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[54] **PRODUCTION OF LOW POUR POINT GAS OIL AND HIGH OCTANE NUMBER GASOLINE**

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 391,380, Aug. 24, 1973.

[52] **U.S. Cl.** ..... **208/111;** 208/138; 208/141; 260/671 R

[51] **Int. Cl.**[2] **C10G 13/02;** C07C 3/52

[58] **Field of Search** ..... 208/111, 15, 102, 82, 264, 208/299; 260/671 R

[56] **References Cited**

UNITED STATES PATENTS

3,597,493	8/1971	Frilette et al.	260/666
3,700,585	10/1972	Chen et al.	208/111
3,729,409	4/1973	Chen	208/135
3,753,891	8/1973	Graven et al.	208/62
3,758,402	9/1973	Oleck et al.	208/111
3,767,568	10/1973	Chen	208/134
3,804,746	4/1974	Chu	208/111

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[57] **ABSTRACT**

A process for the simultaneous dewaxing of high pour point gas oil and upgrading of an aromatic containing naphtha by contact of a mixture of the gas oil and naphtha with a high silica to alumina ratio synthetic aluminosilicate zeolite catalyst, which is derived from a zeolite which was synthesized with an organic cation, incorporating a hydrogenation dehydrogenation component, and a hydrogen atmosphere at about 500° to 1,000°F followed by distillation of the product in order to recover a lower pour point gas oil fraction and a higher octane gasoline fraction.

11 Claims, No Drawings

PRODUCTION OF LOW POUR POINT GAS OIL AND HIGH OCTANE NUMBER GASOLINE

This is a continuation in part of Application Ser. No. 391,380 filed Aug. 24, 1973.

This invention relates to petroleum processing. It more particularly refers to the upgrading of various petroleum fractions.

Light gas oil, particularly the 330°F and heavier fractions find particular use as jet fuel, Diesel fuel and home heating oil. In at least some locations, there is a specification with respect to maximum pour point (temperature) of these distillate fuels which many light gas oils cannot meet. As a result, the gas oil is down graded to lower value use such as residual fuel.

There has recently been developed a process referred to as catalytic hydrodewaxing in which the gas oil is contacted with hydrogen and a shape selective catalyst adapted to selectively crack or hydrocrack the paraffinic molecules in the gas oil. Initially the catalysts used were those zeolite cracking catalysts which had pore openings sized so that they would admit and crack only normal paraffins and exclude all other gas oil components e.g., erionite type zeolite. Later this process was improved through substituting ZSM-5 type of zeolite for the previously used erionite type cracking catalyst. (See U.S. Pat. No. 3,700,585). Using this type catalyst permitted more efficient operation. In addition to the normal paraffins, paraffins with slight branching e.g., with a methyl side group, were also cracked whereby dewaxing was carried out to a greater extent. This permitted lowering of the gas oil pour point in a very efficient manner. The product of hydrodewaxing gas oil is suitably fractionated to produce high yields of dewaxed gas oil boiling in the same range as the feed, some naphtha and some light (C_4^-) ends.

There is a recently discovered process whereby naphtha containing aromatics, particularly reformate, can be upgraded from an octane point of view. This process contacts reformate with a ZSM-5 type of zeolite at about 500° to 1,000°F and space velocities of up to about 15 WHSV whereby some of the normal and singly branched (methyl branched) paraffins are cracked to provide relatively small fragments which alkylate aromatic rings present in the reformate feed. This converts very low octane material, i.e., paraffins, to high octane material, aromatics, by alkylation. Efficiencies in this process are rather high with excellent yields. (See U.S. Pat. No. 3,729,409). The product produced by this process is fractionated to recover high yields of higher octane naphtha as well as some light ends.

The catalyst referred to herein is inclusive of a family of high silica to alumina ratio crystalline aluminosilicate molecular sieve zeolites having an organic cation as produced. These zeolites are known to catalyze the hydrodewaxing of gas oils by inducing hydrocracking of waxy components. They are also known to catalyze the upgrading of aromatic gasoline by causing cracking of low octane components and alkylation of the fragments onto existing aromatics. Exemplary members of the zeolite family useful in this invention are ZSM-5 (U.S. Pat. No. 3,702,886), ZSM-11 (U.S. Pat. No. 3,709,979), ZSM-12 (West German Offenlagenschrifft 2,213,109 and U.S. Pat. No. 3,832,449), ZSM-21 (U.S. Application Ser. No. 358,192 filed May 7, 1973) TEA mordenite (U.S. Application Ser. No. 130,442 filed Apr. 11, 1971 and other similarly behaving materials.

