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DESTRUCTIVE HYDROGENATION OF HEAVY CYCLE OILS

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This invention relates to the catalytic destructive hydrogenation of heavy catalytically cracked gas oil using the specific set of process conditions.

It has been the practice in the petroleum industry for a number of years to increase the quantity of gasoline obtained from crude oil by catalytically cracking various heavier-than-gasoline fractions obtained from such oil, generally by distillation. In the course of such cracking, various of the hydrocarbon components of the heavier-than-gasoline fractions undergo molecular cleavage, among other chemical changes, resulting in the formation of compounds which form a relatively high quality gasoline fraction and a certain quantity of gas. The material remaining after these light fractions are drawn off from the cracked product contain a much larger proportion of components which are comparatively resistant to the catalytic cracking treatment (e.g. polycyclic aromatics and high molecular weight resinous ingredients). Despite this fact, various heavy fractions, i.e. the so-called catalytically cracked gas or cycle oils obtained from the cracked product are often recycled to the catalytic cracking operation and the necessity for more frequent regeneration of the catalyst.

As alternatives to the recycling of these refractory cracked products to the catalytic cracker are various physical and chemical treatments of these products, e.g. coking, thermal cracking, solvent extraction, and hydrogenation, to obtain other products which are useful, per se, or are better suited for subsequent treatment, e.g. further catalytic cracking. Of these treatments, hydrogenation, both destructive and non-destructive has been investigated. It was found, however, that this type of treatment is beset with various problems, e.g. the difficulty of obtaining desirable products, low reaction rates, the quickness with which the catalyst becomes inactivated when a hydrogenating catalyst is used, and the refractoriness of the components of the heavy cracked products. To eliminate or minimize these defects, various schemes have been proposed, e.g. dilution of the cracked products with light hydrocarbons, the use of a plurality of stages of hydrogenation in which different reaction conditions and often different catalysts are used, etc. However, these special treatments and agents often render the hydrogenation process economically unfeasible and any type of operation which renders them unnecessary is greatly to be desired.

It has now been found that the resistance of cracked products boiling above the gasoline range to further catalytic cracking is due primarily to the heavier components of such products, i.e. the fraction of the cracked gas oil that boils above 260° C. It is this fraction which results in the greatest amount of catalyst deactivation and production of undesirable products, e.g. gases and coke, during the cracking treatment.

It is an object of this invention to provide an improved process for the destructive hydrogenation of heavy cracked products resulting in a favorable production of

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desirable products. It is a further object of this invention to provide a simple process for the destructive hydrogenation of a heavy catalytically cracked gas oil having an initial boiling point of at least 260° C. to obtain good yields of hydrocarbons boiling in the gasoline range, and those boiling above such range but which, among other desirable attributes, constitute a good feed for subsequent catalytic cracking.

Now, these objects are attained in accordance with this invention by contacting the heavy catalytically cracked material having an initial boiling point of at least 260° C., at least a major proportion of which is in the liquid phase together with a hydrogen-rich gas, at a temperature of at least 350° C., and a pressure of at least 100 atm. with a catalyst comprising cobalt and molybdenum in the form of the free metals and/or various compounds, e.g. oxides and sulfides, and an acidic component, on a carrier comprising at least a major proportion of alumina, so as to obtain appreciable quantities of gasoline having a high aromatic and naphthenic content, and heavier products which are suitable as diesel or other fuel or alternatively provide excellent feed for subsequent catalytic cracking. More specifically, the catalyst contains from 5 to 10% by weight of cobalt and molybdenum, calculated as free metals, the atomic ratio of cobalt to molybdenum being from 1:20 to 18:20 and preferably 1:10 to 7:10 and, preferably, at least 0.5% of fluorine as the acidic component, the percentages being by weight of the total catalyst. A catalyst particularly suitable for obtaining large amounts of hydrocarbons in the gasoline range contains 0.8 part of cobalt and 6.5 parts of molybdenum per 100 parts of alumina, and at least 1.6% of fluorine.

