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(54) Title: UPGRADING OF FISCHER-TROPSCH HEAVY END PRODUCTS

(57) Abstract

High silica to alumina ratio zeolite beta modified with boron, tin, lead or indium and combined with a hydrogenation/dehydrogenation component is used to convert Fischer-Tropsch heavy end products which may contain paraffins, olefins and oxygenates into low pour point distillates with high cetane number and extra high VI lube is described. The lube can be dewaxed by a conventional solvent process, by a catalytic process, or by increasing the severity of the hydroisomerization step.

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UPGRADING OF FISCHER-TROPSCH HEAVY END PRODUCTS

This invention relates to the upgrading of Fischer-Tropsch heavy end products to produce low pour point distillates and lubricants of high viscosity index.

Processes for the production of synthetic hydrocarbon fuels and lubricants from synthesis gas, a mixture of hydrogen and carbon monoxide, have been known for some time and, of them, the Fischer-Tropsch process is probably the best known. An account of the development of the process and its more notable characteristics are given in Kirk-Othmer, Encyclopedia of Chemical Technology, Third Edition, John Wiley & Sons, New York 1980, Vol 11, pp. 473-478 in the article on Synthetic Fuels.

In the Fischer-Tropsch process, synthesis gas is passed over a catalyst at elevated temperature and pressure to produce a number of carbon monoxide reduction products including hydrocarbons, alcohols, fatty acids and other oxygenated compounds. In favorable circumstances, oxygenated materials can comprise less than 1 percent of a total desired liquid product. The hydrocarbon product is highly paraffinic in nature and typically includes hydrocarbon gas, light olefins, gasoline, light and heavy fuel oils and waxy gas oils. Because the higher boiling fractions in the product are generally too waxy for general use either as liquid fuels or lubricants, further processing or upgrading is normally necessary before they can be used, either as such or by being added to the general pool of products.

Upgrading processes of various kinds are described, for example, in U.S. Patent Nos. 4,125,566, 4,133,841 and 4,234,412 and in these processes a high boiling fraction is subjected to cracking followed by other processes such as hydrotreating in order to remove residual quantities of oxygenated materials and to increase the yield of gasoline boiling range products. U.S. Patent No. 4,071,574 describes a process for improving the quality of the high boiling fraction, the decant oil being subjected in this case to an initial hydrogenation to saturate olefinics and to remove oxygenates, especially organic acids, after which the higher boiling materials are treated with a catalyst such as ZSM-5 to produce a material with an acceptable pour point.

A similar process is described in U.S. Patent No. 4,044,064 in which the hydrotreated Fischer-Tropsch product is fractionated and the kerosone fraction together with the heavy oil fraction boiling above about 345°C (650°F) is upgraded using a ZSM-5 type catalyst. In the upgrading process described in U.S. Patent No. 4,080,397, a mixture of light oil and higher boiling decant oil is first hydrogenated and then fractionated to form a light fraction and a heavy fraction which is subjected to selective cracking. A similar process is described in U.S. Patent No. 4,044,063. U.S. Patent No. 4,046,829 describes a process in which the fractionated synthesis product boiling above about 200°C (400°F) is first hydrogenated and then treated with a ZSM-5 type catalyst to obtain a product of lower pour point.

In U.S. Patent No. 4,943,672 issued to Hamner, et al., Fischer-Tropsch wax is converted to a lubricating oil having a high viscosity index and a low pour point by first hydrotreating the wax under relatively severe conditions and thereafter hydroisomerizing the hydrotreated wax in the presence of hydrogen on a particular fluorided Group VIII metal-on-alumina catalyst. The hydroisomerate is then dewaxed to produce a premium lubricating oil base stock.

Degnan, Jr. et al., in U.S. Patent No. 4,995,962 provided a process for hydroisomerizing petroleum or synthetic paraffin wax with a particular catalyst. The catalyst comprises a hydrogenating component and a layered titanate containing an interspathic polymeric oxide such as silica. The hydrogenating component may be a Group VIII metal such as Pt.

