

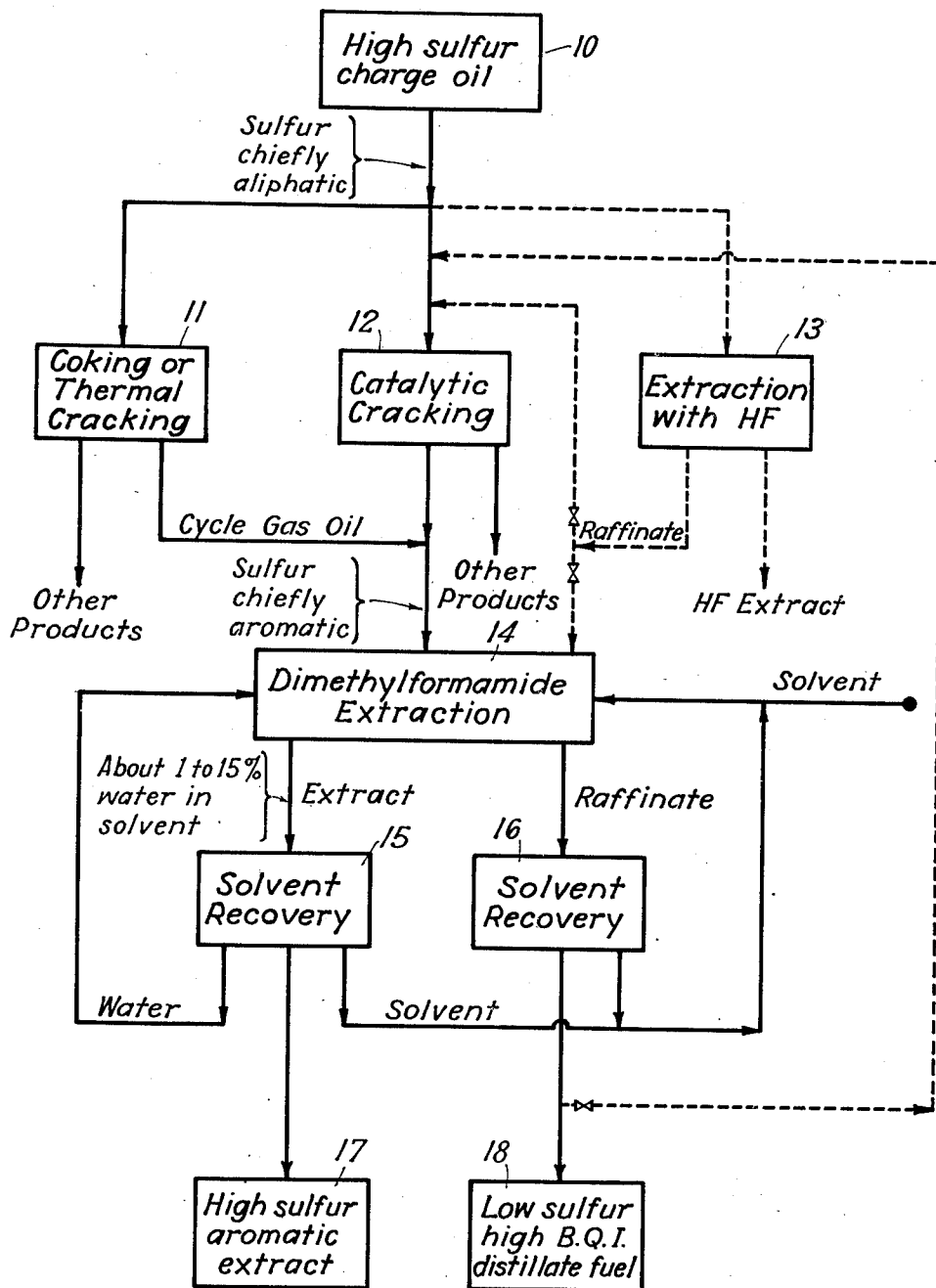
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DESULFURIZATION OF DISTILLATE FUELS

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DESULFURIZATION OF DISTILLATE FUELS

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1

2

This invention relates to desulfurization of hydrocarbons of the distillate fuel boiling range and it pertains more particularly to an improved process employing a dialiphatic formamide solvent, such as N,N-dimethyl formamide wherein a high boiling, sulfur-containing charging stock is first treated to produce a gas oil having a larger proportion of aromatic sulfur compounds to aliphatic sulfur compounds than were present in the original charge, and said gas oil is then extracted with said solvent in an improved extraction system.