The liquid hourly space velocity of the feed is preferably from 0.5 to 5 volumes of oil per volume of catalyst per hour. Although the temperature and pressure may be varied widely above the lower limits stated, a pressure of 200 atm. and a temperature of from 425 to 500° C. have been found to be suitable in many cases.

The starting material used for the hydrogenation may be the whole distillable fraction boiling above approximately 260° C. which is obtained from the catalytic cracking process, whether or not mixed with the residual oil remaining after the distillable material is drawn off. It is also possible to separate specific fractions from the heavy catalytically cracked cycle oil and/or the residual oil and hydrogenate them. This separation may be carried out, for example, by means of distillation or by extraction. In addition, the residual oil may be hydrogenated according to the process of this invention without adding lighter products.

The hydrogen used in the reaction may be in the form of pure hydrogen or as a mixture containing appreciable quantities of hydrogen, e.g. the gas obtained from a catalytic reforming process. Moreover, since the percentage of hydrogen consumed in the process of this invention is relatively small, the gas may often be recycled to the reaction zone either with or without the separation of the hydrogen sulfide and ammonia formed as a result of the hydrogenation of the sulfur and nitrogen-containing compounds.

A particularly satisfactory embodiment of this invention involves carrying out the process by allowing the liquid feed to flow downward through a fixed bed of catalyst at a rate somewhat below that which would cause flooding, i.e. such that a thin film of oil forms around the catalyst particles. The hydrogen may be passed either concurrently or countercurrently with the oil through the catalyst bed. It has been found that concurrent (parallel) flow of hydrogen and liquid feed is very suitable for most purposes. When this so-called trickle technique is used, the hydrogen may be added at a rate of from 500 to 5000 volumes per volume of oil,

The process of this invention, in addition to removing most of the undesirable nitrogen and sulfur from the bed results in the production of a large percentage of desirable gasoline and heavier-than-gasoline products. The gasoline fraction boiling from 100 to 205° C. contains a substantial proportion of aromatics and naphthenes, e.g. from 75 to 90% by weight. This gasoline may be used as such or if a very high octane gasoline is desired, it may be subjected to a catalytic reforming step, e.g. "Platforming," in which a catalyst comprising from 0.05 to 1% platinum on an alumina support is used. Sufficient hydrogen may be obtained from this step if it is used to make up for up to approximately 20% of the hydrogen required for the destructive hydrogenation reaction of the initial material. The selectivity of the hydrocracking reaction of this invention which results in the production of gasoline is very high, e.g. 80% or higher, the selectivity being defined as the percentage by weight of products in the C₅ to 205° C. boiling range based on the total weight of products boiling below 205° C. The degree of hydrocracking may be somewhat controlled by varying the liquid hourly space velocity and/or the temperature at which the process is carried out.

The fraction boiling above the gasoline range has a fairly high diesel index (cetane number), viz. approximately 55, and is therefore an excellent heavy gas oil for use as diesel fuel. Alternatively, this fraction may be wholly or partly returned to the catalytic cracking plant. Since the quantities of polycyclic aromatics and other asphaltic compounds in this fraction are considerably lower than in the starting material, the hydrogenated heavy fraction is cracked with considerably more ease than the starting material for the hydrogenation. In all these uses the low content of sulfur and nitrogen is a very favorable factor.

The effectiveness of the process of this invention is illustrated by the following example.

EXAMPLE

The starting material was a mixture of heavy catalytically cracked cycle oil and the residual oil remaining after the distillation of the cracked product. This mixture was subjected to flash distillation at reduced pressure, 95% by weight of the starting material evaporating. The gaseous product was separated from the unevaporated material and then condensed. The condensate drogenation tests, had the properties referred to in obtained, which was used as initial material for the hydrogenation column IV of Table 3.