According to the invention, there provided a process for upgrading a waxy heavy oil fraction produced by a Fischer-Tropsch type synthesis comprising:

contacting said fraction and hydrogen gas under isomerization conversion conditions including a temperature of 200 to 500°C (400 to 930°F), a pressure of 200 to 13900 kPa (25 to 2,000 psig), and a liquid hourly space velocity (LHSV) of 0.1 to 20, with a catalyst comprising zeolite beta modified with an element selected from boron, tin, lead, and indium and combined with a hydrogenation component for a time sufficient to convert the heavy oil fraction to form a product that contains a hydrocarbon distillate fraction and a heavy hydrocarbon fraction suitable for conversion to a lubricating oil.

When operated under mild hydroisomerization conditions, a hydrotreating step is not required. By increasing the severity, a low pour point lube can be produced directly without a dewaxing step.

Feedstock

The feed for the present conversion process is obtained by means of the Fischer-Tropsch synthesis, in which synthesis gas, comprising hydrogen and carbon monoxide is passed over a suitable catalyst under conditions of elevated temperature and pressure. The catalyst used is typically a metal or a metal oxide, with iron, cobalt, nickel, ruthenium, thorium, rhodium or osmium being preferred. In most cases, cobalt will be used as the metal. Temperatures are typically in the range of 150°C to 500°C (about 300°F to 930°F) and pressures of 100 to 100,000 kPa (1 to 1000 Atm). Further details of the process and of suitable apparatus for carrying it out will be found in Kirk-Othmer, Synthetic Fuels, op cit and U.S. Patent Nos. 4,046,829, 4,044,063, 4,044,064, 4,059,648, 4,080,397 and 4,071,574.

In a typical Fischer-Tropsch operation, the synthesis gas obtained, for example, from coal by means of a suitable gasifier, is introduced into the Fischer-Tropsch converter where the carbon monoxide reduction reactions take place to form the synthesis product comprising hydrocarbons and various oxygenates such as alcohols and acids. The conversion over the Fischer-Tropsch catalyst may take place either over a fixed bed of the catalyst or in a fluidized bed of catalyst, as described in U.S. Patent No. 4,046,829. Generally, the synthesis gas feed will be introduced at a temperature of at least 150°C (about 300°F) and at a pressure of at least 800 kPa (about 100 psig); during the conversion the temperature of the reactants will rise due to the exothermic nature of the reaction. The products of the reaction are then cooled and a preliminary separation of the products made. A physical separation of the products will normally lead to a decant oil stream comprising oil free of catalyst and a slurry oil stream comprising oil mixed with entrained particles of the catalyst. After the oil has been separated from the catalyst in the slurry oil stream, the oil can be combined with the decant oil for fractionation. The separation made at this stage will depend upon the nature of the synthesis product and the subsequent processing steps but typically, a light oil boiling below 250°C (about 480°F) and a higher boiling heavy oil can be obtained. The fractionation cut points may, of course, be adjusted as desired, as is conventional. The light oil may be treated subsequently by further cooling and washing and by other processing steps such as clay treatment and washing, as described, for example, in U.S. Patent No. 4,046,829, which may then be followed by further separation of heavy ends by fractionation. The heavy ends so obtained may be mixed with the other heavy oil fractions which may be treated by the present upgrading process.

Whatever specific synthesis steps may be used, the present upgrading process employs a heavy oil fraction obtained from Fischer-Tropsch synthesis. This fraction is generally in the distillate boiling range or above and therefore may be characterized as having an initial boiling point of at least 150°C (about 300°F), although in some cases, materials of low boiling point (about 125°C) may be included in this fraction. Preferably, the Fischer-Tropsch heavy oil fraction will have an initial boiling point above 174°C and more preferably 343°C (about 650°F) since the use of a gas oil offers the possibility of producing both a distillate and a lubricating oil product. These heavy oil fractions will contain a high proportion of paraffins which give them their waxy character and in addition will contain olefins together with oxygenated compounds such as alcohols, carboxylic acids, esters and other compounds. If desired, the heavy oil fraction may be washed prior to upgrading in order to remove water soluble oxygenated compounds but if this is done, the residual water content should be reduced to an adequately low level if the catalyst used in the upgrading step is sensitive to steam. The fraction may also be passed through a guard chamber to remove contaminants associated with the conversion of the synthesis gas.