It is an object of this invention to provide a novel process for carrying out catalytic hydrodewaxing and reformate upgrading in a more efficient manner.

It is another object of this invention to provide a novel process of upgrading gas oil and reformate.

Other and additional objects of this invention will be apparent from a consideration of this entire specification including the claims hereof.

In accord with and fulfilling these objects, one aspect of this invention resides in a process comprising admixing a gasoline boiling range petroleum fraction such as naphtha or reformate containing at least about 20 weight percent aromatics and gas oil having a pour point of at least about +20°F into a feed having a cumulative boiling range in the range of about C_5 to 850°F or any part thereof; contacting such feed with an organic cation derived, high silica to alumina ratio, crystalline aluminosilicate zeolite at a temperature of about 500° to 1,000°F, a space velocity of about 0.5 to 20, a pressure of about 1 to 70 atmospheres, and a hydrogen to hydrocarbon ratio of about 1 to 20 to 1; and resolving the product thus formed into a gasoline boiling range (e.g., C_5 to about 400°F) fraction having a higher octane number than the corresponding boiling range fed, a gas oil fraction having a boiling range higher than said gasoline (e.g., about 400°F+) and having a lower pour point than the gas oil fed, and a minor C_4^- light gas fraction.

Exemplary of the catalysts which are useful for this process and which fall within the scope expressed hereinabove are ZSM-5 type zeolites, ZSM-12, ZSM-21 and TEA mordenite. ZSM-12 is described in West German Offenlagenschrifft 2,213,109 and U.S. Pat. No. 3,832,449, ZSM-21 is described in U.S Pat. Application Ser. No. 358,192 filed May 7, 1973. TEA mordenite is described in U.S. Patent Application Ser. No. 130,442, filed Apr. 11, 1971. All of these references are incorporated herein by reference.

It has been stated, as a step in the described process, that a gasoline boiling range fraction and a gas oil fraction are mixed as a first step. Since most virgin gasoline fractions do not have sufficient aromatics content to meet the minimum specified herein, this admixture step contemplates a prior refinery operation, such as reforming, in which the aromatics concentration is increased followed by admixture with gas oil. It is to be understood, however, that a separate admixing step is not per se an absolute requirement of this process. It is contemplated that a petroleum cut encompassing both naphtha and gas oil boiling range materials can be taken from appropriate crude sources containing the required minimum aromatics proportion in the gasoline boiling range fraction and this wide cut fraction processed as further set forth herein. The mixing step should be considered as a requirement that mixed gasoline and gas oil be processed but not necessarily that separate fractions thereof be separately mixed.

It is surprising that naphtha upgrading and gas oil catalytic hydrodewaxing can be carried out simultaneously since each process was designed and intended to operate on a significantly different fraction of petroleum. In addition to the significant processing advantage in the single product resolution step for both the upgraded naphtha and the dewaxed gas oil, which results in major cost savings, this process has been found to result in higher gasoline yields and higher gas oil yields at the expense of light gas than were possible

under equivalent conditions operating the two processes individually. This is so even if the processes are separately operated and their products combined for a single product resolution operation.

The catalyst can be used in a fixed, moving or fluidized bed as desired with the reaction zone appropriately designed therefor. The reaction zone may be operated in an upflow or downflow manner utilizing either trickle or flooded operation. The catalyst can be used as such or can be employed in a matrix as per the referred to patents and applications. It is preferred to provide a hydrogenation/dehydrogenation component, such as nickel or other metals having such known activity, in combination with the zeolite catalyst. In addition, the catalyst may be sulfided in known manner.

The zeolite catalyst of this invention should have a silica to alumina ratio of at least about 12 to 1, preferably at least about 60 to 1. It may be used alone or in admixture with a matrixing material such as alumina or silica or the like. When used in a matrix, the proportion of active zeolite material is preferably at least about 25 weight percent.