The catalyst used in the hydrogenation contained 0.8 part by weight of cobalt and 6.5 parts by weight of molybdenum in oxide form supported on 100 parts by weight of alumina. It was fluorinated by impregnating with an ammoniacal NH₄F solution, followed by calcining for two hours at 500° C. In this way two catalysts were obtained, one with 0.54% by weight of fluorine and one with 1.64% by weight of fluorine. In addition, the unfluorinated catalyst was also included in the examination. The particle size of the catalyst used was between 2 and 4 mm.

The hydrogenation was carried out in a vertical tubular reactor containing a fixed catalyst bed. In all tests the trickle technique was used, the gas rich in hydrogen being passed through the reactor concurrently with the oil. At the beginning of each test the catalyst was heated to the operating temperature at 200 kg./cm.² in a hydrogen stream. The oil was not supplied until the operating temperature had been reached. In all tests the gas was recycled without removal of H₂S and NH₃. The liquid product free from butane was subjected to fractional distillation and the fractions obtained were analyzed in the known manner.

Table 1 shows the catalysts, reaction conditions and yields for the various tests. Results were obtained with a catalyst containing 0.54% fluorine in which the maxi-

imum temperature of reaction was 450° C., a catalyst containing 1.64% fluorine wherein the maximum temperature of reaction was 450° C., and a catalyst containing 1.64% fluorine wherein the maximum temperature of reaction was 475° C. These are indicated as cases I, II and III, respectively.

Table 1

Catalyst	I Co-Mo-Al ₂ O ₃ +0.54% by wt. F.	II	III
		Co-Mo-Al ₂ O ₃ +1.64% by wt. F.	
Reaction conditions:			
Pressure, kg./cm. ²	200	200	200
Max. temperature, °C.....	450	450	475
Liquid hourly space velocity v./ v./hr.....	1.0	1.0	1.0
Amount of recycle gas, 1/kg.....	4,000	4,000	4,000
Yields percent by weight of feed:			
Fraction, C ₁ -C ₄	2.5	3.0	5.9
Fraction, C ₅ -100° C.....	3.5	6.2	9.8
Fraction, 100°-205° C.....	8.1	15.0	24.9
Fraction, 205° C.....	85.4	75.9	59.7
H ₂ S.....	2.7	2.7	2.7
Hydrogen consumption (net) m. ³ (0°, 760 mm.)/tons of oil.....	248	318	330

It may be seen from this table that the process of this invention results in an appreciable amount of hydrocarbons boiling in the gasoline range as a result of hydrocracking reactions. Moreover, the hydrocracking appears to be quite selective, the selectivities as defined above being 82.3%, 87.6% and 83.4% for cases I, II, and III, respectively.

The characteristic of the gasoline fractions produced in these three cases are shown in Table 2.

Table 2

Catalyst	I Co-Mo-Al ₂ O ₃ +0.54% by wt. F.	II	III
		Co-Mo-Al ₂ O ₃ +1.64% by wt. F.	
Fraction C ₅ -100°:			
Density, d ₄ ²⁰	0.6971	0.6921	0.6836
Sulphur content, percent by wt.....	0.01	0.01	0.01
A.S.T.M. distillation, °C.:			
Initial boiling point.....	30	26	35
10% by volume.....	49	52	49.5
50% by volume.....	80	80	75.5
90% by volume.....	98	98	93
Final boiling point.....	107	108	98
Composition, percent by wt.:			
Paraffins.....	59	54.5	65
Naphthenes.....	34	37	29
Aromatics.....	7	8.5	6
Fraction 100°-205° C.:			
Density, d ₄ ²⁰	0.8082	0.8050	0.7945
Sulphur content, percent by wt.....	0.01	0.01	0.02
A.S.T.M. distillation, °C.:			
Initial boiling point.....	119	123	125
10% by volume.....	138	137	135
50% by volume.....	166	159	157
90% by volume.....	194	190	188
Final boiling point.....	205	200	195
Composition, percent by wt.:			
Paraffins.....	8	6	22
Naphthenes.....	58	64	50
Aromatics.....	34	30	28

It can be seen that the percentage of the naphthenes and aromatics in the 100 to 205° C. fraction is very considerable so that the gasoline may be used per se as a motor gasoline. However, if a higher grade of gasoline is desired, the gasoline produced by the process of this invention may be subjected to a catalytic reforming step where, among other reactions, most of the naphthenes will be hydrogenated to aromatics resulting in a substantial raising of the octane number.