Feedstock properties of a heavy wax fraction used herein are shown below in Table 1.

TABLE 1
Feedstock Properties

Source:	Paraflint H1 Sasolwaks Batch #5753 (Moore & Munger, Shelton, Conn.)
Oil Content, wt% (D3235)	0.75%
650°F-, wt%	<1
Melting Point, °C	102
Average Molecular Mass	814
Average Carbon Number	58
Carbon Content, wt %	85.4
H2 Content, wt%	14.6
Viscosity @ 120°C, cP (Brookfield)	10
Density: at 25°C, g/cm3	0.94
120°C	0.7662
IBP @ 760mm Hg, °F (°C)	734 (390)
n-Paraffins	90.%
i-Paraffins	10.%
Aromatics	0.%

Catalyst

The catalyst used in the present invention comprises zeolite beta as the acidic component and a hydrogenation-dehydrogenation component supported on the zeolite. Zeolite beta is described in US Patent No. 3,308,069.

The zeolite beta is modified by the inclusion in the framework of the zeolite at least one element selected from boron, tin, lead and indium, with boron being particularly preferred. A method for preparing zeolite beta containing framework boron is disclosed in U.S. Patent No. 4,672,049. As noted therein, the amount of boron contained in the zeolite may be varied by incorporating different amounts of borate ion in the zeolite forming solution e.g. by the use of varying amounts of boric acid relative to the forces of silica and alumina.

Preferably, the zeolite beta contains at least 0.1 weight % framework boron, preferably at least 0.5 weight % boron. Normally, the maximum amount of boron will be about 5 weight % of the zeolite and in most cases not more than 2 weight % of the zeolite. The framework will normally include some alumina and the silica:alumina ratio will usually be at least 30:1, preferably at least 300 to 1 in the as-synthesized conditions of the zeolite.

The zeolite beta employed herein is combined with a hydrogenation-dehydrogenation component which is typically selected from Group VIIIA of the Periodic Table, including the noble metals platinum, palladium, iridium, osmimum, rhodium and ruthenium. The preferred metal is platinum. The hydrogenation-dehydrogenation component may be incorporated with the zeolite by any suitable method such as impregnation or ion exchange. The catalyst preferably contains 0.5 to 2 wt% of the hydrogenation-dehydrogenation component.

The zeolite beta may be composited with a matrix material to form the finished catalyst and for this purpose conventional non-acidic matrix materials such as alumina, silica-alumina and silica are suitable with preference given to silica as a non-acidic binder, although non-acidic aluminas such as alpha boehmite (alpha alumina monohydrate) may also be used, provided that they do not confer any substantial degree of acidic activity on the matrixed catalyst. The use of silica as a binder is preferred since alumina, even if non-acidic in character, may tend to react with the zeolite under hydrothermal reaction conditions to enhance its acidity. The zeolite is usually composited with the matrix in amounts from 80:20 to 20:80 by weight, typically from 80:20 to 50:50 zeolite:matrix. Compositing may be done by conventional means including mulling the materials together followed by extrusion of pelletizing into the desired finished catalyst particles. A preferred method for extruding the zeolite with silica as a binder is disclosed in U.S. 4,582,815. If the catalyst is to be steamed in order to achieve the desired low acidity, it is performed after the catalyst has been formulated with the binder, as is conventional.