It should be noted that invention is not here claimed in any single or group of catalysts pre se, nor in either the hydrodewaxing or the gasoline upgraded processes individually. Rather, invention is here claimed in the combination process described particularly with respect to its unexpectedly improved yield results.

This invention will be illustrated by the following Examples which are not to be considered to be limiting on the scope hereof. Parts and percentages are by weight unless expressly stated to be to the contrary.

EXAMPLE 1

Equal volumes of a Libyan "high pour" (+80°F) gas oil and a midcontinent C_6^+ light reformate were blended, properties of the two materials as follows:

		Libyan Gas Oil	C_6^+ Light Reformate
Gravity, °API		36.6	58.6
Specific		0.8468	0.7443
ASTM Distillation, °F			
IBP		368	155
5%		579	168
10		629	172
30		666	181
50		685	192
70		722	206
90		782	223
95		809	—
EP		—	239
Pour Point,	°F	+80	—
Octane No.,	R+0	—	76.0
	R+3	—	92.1

The blend was processed over sulfided Ni/H/ZSM-5 containing 35% alumina binder at 500 psig, 1.5 LHSV, 5000 SCF hydrogen/Bbl, 600°F, for 14 hours. The product was fractionated to a naphtha cut point of 390°F.

C_1+C_2, wt.%	0.4
C_3, wt. %	6.2
C_4's, vol.%	25.5
C_5's, vol. %	9.1
C_6-390°F gasoline, vol.%	40.9
390°F+ Gas oil, vol.%	25.5

The R+0 and R+3 octane numbers of the C_6-390°F gasoline were 90.3 and 100.7, respectively (compared to 76.0 and 92.1 for the reformate charge), and the pour point of the 390°F$^+$ gas oil was <−75°F (compared to +80°F for the gas oil charge).

EXAMPLE 2

The Libyan gas oil set forth in Example 1 alone was passed over a fresh portion of the same catalyst used in Example 1 at 400 psig, 1.0 LHSV, 2500 SCF hydrogen/bbl, 600°F, for 27 hours. These conditions were chosen so as to produce a gas oil product having about the same pour point as the gas oil product in Example 1. Yields as follows:

C_1+C_2, wt. %	0.5
C_3, wt. %	7.9
$C_{4,06}$'s, vol.%	21.5
C_5's, vol. %	2.9
C_6-390°F gasoline, vol.%	12.0
390°F$^+$ Gas oil, vol.%	58.8

The 390°F+ gas oil again had a pour point of <−75°F, but the R+0 and R+3 octanes of the C_6-390°F gasoline were about 80 and 93.8, respectively, much lower than the octane numbers in Example 1.

EXAMPLE 3

The midcontinent light reformate of Example 1 was contacted with the same catalyst at 600°F, 3.7 LHSV, 5000 SCF hydrogen/bbl, and 500 psig, sufficient conditions to produce a C_6-390°F product having an octane number R+0 of 90.3. Yields as follows:

C_1+C_2 wt. %	0.4
C_3 wt. %	8.4
C_4's vol. %	12.7
C_5's vol. %	5.8
C_6-390°F vol. %	68.7
390°F + vol. %	5.0

In one aspect of this invention a mixture of benzene or aromatics containing gasoline boiling range material such as reformate is mixed with a high boiling range material having a lubricating oil fraction therein such as Foot's oil and the mixture subjected to hydrodewaxing as set forth herein. To convert the mixture to a relatively high octane gasoline boiling range product, a dewaxed fuel oil product and a purified lube oil fraction boiling in the range of about 650°F+.

