it has been found that the separation of normal paraffinic hydrocarbons from hydrocarbon mixtures may be effected by vigorously contacting these mixtures with urea in the absence of any solvent. Where this method is employed, the hydrocarbon mixture and the urea must be very vigorously contacted by a method which applies strong shearing forces to the solid particles in the mixture and the period of contact must be prolonged.

It is an object of this invention to provide a method for separating normal paraffinic hydrocarbons from hydrocarbon mixtures, in which no

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solvent for urea is employed and which, consequently, makes process steps adapted to remove urea from the filtrate and from the normal paraffinic hydrocarbons separated unnecessary.

It is a further object of this invention to provide a process for the separation of normally paraffinic hydrocarbons from hydrocarbon mixtures by which rapid and complete removal of the normal paraffinic hydrocarbons from the mixtures may be obtained without severe agitation and without encountering the process difficulties which are met when a solvent for urea, such as methanol, is employed.

It has now been found that the rapidity and completeness with which the formation of the composite of urea and normal paraffinic hydrocarbons proceeds may be increased by pre-wetting solid urea with a small amount of a low boiling, normally liquid, non-polar material and then contacting the urea so wetted with the hydrocarbon mixture from which it is desired to separate the normal paraffinic hydrocarbons.

Suitable low-boiling, non-polar liquids include aromatic hydrocarbons such as benzene and toluene, paraffinic hydrocarbons such as the pentanes, hexanes, heptanes, and octanes, olefinic hydrocarbons such as the pentenes, hexenes and actenes, naphthenic hydrocarbons such as cyclopentane, methylcyclopentane, dimethylcyclopentanes, cyclohexane and methyl cyclohexane, and halogenated hydrocarbons such as carbon tetrachloride, chloroform, and the like.

According to this invention, solid urea is moistened with a minor amount, of the order of 0.1% to about 10% of its weight, of a low-boiling, non-polar liquid. The urea wetted with the non-polar liquid is then contacted with the hydrocarbon mixture containing normal paraffinic hydrocarbons and other hydrocarbons, and a solid composite comprising urea and normal paraffinic hydrocarbons is rapidly formed.

The process of this invention may be practiced in either batch operation or continuous operation. Where batch operation is employed, the urea, preferably in finely-divided form is slurried with a substantial quantity of the low-boiling, non-polar liquid, and the resulting slurry is then filtered to remove the excess of the non-polar liquid, and to leave on the urea only a sufficient quantity of this liquid to moisten the surfaces of the urea particles. The urea, after filtration in this manner, is contacted with the hydrocarbon feed mixture either by stirring the hydrocarbon and the urea together, or by shaking the mixture of hydrocarbon and urea. After a contact of a

few minutes' duration, the solid composite of urea and normal paraffinic hydrocarbons is formed and the mixture is filtered. The filtrate recovered is a hydrocarbon liquid having a substantially lower content of normal paraffinic hydrocarbons than that of the feed, and the filter cake consists essentially of urea and normal paraffinic hydrocarbons. The filter cake may then be separated into its constituent components by heating or by washing with a hot hydrocarbon liquid. Where the composite is separated into its constituent parts by washing with a hot hydrocarbon liquid, the washing is conducted at a temperature below the melting point of urea and the normal paraffinic hydrocarbons are washed from the composite by the hot hydrocarbon, leaving solid, finely-divided urea which may be used in separating further quantities of the hydrocarbon mixture.

The process may be conducted in a continuous manner either by continuously slurring urea pre-wet with a low-boiling, non-polar liquid with the hydrocarbon mixture, continuously withdrawing the resultant slurry of unreacted hydrocarbons and composite, continuously filtering the slurry, decomposing the composite, and returning the recovered urea to contact further quantities of the feed. The process may also be conducted continuously by disposing finely-divided urea in a fixed bed, wetting the urea with a low-boiling, non-polar liquid in the manner above described, and then percolating the hydrocarbon mixture through the fixed bed. The percolate is characterized by a low content of normal paraffinic hydrocarbons, and the bed of urea is converted to a bed of urea-normal paraffinic hydrocarbon composite. The composite may be separated into its constituent components by washing it with a hot hydrocarbon liquid to remove the normal paraffinic hydrocarbons and leave the finely-divided urea in suitable condition for re-use in the process. In some instances, it is possible to use a hot hydrocarbon liquid for the decomposition of the composite which is also a suitable low-boiling, non-polar liquid for the pre-wetting of the urea. For example, hot toluene may be used to decompose the composite, and the residual toluene remaining on the urea when the normal paraffins have been removed will function as the desired low-boiling, non-polar liquid when the urea is again contacted with the feed.