Preferably, the catalyst employed herein has an alpha value no greater than 10, and more preferably no greater than 5. Alpha Value is an approximate indication of the catalytic cracking activity of the catalyst compared to a standard catalyst and gives the relative rate constant (rate of normal hexane conversion per volume of catalyst per unit time). It is based on the activity of the highly active silica-alumina cracking catalyst taken as an Alpha of 1 (Rate Constant = 0.016 sec-1). The Alpha Test is described in U.S. Patent No. 3,354,078; in the Journal of Catalysis, vol. 4, p. 527 (1965); vol. 6, p. 278 (1966); and vol. 61, p. 395 (1980) The experimental condition of the Alpha test used herein include a constant temperature of 538°C and a variable flow rate as described in detail in the Journal of Catalysis, vol. 61, p. 395.

The desired low alpha value of the catalyst can be achieved steaming. Steaming typically utilizes an atmosphere of 100% steam, at a temperature of 430 to 590°C (800° to 1100°F) and is normally carried out for 12 to 48 hours, typically about 24 hours, in order to obtain the desired reduction in acidity. The use of steaming to reduce the acid activity of the zeolite has been found to be especially advantageous, giving results which are not achieved by the use of a zeolite which has the same acidity in its as-synthesized condition. It is believed that these results may be attributable to the presence of trivalent metals removed from the framework during the steaming operation which enhance the functioning of the zeolite in a manner which is not fully understood. Steaming can be done before or after compositing.

Properties of a typical silica-bound, boron-containing zeolite beta catalyst for use herein are given in Table 2:

TABLE 2
Properties of Beta/SiO_2

Zeolite Beta content, wt%	65
Alpha Value(1)	5-7
Particle Density, g/cc	0.972
Real Density, g/cc	2.238
Pore Volume, cc/g	0.582
Surface Area, m^2/g	357
Hexane Sorption, wt%	10.1
Cyclohexane Sorption, wt%	11.7
Alumina, ppmw	2,900
Boron, ppmw	2,000
Sodium, ppmw	160

(1) Prior to the platinum exchange

Process Conditions

The feedstock is contacted with the catalyst in the presence of hydrogen under conditions of elevated temperature and pressure. The conditions used e.g. temperature, pressure, space velocity and hydrogen ratio, may be similar to those used in conventional hydroisomerization operations although the use of highly siliceous zeolite catalysts may permit the total pressure requirements to be reduced and the absence of polycyclic aromatic materials in the feedstock will preclude the normal hydrocracking reactions from taking place.

Process temperatures of 200°C to 500°C (400°F to 930°F) may conveniently be used although temperatures above 425°C (800°F) will normally not be employed. Generally, temperatures of 300°C to 425°C (570°F to 800°F) will be employed. As is preferred, the temperatures will be 260 to 370°C (500 to 700°F). Total pressure is usually in the range of 200 to 16,000 kPa (25 to 2000 psig), with lower pressures within this range of 2170 to 3550 kPa (300 to 500 psig) being preferred. The process is operated in the presence of hydrogen and hydrogen partial pressures will normally be from 600 to 6,000 kPa (72 to 2305 psig). The ratio of hydrogen to the hydrocarbon feedstock (hydrogen circulation rate) will normally be from 10 to 3,500 normal liters per liter (56 to 19,660 SCF/bbl). The space velocity of the feedstock will normally be from 0.1 to 20 LHSV, preferably 0.1 to 2 LHSV.

During the reaction, substantial conversion to lower boiling products, especially those in the distillate range (165°-343°C, 330°-650°F) takes place. Naphtha and dry gas may also be produced in substantial amounts. At the same time, however, the n-paraffins present in the feed and those produced by cracking are subjected to isomerization to less waxy iso-paraffins, resulting in a lower pour point for the product. As a result, the process of the invention produces a material which, by reason of its lower pour point and good viscosity index (attributable to its substantially paraffinic nature), is highly suitable as a lubricating oil base stock.

The conversion may be conduced by contacting the feedstock with a fixed stationary bed of catalyst, a fixed fluidized bed or with a transport bed. A simple configuration is a trickle-bed operation in which the feed is allowed to trickle through a stationary fixed bed. With such a configuration, it is desirable to initiate the reaction with fresh catalyst at a moderate temperature which is of course raised as the catalyst ages, in order to maintain catalytic activity. The catalyst may be regenerated by contact at elevated temperature with hydrogen gas, for example, or by burning in air or other oxygen-containing gas.

