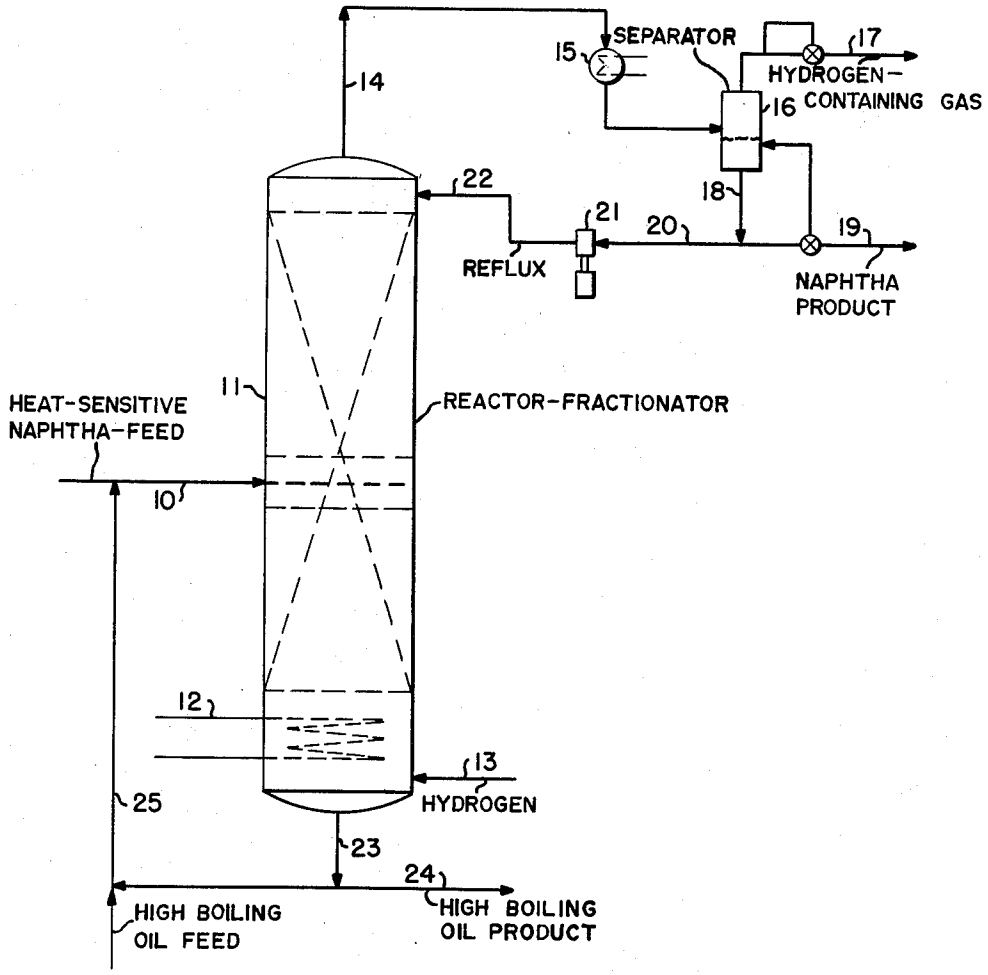
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HYDROFINING PROCESS

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HYDROFINING PROCESS

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This invention relates to a hydrocarbon conversion process and more particularly to an improved process for the catalytic conversion of heat sensitive naphthas in the presence of added hydrogen.

It is known that the quality of virgin or straight run as well as cracked or thermally reformed naphthas and middle distillates can be improved by reacting such feedstocks with added hydrogen at elevated temperatures and superatmospheric pressures in the presence of hydrogenation-dehydrogenation catalysts. Such operations are referred to as hydroforming, hydrofining, hydrocracking, hydrodesulfurizing, and the like. The purpose and result of these treatments are to effect a substantial reduction in the sulfur content, to saturate certain highly unsaturated gum-forming constituents and to saturate at least a part of the olefins present, to improve the color and odor of the product and to produce aromatic hydrocarbons by the catalytic dehydrogenation of naphthenic and cyclic olefin components.