The characteristics of the heavier-than-gasoline hydrocarbons produced by the process of this invention as carried out in cases I, II and III are shown in Table 3 together with the properties of the initial material, listed in column IV.

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Table 3

Catalyst	I Co-Mo-Al ₂ O ₃ +0.64% by wt. F.	II	III	IV Initial Material
		Co-Mo-Al ₂ O ₃ + 1.64% by wt. F.		
Fraction 205+° C.:				
Density, d_4^{20}	0.868	0.852	0.851	0.935
Refractive index, n_D^{70}	1.468	1.456	1.460	1.523
Mol. weight.....	264	263	226	299
Sulphur content, per- cent by wt.....	0.03	0.01	0.02	2.59
Nitrogen content, per- cent by wt.....	0.002	0.002	0.002	0.043
Dieselindex.....		60.4	55	32
A.S.T.M. distillation:				
Percent by vol. dis- tilled over at 350° C.....				15
Percent by vol. dis- tilled over at 371° C.....				44
Carbon distribution, percent:				
Paraffinic.....	57	60	61	56
Naphthenic.....	24	25	18	
Aromatic.....	19	15	21	44
Type analysis (Chromato- graphic) percent by weight:				
Saturated compounds.....	66	76	69	49
Monocyclic aromatics.....	25	16	21	5
Bi- and polycyclic aro- matics.....	9	8	10	44
Resinous compounds.....	0.5	0.5	0.5	2

The substantial improvement in the diesel index of the heavier-than-gasoline fraction resulting from the process of this invention over the initial heavy catalytically cracked gas oil indicates that the former material is much better suited as a diesel or other type of fuel than the initial cracked gas oil. Moreover, the reduction of the polycyclic aromatics and resins in the initial material to less refractory components and the elimination of sulphur and nitrogen from such material results in the production of a gas oil which is very well suited for catalytic cracking.

The process of this invention makes possible the production of optimum quantities of gasoline and gas oil of very favorable properties from an extremely refractory material, which prior to this invention could only be treated by wasteful thermal methods to obtain products in general less useful than those resulting from the process of this invention. It should be pointed out, moreover, that unlike other hydrogenation catalysts, the catalysts of this invention do not become rapidly inactivated under the harsh conditions of the process.

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We claim as our invention:

1. Process for the conversion of heavy catalytically cracked cycle oil by destructive hydrogenation which comprises contacting a heavy catalytically cracked cycle oil having an initial boiling point of at least 260° C. while maintaining at least a major proportion in the liquid phase, in the presence of hydrogen and at a pressure of at least 100 atm. and a temperature between about 425 and 500° C., with a catalyst comprising cobalt and molybdenum in a form taken from the group consisting of the free metals, oxides, sulfides and mixtures thereof, and at least 0.5% of chemically combined fluorine, on a carrier comprising at least a major proportion of alumina, the amount of the total of the cobalt and molybdenum being from 5 to 10% by weight of the catalyst based on the free metals, and the atomic ratio of cobalt to molybdenum being from 1:10 to 7:10.

2. The process of claim 1 wherein the catalyst comprises 0.8 parts by weight of cobalt and 6.5 parts by weight of molybdenum per 100 parts of alumina, and at least 1.6% by weight of fluorine.

3. The process of claim 1 wherein a pressure of at least 200 atm., temperature of about 450° C., and a liquid hourly space velocity of 0.5 to 5 volumes per volume per hour is employed.

4. The process of claim 1 wherein the hydrocarbon oil and the hydrogen are passed concurrently downward through a fixed bed of catalyst, the oil being sent into the reaction zone at a rate below that which is necessary to flood the said zone so that a thin film of oil surrounds the catalyst particles.

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