The production of high quality distillate fuels, such as diesel fuels, furnace oils, heater oils, etc., from high sulfur charging stocks of the gas oil boiling range presents a problem which is very different from that of producing lubricating oils from heavier charging stocks or extracting aromatics from lighter charging stocks. Conventional lubricating oil extraction solvents, such as phenol, dichlorethyl ether, nitrobenzene, etc., give such poor performance when used for gas oil extraction that they are unsuited for such purpose, and extensive research has been conducted by the petroleum refining industry on the problem of preparing high quality distillate fuels from high sulfur gas oils. An object of my invention is to provide a solution for that problem.

Another object is to provide an improved method and means for refining high sulfur charging stocks in a multi-step process wherein the first step produces a gas oil boiling range material containing an enhanced proportion of aromatic sulfur compounds and the second step removes most of said sulfur compounds. An important object is to provide an improved method and means for producing high quality distillate fuels from the so-called "cycle gas oils" which are produced as by-products in thermal and catalytic cracking processes. A further object of the invention is to provide an improved method and means for obtaining a maximum yield of a raffinate of a low sulfur content in a process for extracting hydrocarbons of the gas oil boiling range with dimethyl formamide and added water. Other objects will be apparent as the detailed description of the invention proceeds.

While dimethyl formamide is known to be a selective solvent for the naphthenic components of lubricating oil charging stocks (note U. S. 2,166,140 and 2,183,852), it has not been considered useful as a desulfurizing agent. It apparently effects no substantial amount of desulfurization when applied to lubricating oils, and even when applied to high sulfur virgin gas oils, it ef-

fects removal of only about 25% of the sulfur. I have discovered, however, that dimethyl formamide will remove as much as 80% to 90% of aromatic sulfur compounds (even though it removes only about 25% to 35% of the aliphatic sulfur compounds) of the gas oil boiling range. When a high sulfur virgin gas oil is subjected to either thermal or catalytic cracking, there is a marked conversion of certain of the sulfur compounds contained in said charging stock so that while the original charging stock contains predominantly aliphatic sulfur compounds, the cycle gas oil contains predominantly aromatic sulfur compounds. Cracking thus produces a cycle gas oil containing sulfur compounds in a form amenable to separation by extraction with dimethyl formamide and the combination of steps results in the production of distillate fuels of remarkably high quality.

While hydrogen fluoride is recognized as one of the best available desulfurizing agents, I have found that a hydrogen fluoride raffinate of West Texas gas oil can be further desulfurized with dimethyl formamide, apparently because the latter possesses the remarkable ability to remove aromatic sulfur compounds.

In the dimethyl formamide extraction step itself, I have found that the injection of water or aqueous solvent into the extract increases raffinate yields without materially decreasing desulfurization if the amount of water introduced is sufficiently small, e. g., is in the range of about 1% to 15%. To avoid emulsification difficulties, the water, if used in appreciable quantities, should be introduced into the extract material as aqueous solvent mixture.

The invention will be more clearly understood from the following detailed description read in conjunction with the accompanying drawing which forms a part of this specification and which is a process flow chart illustrating the sequence of steps employed.

Before proceeding with the detailed description of the invention, it may be well to point out the required characteristics of a high quality distillate fuel. Distillate fuels should boil chiefly in the range of about 400° F. to 650° F.; in other words, they are essentially of the gas oil boiling range. It is important that distillate fuels have a low sulfur content, i. e., a sulfur content below about .5 per cent. When employed as diesel fuel, they should have a cetane number of at least about 40 and preferably about 50 or more. An important characteristic of a distillate fuel (particularly furnace oils, heater oils, and the like) is its freedom from coke and soot deposits; this

characteristic is rated by burning quality index or "BQI" and a high quality fuel should have a BQI of at least about 60 for most purposes.

The BQI as an index of distillate fuel quality is comparable to "octane number" as an index for gasoline quality. The BQI of a distillate fuel is determined by a standard burner test in a Coleman model 821B heater. The test involves determining the weight of total burner deposits when 100 gallons of fuel are burned at a rate of .3 gallon per hour employing a draft of 0.06 inch of water. A theoretically perfect fuel would give no burner deposits; such a fuel would arbitrarily be defined as having a BQI of 100. The BQI of any actual fuel is determined by subtracting from 100 the number of grams of burner deposits which accumulate under the above test conditions. Any fuel which deposits more than 40 grams of deposit (and hence has a BQI lower than about 60) does not meet the BQI requirements of a high quality distillate fuel, even though it may be a satisfactory fuel for many purposes.

While dimethyl formamide is the preferred solvent, it should be understood that other di-aliphatic formamide solvents, such, for example, as methyl ethyl formamide, diethyl formamide, etc., may be used. Dimethyl formamide is a liquid boiling at 153° C. (approximately 308° F.), it is heat stable, will not polymerize or form tars when heated, is non-corrosive, and is completely miscible with water. In addition, its density of 0.953 gm./ml. is such that it is easily separated from petroleum stocks.