In most of these processes the feed is supplied alone or in admixture with the added hydrogen-rich treat gas to the catalyst-containing reaction zone at temperatures in the range of from about 450° F. to 950° F. It is the general practice to obtain such temperatures by passing the feed through a heat exchanger or furnace provided with a large number of tubes of small diameter. It has been found, however, that as temperatures above about 250–350° F. are reached, many naphtha feeds tend to form deposits upon the walls of the heat exchanger which in some cases have completely plugged the heat exchanger tubes. In addition, these feeds have a tendency to form excessive amounts of carbonaceous deposits upon the catalyst severely reducing the activity thereof.

It has been proposed to overcome these difficulties in various ways such as by passing an inert gas through the feed stock to strip off the free oxygen content, by blanketing the feed stock with an inert gas to minimize contact with air and by giving the feed stock a pretreatment with hydrogen in contact with a hydrogenation-dehydrogenation catalyst at temperatures above about 300° F. but below the temperature at which substantial deposits are formed.

It is the object of this invention to provide an improved process for hydrofining heat-sensitive naphthas.

It is a further object of this invention to provide a process for hydrofining heat-sensitive naphthas which avoids the problems of deposit formation on heat exchanger surfaces and overcomes the problem of excessive carbonaceous deposit formation upon the catalyst.

These and other objects will appear more clearly from the detailed specification and claims which follow.

It has now been found that heat-sensitive naphthas such as cracked or coker naphtha can be effectively hydrofined without the usual heat exchanger and catalyst fouling by mixing the naphtha feed with a suitable gas oil, pumping the feed mixture in the liquid phase into the center section of a high pressure reactor-fractionator tower which is suitably packed with hydrofining catalyst. The hydrogen or hydrogen-rich treat gas stream is injected into the reboiler at the bottom of the tower whereupon the treat gas passes upwardly through the tower, countercurrently to the descending gas oil in the lower portion of the tower and concurrently with the naphtha in the upper section of the tower. The operation of the reactor-fractionator

tower is very much like any fractionator. The pressure, hydrogen rate and the boil-up rate are chosen so as to give the desired separation as well as the desired degree of hydrofining. The hydrofined naphtha product is taken overhead from the tower while the gas oil is removed as bottoms. The principal advantages of the process in accordance with the present invention is that vaporization of the heat-sensitive naphtha feeds in heat exchanger or preheat furnace tubes is avoided and moreover the entire catalyst bed is being continuously washed with a hot liquid oil phase.

The feed stocks that can be treated advantageously by the process of the present invention are those hydrocarbons which boil within the range of from about 150 to 450° F. and may be straight run naphtha, coker naphtha, thermally cracked naphtha and catalytically cracked naphtha. The process of this invention is particularly adapted for the treatment of cracked or coker naphthas, especially those which tend to form deposits when heated to temperature of about 250–350° F. in heat exchangers or preheat furnace tubes.

The higher boiling oil which is added to the naphtha feed stock in accordance with the present invention should boil within the range of from about 450 to 800° F. preferably 550 to 650° F. The higher boiling oil may be a virgin gas oil which will be desulfurized in the operation or the higher boiling oil may, if desired, be recycled in whole or in part.

For operability of the invention the ratio of heavy oil to naphtha in the feed is not very critical. The reason for this is that by refluxing vapor up the column from the reboiler the heavy oil concentration may be maintained even though it is not being added in large quantities in the feed. However, in order to prevent the accumulation of extracted polymer in the reboiler some constant addition and withdrawal of heavy oil is necessary. The minimum quantity of this heavy oil addition will depend upon the materials being processed, the particular catalyst being used and upon the severity. In general, it is expected that most operations will require a minimum of about 0.1 volume of heavy oil per volume of naphtha.

There is no maximum to the amount of heavy oil which can be added and the quantity used will be controlled by its availability together with economic comparisons with other methods of treatment.