The process of this invention is especially applicable to petroleum distillates having a 50% point on an ASTM D-158 distillation above about 300° F., such as gas oils, kerosenes, lubricating oil distillates, and heavy naphthas. The low-boiling, non-polar liquids which have been found suitable for use in the process of this invention boil below about 250° F. These liquids, even though they are used in small amount in the process, are desirably recovered from the process products and re-used. Where petroleum distillates of the type described constitute the feed material to the process, recovery of the low-boiling, non-polar liquids from the process products is readily effected by fractional distillation.

When lower boiling petroleum distillates, such as a straight run gasoline, are to be contacted with urea to separate normal paraffinic hydrocarbons according to the method of this invention, the urea is pre-wet with a non-polar liquid boiling below about 250° F. and boiling in a range below the boiling range of the distillate. For example, the urea is wetted with a C<sub>6</sub> hydro-

carbon or with petroleum ether prior to contacting it with gasoline.

The following table is illustrative of the improved results obtained in treating a California gas oil with urea according to the process of this invention. The gas oil constituting the feed in the experiments summarized in the table had the following properties:

API gravity	31.1
Aniline point	170
Four point	+45 ° F.
ASTM D-158 distillation:	
Start, 540° F.; 10%—590° F.; 30%—602° F.; 50%—614° F.; 70%—626° F.; 90%—647° F.; end point, 675° F.	

The non-polar liquids illustrated in the table include low-boiling petroleum fractions described as petroleum ether, 200 Thinner, and 250 Thinner. The ineffectiveness of higher-boiling, non-polar materials is illustrated in the table by the employment of a petroleum distillate designated as 300 Thinner. Inspections of these petroleum distillates are as follows:

Petroleum ether, a straight run distillate of California crude oil:

API gravity	82.8
ASTM D-86 distillation:	
Start, 95° F.; 10%—106° F.; 50%—120° F.; 70%—130° F.; 90%—149° F.; end point, 155° F.	

Content of hydrocarbon types as determined by ASTM Method D-875:

	Per cent
Paraffins	89
Naphthenes	8
Aromatics	3

200 Thinner, straight run distillate of California crude oil:

API gravity	60.8
ASTM D-86 distillation:	
Start 162° F.; 10%—177° F.; 50%—190° F.; 70%—198° F.; 90%—212° F.; end point 255° F.	

Content of hydrocarbon types as determined by ASTM Method D-875:

	Per cent
Paraffins	49
Naphthenes	44
Aromatics	7

250 Thinner, straight run distillate of California crude oil:

API gravity	56.4
ASTM D-86 distillation:	
Start 186° F.; 10%—199° F.; 50%—212° F.; 70%—222° F.; 90%—244° F.; end point 290° F.	

Content of hydrocarbon types as determined by ASTM Method D-875:

	Per cent
Paraffins	43
Naphthenes	48
Aromatics	9

300 Thinner, straight run distillate of California crude oil:

API gravity	49.5
ASTM D-86 distillation:	
Start, 240° F.; 10%—261° F.; 50%—295° F.; 70%—313° F.; 90%—329° F.; end point 366° F.	

Content of hydrocarbon types as determined by ASTM Method D-875:

	Per cent
Paraffins .....	35
Naphthenes .....	49
Aromatics .....	16

In each of the experiments recorded in the table, 50 grams of approximately 100-mesh urea were stirred up with 200 cc. of the low-boiling, non-polar liquid, and the mixture was filtered on a vacuum filter. The urea was weighed after filtration to determine the amount of the non-polar liquid retained on the urea surface. The urea and 100 cc. of the gas oil described above were then stirred with a glass rod in a beaker. After 10 minutes, the resulting mixture was filtered, the filtrate was heated and blown with nitrogen to expel any of the non-polar liquid carried into it, and the pour point of the filtrate was then determined.