Referring to the drawing, a high sulfur charge oil from source 10 may be any reduced crude or gas oil which has a sulfur content of more than one per cent. In this example, the charge oil may be a West Texas crude or high boiling fraction thereof. This high boiling fraction may be subjected to coking or thermal cracking in any known manner in cracking system 11 to produce products lighter and heavier than gas oil and to produce a fraction of gas oil boiling range commonly referred to as cycle gas oil (which expression is intended to include coke still gas oil). Alternatively, a West Texas reduced crude or West Texas virgin gas oil may be cracked in system 12 which represents any conventional catalytic cracking process of the fixed bed, moving bed, or fluid type employing solid catalyst of the natural or synthetic silica alumina or silica magnesia type. Here again the gas oil boiling range product is conventionally called cycle gas oil. As above stated, the sulfur compounds in the crude oil or virgin gas oil are chiefly present in the form of aliphatic sulfur compounds. The cracking step apparently alters these compounds to a considerable extent and the sulfur content of the cycle gas oils is chiefly in the form of aromatic sulfur compounds. At any rate, the proportion of aromatic to aliphatic sulfur compounds in gas oil boiling range materials is markedly increased by the cracking steps.

If the West Texas virgin gas oil is extracted with hydrogen fluoride for removal of sulfur in system 13, the raffinate produced apparently contains a considerable amount of aromatic sulfur compounds not removable by hydrogen fluoride. As above stated, even this so-called "desulfurized gas oil" can be further desulfurized by extraction with dimethyl formamide. It is also known to be an excellent charging stock for catalytic cracking.

The cycle gas oil (or HF raffinate) produced as hereinabove described and containing large

amounts of aromatic sulfur compounds is introduced to dimethyl formamide extraction system 14. The extraction may be effected batchwise, in a multiple batch system, in a countercurrent batch system or in a countercurrent extraction tower, all of which extraction means are well known to those skilled in the art. I prefer to employ the type of extraction system which is conventionally used to extract lubricating oil with phenol and which is described, for example, in the "National Petroleum News," Monthly Technical Section Devoted to Refinery Management and Petroleum Chemical Technology, section 2, December 6, 1944, pages R-830 to R-840. In such a system, substantially anhydrous solvent is introduced at the top of a baffled countercurrent tower, oil charge is introduced at a level spaced from the bottom of the tower and water or aqueous solvent is introduced into the extract phase in the tower at about, but preferably below, the oil inlet level, raffinate being withdrawn from the top of the tower and extract from the bottom thereof.

Unless the amount of water or aqueous solvent introduced into the extract phase for increasing raffinate yield is held within a rather narrow range, there will be a substantial loss of desulfurization efficiency. With a solvent to oil ratio of the order 1:1, the amount of water introduced should not substantially exceed 5%, but amounts of water may be as high as 15% when sufficiently higher solvent to oil ratios are employed. A small amount of water may be introduced with the solvent at the top of the tower; this amount should not exceed about 1% to 2% since the water is most effectively utilized when introduced into the extract phase near the bottom of the extraction tower. By per cent of water introduced, I refer to the weight per cent of water in the total solvent which is removed with the extract since some of this solvent may be introduced with the water at the base of the tower for avoiding emulsification difficulties. If large amounts of water are introduced at the base of the extraction tower, such water should contain an amount of solvent from about one-half to twice its volume in order to avoid objectionable emulsification.

The extract from the base of the extraction tower is freed from solvent in solvent recovery system 15, which is preferably a conventional extract stripper which is operated at a sufficiently high bottom temperature to insure substantially complete removal of solvent. When water is employed, a separation between water and solvent may be effected in the top of the extract stripper or distillation column; however, a separate column may be employed for removing water from solvent. The cycle gas oil charging stock to the dimethyl formamide extraction system should not contain components lower boiling than about 350° F. because lower boiling components might accumulate in the solvent and thus require additional equipment for solvent recovery. The water or aqueous solvent recovered from system 15 is preferably returned to the lower or extract portion of the extraction system while the solvent is returned to the raffinate or upper part of the extraction system. An alternative method of solvent recovery is simply to wash the extract with water and subsequently remove the water from the resulting aqueous solution. A stripped raffinate and/or extract may be additionally washed with water for removing any small amounts of solvent which may be retained therein. Solvent is removed from the raffinate in solvent recovery system 16 in the

same general manner as described in connection with solvent recovery system 15.