Products

The distillate boiling range products which may be obtained by the present upgrading process are characterized by a high content of isoparaffins and a very low content of sulfur- and nitrogen-containing compounds. Because of the high isoparaffin content, the pour point (ASTM D-97) of the distillate products is generally at or below -18°C (about 0°F). In addition, these products are extremely low in aromatics so that they are highly suitable as premium quality jet fuels. Their high Cetane Index will also make them good diesel fuels, a utility which is, of course, enhanced by their low sulfur content.

The higher boiling fractions (343°C+, 650°F+) which are obtained from the upgrading process are also highly paraffinic materials which confer a high viscosity index (ASTM D-2270) upon them, making them highly desirable lubricant base stocks. However, because the paraffins are present mainly as isoparaffins, the product will have a low pour point in addition to the desired high viscosity index. In general, the pour point (ASTM D-97) will be below 0°C (32°F) and in some cases below -18°C (about 0°F). Viscosity Indices will normally be above 150 and may even be as high as 170 or even higher. A VI of 175 has been obtained.

The present process is therefore notable for its ability to upgrade Fischer-Tropsch heavy fractions to produce both distillate and lubricant products which are notable for their low pour point and their minimal content of heterocyclic (nitrogen and sulfur) compounds. The process may be operated under conditions of high severity to increase the proportionate yield of distillate range product, if this is desired or, alternatively, the proportion of lube product may be maximized by operation under low severity conditions. By suitable choice of operating conditions, both distillate and lube products may be obtained.

The invention is illustrated by the following Examples in which all parts, proportions and percentages are by weight unless stated to the contrary. Examples 2 and 3 below illustrate the preparation of the highly siliceous zeolite catalysts.

EXAMPLE 1

The Pt/[B]zeolite beta catalyst described in Table 2 was used to upgrade a Fischer-Tropsch wax by hydroisomerization to form high-quality diesel fuel and potentially premium lubes. The wax was isomerized and cracked over the catalyst at moderate conditions, namely 2860 kPa (400 psig), 315-330°C (600-630°F), 0.5 LHSV, to produce the following:

Cracking Severity	Low	High
650°F+ (343°C+)Conversion	24	62
Wax Conversion	83	100
Diesel Fuel		
330-650°F (165-343°C) Yld	20	46
Cetane Number*	74	72
650°F+ (343°C) Distilled Btms		
MEK dewaxing yield	77	100 - no dewaxing required
Lube Yld, wt% feed	59	38
Lube kV@100°C, cSt	5.5	4.4
Lube VI	170	151
Lube Pour Point,°F (°C)	+10 (-12)	0 (-18)

*Estimated from ^{1}H NMR.

At low severity, lube yield is optimized at 59 wt% with a VI of 170. Increasing severity increases diesel yield at the expense of lower lube yield, viscosity, and VI. However, these debits to the lube yield/quality may be off-set by the higher dewaxing yield, especially at the point (~60 wt% 650°F+ [343°C+] conversion) where no further dewaxing of the distilled bottoms is required to produce a lubes base stock. Cetane numbers of the distillate fractions were estimated by a nuclear magnetic resonance(NMR) technique.

This example illustrates that Fischer-Tropsch wax can be processed over Pt/[B]zeolite beta at 24% 650°F+ (343°C+) conversion to yield 60% lube (170 VI) and 20% diesel (70+ cetane number). Increasing conversion to increase diesel yield results in decreased lube yield and VI. However, at high conversion (~60%), high quality lube (VI>150) can be produced directly upon distillation without the need of additional dewaxing.

The following examples illustrate the preparation of the Pt/[B]zeolite beta catalyst which is used above.