Any conventional hydrofining or hydrogenation-dehydrogenation type catalyst may be used. Such catalysts include various oxides and sulfides of metals of groups VI and VIII such as molybdenum, tungsten, chromium or the like or mixtures such as nickel-tungsten sulfide and cobalt molybdate or mixtures of cobalt oxide and molybdenum oxide preferably deposited upon a support or carrier material such as activated alumina, silica gel, or activated alumina containing small amounts (2 to 10 wt. percent) of silica. The preferred catalyst is one containing from about 5 to 25 wt. percent of cobalt oxide and molybdenum oxide with the ratio of the former to the latter in the range of from about one to five to about five to one, supported upon an adsorptive or activated alumina containing about 0 to 5 wt. percent of silica. Such catalysts are prepared by first forming adsorptive alumina, containing silica if desired, in any suitable or known way and then compositing molybdenum oxide and cobalt oxide therewith. The molybdenum oxide can, for example, be added as a slurry or it may be applied as a solution of ammonium molybdate. The cobalt oxide is conveniently added as a salt such as cobalt nitrate or acetate, salts which are readily decomposed to cobalt oxide and volatile materials. The catalysts may, if desired, be given an activation treatment prior to use in the hydrofiner by reacting the same with a suitable sulfiding agent such as a sulfur-containing feed stock,

hydrogen sulfide, carbon disulfide and the like. The amount of sulfur added for preactivation of the catalyst may vary from about 100% up to about 1500% of the stoichiometric quantity necessary to convert the cobalt oxide and molybdenum oxide to the corresponding sulfides.

The reaction conditions maintained in the reactor fractionator vessel vary somewhat depending upon the nature of the feed stock, the character and quantity of the impurity or contaminant being removed and the degree of improvement desired. In general, the reaction temperature is about 400 to 800° F. preferably 500 to 650° F., reaction pressure 50–500 p.s.i.g., preferably 200–250 p.s.i.g. and feed rate is 0.5 to 20 v./v./hr.; preferably about 1–3 v./v./hr. The hydrogen-rich treat gas, which should contain at least about 30 volume percent hydrogen is supplied to the bottom of the reactor-fractionator column at the rate of about 50 to 2000 s.c.f./b., preferably about 1000 s.c.f./b. and the hydrogen consumption in the hydrofining operation is about 100 to 500 s.c.f./b., usually about 300 s.c.f./b.

Reference is made to the accompanying drawing illustrating diagrammatically the reactor-fractionator used in the present invention.

In the drawing, liquid feed stock comprising a mixture of a naphtha fraction and a gas oil or higher boiling fraction is supplied at system pressure through inlet line 10 at temperatures of about 200 to 600° F. The liquid feed mixture is supplied at or about the midpoint of the reactor-fractionator 11 which is charged with a suitable hydrofining or hydrogenation-dehydrogenation type catalyst.

The catalyst bed and/or inert packing provided in the vessel 11 serve to pack the vessel so that it can serve as a fractionator. For example, 1/16" diameter, 1/8" long hydrofiner catalyst particles as a packing is about 1 to 2 feet HETP (height equivalent to a theoretical plate). A heating coil 12 is arranged at the bottom of the vessel to supply the necessary heat for vaporizing the higher boiling oil fraction. Hydrogen-rich treat gas is supplied through inlet line 13 at the bottom of the vessel 11 and serves to assist in the vaporization of the higher boiling oil fraction. The hydrogen-containing gas passes upwardly through the column counter currently to the downflowing heavy oil and reflux in the lower portion of the column and concurrently with the lighter naphtha vapors in the upper part of the column. Temperatures at the bottom of the column are about 600–750° F. while temperatures at the top are in the range of from about 400–600° F. Pressures within the column are about 50–500 p.s.i.g., preferably 200–250 p.s.i.g. and under these conditions the hydrogenation of sulfur, nitrogen, and, to some extent, the olefinic compounds in the oils are promoted.