#### Hydrocarbon separation

Non-polar Liquid	Weight of Urea Before Wash, grams	Weight of Urea After Wash, grams	Temperature at 30 sec., ° F.	Maximum Temp., ° F.	Time to Thicken	Total Reaction Time, minutes	Filtrate Pour Pt., ° F.
None.....	50	-----	77	79	Stirred 7 min. No thickening.	10	+45
Benzene.....	50	54	73	99	3 min. 02 sec.-----	10	-30
Petroleum Ether.....	50	50.2	75	104	3 min. 55 sec.-----	10	-25
n-heptane.....	50	54	82	93	1 min. 20 sec.-----	10	-15
n-pentane.....	50	50.3	70	96	3 min. 40 sec.-----	10	-25
isooctane.....	50	57	72	95	5 min. 35 sec.-----	10	-15
Cyclohexane.....	50	51	72	99	5 min. 45 sec.-----	10	-25
Toluene.....	50	54	73	96	3 min. 10 sec.-----	10	-30
200 Thinner.....	50	50.6	73	102	4 min. 40 sec.-----	10	-25
Carbon Tetrachloride.....	50	53	71	99	3 min. 45 sec.-----	10	-25
250 Thinner.....	50	53	75	93	2 min. 00 sec.-----	10	-18
300 Thinner.....	50	55	73	75	Stirred 7 min. No thickening.	10	+40
Decahydronaphthalene.....	50	58	-----	-----	Stirred 7 min. No thickening.	10	+45

The formation of the composite of urea with the normal paraffinic hydrocarbon contained in the gas oil in the experiments tabulated above is evidenced by a visible thickening of the mixture of urea and the gas oil as it is stirred and by an apparent swelling of the solid urea. The time at which this thickening was observed has been recorded to indicate the rapidity with which the composite formed.

No non-polar liquid which boils above 250° F. has been found which is effective in bringing about the rapid formation of the urea-normal paraffinic hydrocarbon composite. The ineffectiveness of higher-boiling, non-polar materials for this purpose is well illustrated by the results obtained with 300 Thinner and with decahydronaphthalene recorded in the above table.

From the column of data indicating the weight of the urea after wetting with a non-polar liquid, it is clear that it need be present in only very small amounts in order to exert a remarkable effect on the rate and completeness of the composite formation. The amount of the low-boiling, non-polar liquid employed does not ordinarily exceed 10% by weight of the solid urea. Larger amounts may be used, but unless they are desirably present in the filtrate which is obtained as a process product, their use is undesirable.

Experiments similar to those summarized in the above table conducted with kerosene, naphtha, Arabian gasoline, and light lubricating oil fractions demonstrate that the employment of low-boiling, non-polar liquids to wet the urea prior to contacting it with these stocks to effect the removal of normal paraffinic hydrocarbons

from them is effective in increasing the completeness and rapidity with which the urea-normal paraffinic hydrocarbon composite is formed. The magnitude of the effect with these stocks is comparable to that obtained with the gas oil in the experiments summarized in the above table.

Experiments have been conducted in which low-boiling, non-polar hydrocarbons were mixed with the feed and the mixture was then contacted with finely-divided urea. The results obtained in these experiments indicate that the addition of a low-boiling, non-polar liquid to the feed is either ineffective, or much less effective, in bringing about the rapid and complete formation of the urea-normal paraffinic hydrocarbon composite than is the method of pre-wetting the urea with the non-polar liquid and thereafter contacting the urea so wetted with the hydrocarbon feed.

It has been found that the employment of low-boiling, non-polar liquids to pre-wet urea in the

manner above described is especially effective with finely-divided urea. If urea particles which pass through a 100-mesh sieve are used, the combination of the non-polar liquid with the small average particle size of the urea makes possible very rapid formation of the composite.

#### I claim:

1. In a process for separating normal paraffinic hydrocarbons from a petroleum distillate having an ASTM D-158 fifty per cent point above about 300° F. by contacting said distillate with solid urea, the improved method which comprises wetting the urea with 0.1 to 10% by weight, based on urea content, of a hydrocarbon liquid boiling below about 250° F. and then contacting the distillate with the urea so wetted.

2. The method as defined in claim 1 wherein the hydrocarbon liquid consists predominantly of low-boiling normal paraffins.

3. In a process for separating normal paraffinic hydrocarbons from petroleum distillates having an ASTM D-158 fifty per cent point above about 300° F. by contacting said distillates with solid urea, the improved method which comprises wetting the urea with 0.1 to 10% by weight, based on urea content, of a normally liquid halogenated hydrocarbon boiling below about 250° F. and then contacting the distillate with the urea so wetted.

4. The method as defined in claim 1 wherein the hydrocarbon liquid is an aromatic hydrocarbon.

5. The method as defined in claim 1 wherein the hydrocarbon liquid is a paraffinic hydrocarbon.

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6. The method as defined in claim 1 wherein the hydrocarbon liquid is a naphthenic hydrocarbon.

7. The method as defined in claim 1 wherein the hydrocarbon liquid is a petroleum distillate.

8. The method as defined in claim 4 wherein the petroleum distillate is a naphtha.

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