EXAMPLE 4

Foot's oil having the following properties:

Specific Gravity at 70°C		0.8266
Kinematic Viscosity at 210°F, cs		4.06
Boiling Range, °F.	approx.	700–900

was mixed with 10% (based upon the total composition) benzene and the mixture treated at 750 psig, 750°F, 2 to 0.5 LHSV and 2000 SCF H/bbl for 11 days. The catalyst was ZSM-5 containing 0.47 wt. % zinc admixed with a 35% alumina binder. The product was composed of some light gas, a significant naphtha fraction, a fuel oil fraction boiling in the range of about 390° to 650°F and a 650°F + lube oil fraction. The lube oil fraction averaged about 30 vol. % of the charge and had the following properties:

Gravity, °API	26.7
Gravity, Specific	0.8944
Pour Point, °F	−35
K.V. at 100°F, cs	50.77
K.V. at 210°F, cs	6.26
Viscosity Index	70
Composition, Wt %	
Paraffins	15.2
Naphthenes	52.4
1-Ring	21.4
2-Ring	14.0
3-Ring	9.0
4,5,6-Ring	8.0
Aromatics	32.4
Alkybenzenes	7.7
Tetralins, Indanes	8.7
Naphthalenes	2.6
Acenaphthenes, etc.	2.9
Phenanthrenes, etc.	2.7
Pyrenes	2.9
Chrysenes	1.4
Benzopyrenes, etc.	3.5
Total	100.0

The naphtha fraction boiling in the range of 125° to 390°F had the following composition:

Paraffins, Wt. %	18.5
Naphthenes	15.7
Olefins	3.5
Indanes & Tetralins	4.4
Naphthalenes	0.2
Alkybenzenes	57.7
Benzene	11.4
Toluene	9.0
C_8 Alkybenzenes	15.8
C_9 Alkybenzenes	14.0
C_{10} Alkybenzenes	5.0
C_{11} Alkybenzenes	2.1
C_{12} Alkybenzenes	0.4
Total	100.0

while the fuel oil boiling in the range of 390° to 650°F had the following properties;

Gravity, °API	26.3
Gravity, Specific	0.8967
Pour Point, °F	−65
Aniline No., °F	70.0
Diesel Index	18.4

What is claimed is:

1. A process of upgrading petroleum fractions which comprises contacting an admixture, containing at least 10% benzene, of gasoline boiling range fraction having a boiling range of at least about C_6 to 239°F which contains at least about 20 weight percent aromatics and a gas oil fraction having an end point up to about 850°F and a pour point of at least about +20°F with a catalyst comprising a zeolite consisting essentially of a synthetic crystalline aluminosilicate zeolite derived in an organic cation containing form, having a silica to alumina ratio of at least about 12 to 1 and having a hydrogenation/-dehydrogenation component; converting said admixture in the presence of hydrogen at a space velocity of about 0.5 to 20 WHSV, at a temperature of about 500° to 1,000°F and at a hydrogen to hydrocarbon ratio of about 1 to 20 to 1 to a product comprising a gas oil fraction having a lower pour point, a gasoline fraction having a higher octane and a light gas fraction; and resolving said product into said gas oil fraction, said gasoline fraction and said light gas fraction.

2. A process as claimed in claim **1** wherein said gasoline boiling range fraction is reformate.

3. A process as claimed in claim **1** wherein said gas oil fraction has an end point of about 850°F.

4. A process as claimed in claim **1** wherein said gas oil fraction has a pour point of about 80° to 100°F.

5. A process as claimed in claim **1** wherein said catalyst comprises a ZSM-5 type zeolite.

6. A process as claimed in claim **1** operated at a pressure of about 1 to 70 atmospheres.

7. A process as claimed in claim **1** wherein said admixture is a wide cut petroleum fraction having a boiling range in the range of about C_5 to 850°F.

8. A process as claimed in claim **7** wherein said admixture is a virgin petroleum fraction.

9. A process as claimed in claim **2** wherein said gas oil is a virgin petroleum fraction having a boiling range up to about 850°F.

10. A process as claimed in claim **1** wherein said gas oil is a lubricant containing material and wherein said product is resolved to additionally contain a purified lube oil fraction boiling in the range of 650°F+.

11. A process as claimed in claim **10** wherein said lube oil containing fraction is Foot's oil and wherein the gasoline boiling range fraction comprises benzene.

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UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,893,906
DATED : July 8, 1975
INVENTOR(S) : WILLIAM EVERETT GARWOOD and JOHN J. WISE

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 24 "pre se" should read --per se--

Column 4, line 18 "$C_{4.06}$'s, vol.%" should read --C_{4}'s, vol.%--

Signed and Sealed this

twenty-seventh Day of *January 1976*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks