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3,470,086

HYDROREFINING OF AROMATIC-CONTAINING HYDROCARBON DISTILLATES

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3 Claims

ABSTRACT OF THE DISCLOSURE

Ring saturation of aromatic compounds contained in a hydrocarbon mixture is prevented during a process for hydrorefining to (1) saturate olefins to produce aliphatic hydrocarbons and (2) convert nitrogenous and sulfurous contaminants into hydrocarbons, ammonia, and hydrogen sulfide. An oxide of carbon is added to the hydrogen-hydrocarbon charge, in an amount of from about 0.5 mol percent to about 5.0 mol percent (based upon the quantity of hydrogen), prior to introducing the mixture into the reaction zone.

APPLICABILITY OF INVENTION

The inventive concept described herein is applicable for use in a process for effecting the hydrorefining (often referred to as "decontamination" or "treating") of various hydrocarbon fractions and/or distillates. It is well known in petroleum technology that hydrorefining processes are designed primarily for the hydrogenation of olefins (principally mono- and di-olefins) and destructive hydrogenation of nitrogenous and sulfurous compounds to produce ammonia, hydrogen sulfide and hydrocarbons. The object of such a process is to improve the chemical and/or physical characteristics of the hydrocarbon charge stock such that the same may be readily utilized as a fuel or lubricant, or subsequently subjected to further conversion—i.e. as in catalytic reforming.

Hydrocarbon distillates, or fractions, highly olefinic and contaminated through the inclusion of nitrogenous and sulfurous compounds, result from diverse conversion processes including catalytic and/or thermal cracking, coking, shale oil retorting, the destructive distillation of coal, etc. They exhibit a variety of boiling ranges such as (1) a light naphtha gasoline range fraction having an initial boiling point of less than 120° F. and an end boiling point of about 280° F., or less; (2) a heavy naphtha gasoline fraction boiling from about 260° F. to 380° F.; (3) a full range naphtha boiling from 150° F. to 400° F.; and, (4) heavier than gasoline distillates including kerosene fractions, light gas oils, cycle stocks, heavy gas oils, etc. In addition, the majority of such hydrocarbon fractions also contain significant quantities of aromatic and alkylaromatic hydrocarbons. The aromatics will be included in amounts which range from about 20.0% to as high as about 95.0% by volume, the precise quantity being dependent upon the source; e.g. a coke oven by-product will generally consist of about 95 volume percent, whereas a catalytically cracked full boiling range naphtha fraction will contain about 50% by volume of aromatics.

Present-day hydrorefining processes are preferably conducted catalytically, and under conditions of temperature, pressure, etc., such that a significant proportion of the aromatic hydrocarbons experience at least partial saturation of the aromatic nucleus. That is, hydrorefining catalysts are generally selected from the oxides and/or sulfides of the Group VI-B and Group VIII metals—Periodic Chart of the Elements, Fisher Scientific Com-

pany, 1953—and, at temperatures of from 500° F. to 1000° F., pressures from 300 p.s.i.g. to 3,000 p.s.i.g., liquid hourly space velocities of 1.0 to about 5.0 and hydrogen concentrations of 1,000 to about 25,000 s.c.f./bbl., not only achieve decontamination and olefin saturation, but also effect a considerable saturation of the aromatic nuclei. The present invention is directed toward a scheme which permits hydrorefining for decontamination and olefin saturation without the usually attendant saturation of aromatic nuclei.

An object of the present invention is, therefore, to effect the hydrorefining of hydrocarbon mixtures without the simultaneous excessive saturation of aromatic hydrocarbons.

A corollary objective is to prevent significant aromatic saturation during hydrorefining without experiencing adverse effects with respect to decontamination and olefin saturation.

Another object resides in effecting a hydrorefining process with a decrease in the catalyst deactivation rate attributed to coke laydown.

These objects are achieved through the present invention, as hereinafter set forth in greater detail, one embodiment of which involves an improvement in a process for hydrorefining a hydrocarbon charge stock contaminated by the inclusion of sulfurous and/or nitrogenous compounds and containing aromatic hydrocarbons, in which process said charge stock is admixed with hydrogen and catalytically reacted at conditions selected to convert said contaminants into ammonia, hydrogen sulfide and hydrocarbons, and wherein said aromatic hydrocarbons are at least partially saturated, the improvement comprising adding an oxide of carbon to said hydrogen and charge stock prior to effecting the catalytic reaction thereof, and recovering a hydrorefined product effluent of increased aromatic content. "Increased aromatic content" is employed in the sense that a lesser degree of aromatic nuclei saturation takes place with the result that the product effluent is higher in aromatic content than that obtained in the absence of the carbon oxide additive.

Other embodiments are directed toward the use of from about 0.5 mol percent to about 5.0 mol percent of carbon monoxide, carbon dioxide and mixtures thereof, the concentrations being based upon the concentration of hydrogen. The variety of operating variables usually attendant a hydrorefining process, are selected on the basis of the charge stock, the degree of contamination thereof, the concentration of aromatic hydrocarbons therein and the composition of the catalyst employed, and do not form an integral part of my invention.

PRIOR ART

Acknowledgment must be made of the fact that the prior art is replete with ways and means for hydrorefining various hydrocarbonaceous charge stocks, at least some of which have been hereinbefore described. Further, it must be said that the prior art abounds with a variety of processes designed to treat such charge stocks for the purpose of converting nitrogenous and sulfurous compounds to provide hydrocarbons free therefrom and to saturate olefins to produce aliphatic hydrocarbons.

Thus, U.S. Patent No. 2,767,121, teaches the manner in which a naphtha boiling range charge stock is treated for sulfur and nitrogen removal, and to saturate olefins, in order to provide a suitable charge stock for a catalytic reforming unit.

Similarly, U.S. Patent No. 3,215,618 is directed toward multi-stage processing of highly contaminated hydrocarbon distillates derived from various processes—i.e., thermal cracking for ethylene production—which tend to

results in products containing large quantities of aromatic hydrocarbons. Likewise, aromatic-containing coal tar distillates are treated in U.S. Patent No. 2,990,364 (Cl. 208-209) for desulfurization and nitrogen removal.

In U.S. Patent No. 2,717,857, a process for desulfurizing gas oil fractions (containing material boiling above the nominal end boiling point of gasoline, 400° F.) is discussed.

An examination of this prior art reveals that processes are available for treating hydrocarbonaceous material to effect the removal of contaminating influence such as sulfur and nitrogen. However, it must be noted, in those processes where the charge stock contains quantities of aromatics, that there is no attempt to preserve the aromatic nuclei for possible recovery from the treated product. Obviously, there is no concurrent recognition of the concept encompassed by the present invention wherein an oxide of carbon is employed as an additive to the reaction zone for the avowed purpose of significantly decreasing the degree of aromatic saturation. To the contrary, since the prior art stresses hydrogen purity in the recycled gaseous phase, one would not normally consider the addition of a constituent which would effectively lower the hydrogen concentration.

SUMMARY OF INVENTION

The foregoing representations of prior art processes typify those to which the present invention is applicable, and in which the present concept may be advantageously integrated. This is not to say, however, that my invention is to be restricted to the illustrations presented.

Therefore, by way of a brief summary, my inventive concept involves the intentional addition of an oxide of carbon, or a mixture of the carbon oxides, to a hydrocarbon/hydrogen mixture prior to effecting the catalytic reaction thereof. From the standpoint of the ease of measurement and control, the oxide of carbon is preferably introduced to the process via the recycled hydrogen-rich stream before commingling the same with the charge stock. Thus, a light cycle oil having an initial boiling point of about 400° F. and an end boiling point of about 650° F., containing about 40.0% by volume of aromatic hydrocarbons is admixed with about 10,000 s.c.f./bbl. of hydrogen, the mixture being heated to a temperature such that the catalyst bed inlet temperature is about 700° F. The recycled hydrogen stream contains about 2.5 mol percent of carbon dioxide, and is circulated at a pressure of 1500 p.s.i.g.

By way of contaminating influences, the cycle oil contains about 1,000 p.p.m. (by weight) of total sulfur, about 150 p.p.m. of nitrogen and approximately 5.8% by volume of olefins. The desired product is intended to be substantially free from sulfur and nitrogen, reduced inolefin concentration and virtually unchanged in boiling range. Furthermore, it is intended that the aromatic hydrocarbons be recovered as a subsequent product stream. To achieve this end result, the mixture of charge stock, hydrogen and carbon dioxide is contacted with a catalytic composite of alumina, 0.06% cobalt, 7.0% molybdenum and 3.5% nickel, on a weight basis of the finished catalyst.

The total product effluent, at an elevated temperature of about 760° F., due to the exothermicity of the overall reactions, is passed into a high pressure separator maintained at a temperature in the range of 60° F. to 130° F. The separator serves to provide a hydrogen-rich gaseous phase, at least a portion of which is recycled to the reaction zone, and a normally liquid hydrocarbon phase which constitutes the end product. The product effluent is admixed with water in order to absorb the ammonia resulting from the conversion of the nitrogenous compounds, and the high pressure separator designed to provide a sour water dip leg. Other schemes for removing the ammonia from the system will become evident to those possessing the requisite skill in the art. Similarly, the gaseous phase, generally free from butanes and

heavier hydrocarbons, may be treated by any suitable means for the purpose of removing hydrogen sulfide.

The pressure control point is usually located at the high pressure separator, and controlled by venting a minor amount of the gaseous phase, the remainder of which is recycled by compressive means to combine with the fresh hydrocarbon charge stock. Make-up hydrogen, to compensate for that consumed in the process, may be added either up-stream or down-stream from the compressor, and may stem from any external source such as a "hydrogen-producing" process—i.e., a catalytic reforming unit. Likewise, the carbon dioxide may be introduced at this point, in an amount to maintain the 2.5 mol percent based upon the hydrogen recycle. With the light cycle stock above described, the hydrogen consumption is about 950 s.c.f./bbl.

Analyses of the normally liquid product effluent (including any butanes formed as a result of the minor degree of cracking reactions) indicates a nitrogen concentration less than one part per million, "nil" with respect to olefinic hydrocarbons and about 2.0 p.p.m. of sulfur. Significantly, however, periodic checks show an aromatic content ranging from about 38.0% to 39.0% or up to 97.5% aromatic preservation.

Although the foregoing is believed sufficient to permit the practical use of my invention in a process for hydrorefining an aromatic-containing hydrocarbon distillate, the following examples are presented in further illustration, and to indicate actual results obtained. It is understood that these illustrative examples are not intended to restrict the present invention beyond the scope and spirit of the appended claims.

Examples

(I) A cycle oil, having the properties shown in the following Table I, was subjected to hydrorefining in a 200 cc.-capacity pilot plant-scaled unit.

Gravity, ° API at 60° F. -----	30.0
ASTM Distillation, ° F.:	
IBP -----	418
10% -----	470
50% -----	532
90% -----	600
EP -----	632
Sulfur, p.p.m. -----	1020
Nitrogen, p.p.m. -----	154
Bromine No. -----	8.6
Aromatics, vol. percent -----	38.5
Olefins, vol. percent -----	4.7
Paraffins and naphthenes, vol. percent -----	56.8

The catalyst, disposed in a stainless steel reactor of 5/8-inch nominal diameter, equipped with a spiral inner heater, consisted of 0.25% by weight of cobalt, 5.7% by weight of molybdenum and 2.2% by weight of nickel, all of which were combined with a carrier material of 88% by weight of alumina and 12.0% by weight silica. Silica was used as a component of the carrier material in order to impart an acid-acting function to the catalyst for the purpose of broadening the boiling range of the hydrorefined product.

Throughout the entire operation, the maximum catalyst temperature was controlled at a level of 725° F., the reactor pressure at 1,500 p.s.i.g. by compressing hydrogen recycle in the amount of 3,000 s.c.f./bbl., and the liquid hourly space velocity was 1.0. The addition of carbon dioxide into the hydrogen make-up stream was accomplished by pressuring a metered quantity of a carbon dioxide/hydrogen blend into the recycle hydrogen stream.

Water was injected into the reactor effluent line up-stream of a high-pressure separator which was equipped with a sour-water dip leg. This technique constitutes a convenient method for removing the ammonia formed

from the conversion of nitrogenous compounds. The high-pressure separator was maintained at a temperature of about 80° F. The normally liquid stream was passed into a nitrogen-stripping column functioning at a pressure of about 200 p.s.i.g., in order to remove hydrogen sulfide.

In the following Table II, analyses of the product stream are presented to indicated the results of carbon dioxide addition in amounts of "zero," 0.5 and 2.5 mol percent based upon the quantity of hydrogen.

TABLE II—PRODUCT ANALYSES, CO₂ ADDITION

Carbon Dioxide Concentration.....	0	0.5	2.5
Gravity °API at 60°F.....	35.3	34.9	34.5
ASTM Distillation, ° F.:			
IBP.....	353	390	362
10%.....	450	458	455
50%.....	515	518	515
90%.....	592	594	588
EP.....	631	636	637
Sulfur, p.p.m.....	2.5	1.2	2.1
Nitrogen, p.p.m.....	1.0	<1	<1
Bromine No.....			
Aromatics, vol. percent.....	31.5	34.5	38.0
Olefins, vol. percent.....			
Paraffins plus naphthenes, vol. percent.....	68.5	65.5	62.0

From the foregoing data, the results of adding carbon dioxide, with respect to aromatic retention, are readily ascertained. In the absence of CO₂, there was a decrease from 38.5% in the fresh charge stock to 31.5% in the product, or about 18.2%. With 0.5 mol percent CO₂, the aromatic content decreased to 34.5%, or a loss of about 10.4%. In the operation with 2.5 mol percent CO₂, the aromatic content decreased only to 38.0%, representing a retention of 98.7% of the aromatics in the charge stock. Of further interest is the fact that there has been no indication of an adverse effect with respect to the capability of the catalyst to remove sulfur and nitrogen.

(II) For this example, the charge stock was a blend of a light naphtha having an end boiling point of 314° F., (an aromatic light oil) and a 680° F. end point diesel fuel. The charge stock blend exhibited the characteristics shown in the following Table III.

TABLE III.—BLENDED CHARGE STOCK ANALYSES

Gravity, ° API at 60° F.	31.7
ASTM Distillation, ° F.:	
IBP	192
5%	210
10%	225
50%	469
90%	571
95%	598
EP	650
Aromatics, vol. percent	55.8
Olefins, vol. percent	1.1
Paraffins plus naphthenes, vol. percent	43.1
Sulfur, wt. p.p.m.	7240
Nitrogen, wt. p.p.m.	17

The blend was formed from 26.5% of the aromatic light oil and 73.5 vol. percent of the diesel fuel.

The catalytic composite consisted of 2.2% cobalt and 5.7% molybdenum combined with alumina in the form of 1/8-inch cylindrical pills. This catalyst was disposed in the reaction chamber in an amount of 200 cc. (as in the previous example), and maintained under a pressure of about 800 p.s.i.g. Tests were conducted at a liquid hourly space velocity of 3.0, using a hydrogen recycle rate of 2000 s.c.f./bbl. and maximum catalyst temperatures of 700° F., 725° F. and 750° F. The normally liquid product was separated into a 380° F. end point

naphtha and a 380° F.-plus diesel fuel. Analyses were obtained on the total product and the two fractions thereof. Carbon monoxide was introduced into the hydrogen recycle system from pressurized cylinders in an amount of 4.0 mol percent.

In the absence of the carbon monoxide, the naphtha fraction (end point of 380° F.) was 28.3% by volume of the total product, contained 31 p.p.m. of total sulfur and 1.0 p.p.m. of nitrogen, and consisted of 1.4% by volume of olefins. The total product consisted of 52.4% paraffins and naphthenes, 1.7% olefins and 45.9% aromatics. The latter represents aromatic retention of only 82.2%. Analyses performed on the catalyst showed 3.71% by weight of carbon at a catalyst life of 0.42 (barrels of charge per pound of catalyst disposed in the reaction zone).

The results obtained during the carbon monoxide addition indicated a significantly improved operation. The naphtha fraction was 32.2% by volume of the total product, contained 38 p.p.m. of sulfur and 0.3 p.p.m. of nitrogen, and consisted of 0.7% by volume of olefins. The total product indicated 47.5% paraffins plus naphthenes, 0.9% olefins and 51.6% aromatics, the latter representing an aromatic retention of 92.6%. At a catalyst life of about 0.46, the carbon content of the catalyst was 1.20% by weight. Thus, it is readily noted that the benefits afforded through the addition of carbon monoxide resides in a greater degree of aromatic preservation accompanied by a significantly lesser degree of carbon deposition.

The foregoing specification, and particularly the comparative examples, indicates the method by which the present invention may be integrated into a hydrorefining process, and clearly illustrates the benefits to be afforded therefrom.

I claim as my invention:

1. In a process for hydrorefining a hydrocarbon charge stock contaminated by the inclusion of sulfurous and/or nitrogenous compounds and containing aromatic hydrocarbons, in which process said charge stock is admixed and catalytically reacted with hydrogen at conditions selected to convert said contaminants into ammonia, hydrogen sulfide and hydrocarbons, and wherein said aromatic hydrocarbons tend to become at least partially saturated, the improvement which comprises substantially preventing aromatic saturation by adding a carbon oxide to said hydrogen and charge stock in an amount of from 0.5 mol percent to about 5.0 mol percent, based upon the quantity of hydrogen admixed with said hydrocarbon charge stock, prior to effecting the catalytic reaction thereof, subjecting said charge stock to hydrorefining conditions, and recovering the resulting hydrorefined product effluent.

2. The improvement of claim 1 further characterized in that said oxide of carbon is carbon dioxide.

3. The improvement of claim 1 further characterized in that oxide of carbon is carbon monoxide.

References Cited

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