The final extract 17 is highly aromatic and is characterized by a high sulfur content which may be of the order of 2% to 4% or more. The finished raffinate 18, on the other hand, is char-

Heretofore hydrogen fluoride has been considered to be the most outstanding and best solvent for effecting desulfurization of hydrocarbon oils. The following results show the improvement that can be obtained by extracting an HF raffinate of West Texas gas oil and dimethyl formamide:

	Percent Yield	Percent S	Percent Desulf.	D ₄ ²⁵	n _D ²⁰	Sp. Disp.	Cetane No.
HF-Raffinate of W. T. Gas Oil		0.51		0.846	1.4748	123	57
Dimethyl formamide Raffinate	83.4	0.38	22.4	0.839	1.4641	106	62

acterized by a sulfur content below .5 weight per cent and is characterized by a remarkably high BQI and usually by a high cetane number. This finished raffinate may be further distilled to meet any specific distillate fuel specifications, and the resulting distillate fuel is of remarkably high quality. The finished raffinate is also exceptionally well suited as a catalytic cracking charging stock.

As previously pointed out, the invention is not limited to extraction in a countercurrent tower and the data set forth in the following examples were obtained by batch extraction runs. In any case, the solvent to oil charging stock ratio should usually be in the range of 20 to 150 volumes or more of solvent per 100 volumes of charging stock. Extraction temperatures should be in the range of about 35° F. to 140° F. and preferably from about 60° F. to 120° F. at approximately atmospheric pressure.

When a West Texas virgin gas oil was extracted with an equal volume of dimethyl formamide at 77° F., the results were as follows:

	Yield Percent	Percent S	Percent Desulf.	D ₄ ²⁵	n _D ²⁰	Sp. Disp.	Cetane No.
W. T. virgin gas oil		1.48		0.870	1.4818	127.4	50
Raffinate	78.8	1.10	25.7	0.849	1.4683	108	61
Extract	21.2	3.86			1.5408		

While a relatively high yield was obtained of a raffinate characterized by low refractive index and high cetane number, it will be noted that only about 25.7 per cent of the sulfur was removed, and that the raffinate would fail to meet specifications from this standpoint. However, when a catalytic cycle gas oil was extracted in the same way with an equal volume of dimethyl formamide at 77° F., the following results were obtained:

	Percent Yield	Percent S	Percent Desulf.	D ₄ ²⁵	n _D ²⁰	Sp. Disp.	Cetane No.	BQI
Lt. Cat. Cycle Oil		1.15		0.872	1.4967	154	135	20
Raffinate	57.7	0.39	66.1	0.835	1.4680	122	49	81
Extract	42.3	1.96		0.945	1.5365			

¹ Calculated.

Here it will be noted that in addition to obtaining a raffinate of 1.4680 refractive index, the raffinate sulfur content was reduced to .39, the cetane number was approximately 50, and the BQI was approximately 80. It is most remarkable that the per cent desulfurization on this catalytic cycle gas oil was approximately three times that obtained on virgin gas oil, and it is most unique that any solvent could produce from by-product catalytic cycle gas oil a product having the desirable distillate fuel characteristics which are exhibited by the raffinate in this case.

The HF raffinate itself was too high in sulfur to meet the .5 per cent requirement, but re-extraction of this raffinate with dimethyl formamide lowered the sulfur content to .38 per cent, lowered the refractive index to 1.4641 and increased the cetane number to 62.

As above stated, the raffinate obtained by extracting a thermal or catalytic cracking cycle oil with dimethyl formamide is also exceptionally well suited as a catalytic cracking charging stock. The solvent apparently extracts from the cycle gas oils those substances which are most detrimental in catalytic cracking systems. The raffinate thus produced, when charged to a fixed bed, moving bed, or fluid type catalytic cracking process employing natural or synthetic silica alumina catalysts of known composition, gives a remarkably high conversion to high octane number gasoline. It avoids catalyst deactivation which would otherwise be caused when high sulfur stocks are charged to a unit employing natural catalyst. It results in remarkably low losses to coke and gas formation. The removal from cycle gas oils of

components which are so deleterious to distillate fuels apparently results in a catalytic cracking charging stock which is superior even to virgin gas oil.

I claim:

1. The method of producing a high quality distillate fuel, which method comprises cracking a virgin gas oil which contains more than 1 percent sulfur and in which the sulfur content is chiefly in the form of aliphatic sulfur compounds to

convert sulfur compounds contained in the virgin gas oil and to produce a cracked product oil of which the fraction boiling chiefly in the range of 400° F. to 650° F. contains at least about .5% by weight of sulfur which is chiefly in the form of aromatic sulfur compounds, extracting said product oil fraction which boils chiefly in the range of 400° F. to 650° F. and which contains sulfur chiefly in the form of aromatic sulfur compounds produced in the cracking step with dimethyl formamide at a temperature in the range of 35° to 140° F. with a solvent to charging stock ratio

7

in the range of .2:1 to 1.5:1 to effect formation of separate extract and raffinate phases, separating the raffinate phase from the extract phase and recovering dimethylformamide solvent from each of the separated phases.

2. The method of claim 1 which includes the further step of employing in the extraction step an amount of water in the range of about 1 to 15 volume percent based on total solvent mixture in the extract phase.

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8

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