EXAMPLE 2

A representative boron-containing zeolite beta catalyst can be prepared by crystallizing the following mixture at 285°F (140°C) for 13 days, with stirring:

Boric acid, g.	57.6
NaOH, 50%, ml.	66.0
TEABr, ml.	384
Seeds, g.	37.0
Silica, g.	332
Water, g.	1020

Notes:

1. TEABR = Tetraethylammonium bromide, as 50 % aqueous solution.
2. Silica = Ultrasil^R silica.

The calcined product is expected to have the following analysis and conform to the structure of zeolite beta by X-ray diffraction:

SiO_2	76.2
Al_2O_3	0.3
B	1.08
Na, ppm	1070
N	1.65
Ash	81.6

EXAMPLE 3

The as-synthesized boron-containing zeolite beta of Example 2 is mulled and extruded with silica in a zeolite:silica weight ratio of 65:35, dried and calcined at 900°F (480°C) for 3 hours in nitrogen, followed by 1,000°F (540°C) in air for three hours. The resulting extrudate is exchanged with 1N ammonium nitrate solution at room temperature for 1 hour after which the exchanged catalyst was calcined in air at 1,000°F (540°C) for 3 hours, followed by 24 hours in 100 percent steam at 1,025°F (550°C). The steamed extrudate is found to contain 0.48 weight percent boron (as B_2O_3), 365 ppm sodium and 1920 ppm Al_2O_3. The steamed catalyst is then exchanged for 4 hours at room temperature with 1N platinum tetraammine chloride solution with a final calcination at 660°F (350°C) for three hours. The finished catalyst is found to contain 0.87 weight % platinum and have an alpha value of 4. The catalyst is sized to 20/40 mesh and 10 cc (5.46 g) is loaded into a standard 1/2 inch inside diameter reactor. If desired it can be sulfided at atmospheric pressure with 2% H_2S/H_2 programmed up to 400°C (750°F) and held overnight.

CLAIMS:

1. A process for upgrading a waxy heavy oil fraction produced by a Fischer-Tropsch type synthesis comprising:

   contacting said fraction and hydrogen gas under isomerization conversion conditions including a temperature of 200 to 500°C (400 to 930°F), a pressure of 200 to 13900 kPa (25 to 2,000 psig), and a liquid hourly space velocity (LHSV) of 0.1 to 20, with a catalyst comprising zeolite beta modified with an element selected from boron, tin, lead, and indium and combined with a hydrogenation component for a time sufficient to convert the heavy oil fraction to form a product that contains a hydrocarbon distillate fraction and a heavy hydrocarbon fraction suitable for conversion to a lubricating oil.

2. A process as claimed in claim 1 wherein the zeolite beta is modified with boron.

3. A process as claimed in claim 1 or claim 2 wherein the hydrogenation metal is platinum.

4. A process as claimed in any preceding claim wherein the catalyst has an alpha value less than 10.

5. A process as claimed in any preceding claim wherein said zeolite beta catalyst has a silica to alumina ratio of at least 300:1.

6. A process as claimed in any preceding claim wherein the conversion conditions include a temperature of 260 to 370°C (500 to 700°F), a pressure of 1480 to 13900 kPa (200 to 2,000 psig), and a liquid hourly space velocity (LHSV) of 0.1 to 2.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/08356

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :C07C 1/04, 5/13
US CL : 208/950; 585/733, 750, 751
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 208/950, 137, 138; 585/733, 750, 751,310

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS
search terms: fisher tropsch, isomeri?, hydrogen & carbon monoxide, zeolite(2a) beta, boron or tin or lead or indium

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 5,292,983 (SIE) 08 March 1994, col. 3, line31; col. 4, lines 6-14, claim 1-b.	1-6
Y	US, A, 5,082,988 (HOLTERMANN) 21 January 1992, col. 2, lines 6-13, 46-47, 56-63; col. 3, lines 18-20.	1-6
Y	US, A, 4,672,049 (CHEN ET AL) 09 June 1987, col. 3, lines 20-27, 62-65; col. 4, lines 36-37.	1-6
A	US, A, 4,523,047 (CHESTER ET AL) 11 June 1985, particularly col. 4, lines 24-29.	1-6
A	US, A, 4,943,672 (HAMNER, DECEASED ET AL) 24 July 1990.	1-6

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

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