The hydrofined naphtha, excess treat gas and gaseous reaction products pass overhead from vessel 11 through line 14, cooled in condenser 15 and discharged into separator 16. Gaseous products are released from the top of separator 16 via line 17 and after absorption may be used as fuel or, if desired, scrubbed of hydrogen sulfide and the like and recycled to the reactor-fractionator. Naphtha product is withdrawn from separator 16 through line 18 and 19 and discharged to a stripper and/or further processing such as hydroforming. A portion of the naphtha product is recycled via line 20, pump 21 and line 22 as reflux to the top of the reactor-fractionator. It should be noted that in the arrangement shown, all of the catalyst within the vessel is continuously washed by the flow of liquid oil thereover. This is especially advantageous since the heat sensitive naphthas such as coker or catalytically cracked naphthas normally tend to form large amounts of carbonaceous deposits upon the catalyst which in the present invention are continuously removed by the washing action of the oil. Moreover, by mixing the heat sensitive naphtha which tends to form deposits on heat transfer surfaces when vaporized, with gas oil and supplying the feed stream to the reactor fractionator vessel in liquid form, the vaporization of the naphtha is effected in an area where the surfaces of the catalyst, filler or packing materials as well as the walls of the vessel itself are continuously washed with liquid oil. This should give high heat economy with small capital investment.

The higher boiling oil is withdrawn from the bottom of the column through line 23 and discharged to product storage via line 24 or, if desired, a portion of the heavy oil may be pumped via line 25 back to the feed inlet line 10 as recycle.

The following example is illustrative of the present invention.

Example

A heat sensitive C_5/430 steam cracked naphtha is to be hydrofined to improve stability by the partial saturation of diolefins. It is mixed in approximately equal volumes with a 430/650 virgin gas oil. This virgin gas oil is to be desulfurized for use as diesel fuel. The mixed feed is fed at a temperature of about 300° F. into the center of the combination reactor-fractionator. This vessel is packed with a mixture of cobalt molybdate on alumina catalyst and a suitable distillation packing such as Berl saddles. The catalyst may be in the form of pellets, cylinders, spheres or in various extruded shapes such as hollow cylinders, saddles, etc. The height and diameter of the tower may be chosen by methods well known to those skilled in the art. The diameter must be sufficient so that with the vapor and liquid loadings required, flooding will not occur. The height must be sufficient to provide adequate fractionation. These requirements fix the total volume of catalyst and inert packing. The volume of active catalyst required in each section, i.e. above and below the feed injection point, will be determined by the required qualities for the naphtha and gas oil products. In general, the total volume of catalyst will be in the range of 0.1 to 1.0 multiplied by the total hourly liquid volume of feed.

For the particular example described here, the reactor operating pressure is 200 p.s.i.g., the hydrogen gas treat rate is 1000 s.c.f./b., the temperature is 650° F. in the reboiler, and at the top of the tower 490° F. An external reflux ratio of 1:1 is employed. The inspections on the feed components are given below:

	Steam Cracked Naphtha	Virgin Gas Oil
Gravity, ° API	35.2	33.6
Percent Sulfur	0.17	0.8
Bromine No.	133	----------
Diene No.	26	----------
Research Octane No.	98.0	----------

The naphtha is to be treated to a diene number of less than 2. The gas oil sulfur content is to be reduced to less than 0.4.

For these requirements, it is found that an equal volume of catalyst should be used both above and below the feed plate and that the total volume of catalyst should be in the range of 0.5 to 1.0 times the total hourly liquid feed rate. A total column height of 30 to 40 feet would give fractionation satisfactory for most purposes.

The foregoing description contains a limited number of embodiments of the present invention. It will be understood that numerous variations thereof are still within the scope of the present invention.

What is claimed is:

1. The method of catalytically hydrogenating heat sensitive naphtha feed stocks that tend to form a deposit upon a heat transfer surface when preheated to a temperature above about 250–350° F. and which tend to form an excessive amount of carbonaceous deposit upon

hydrogenating catalyst in a reaction zone, which comprises mixing the said naphtha feed stock with a higher boiling gas oil, introducing the resultant mixture at about the mid-section of a vertical reaction zone containing a hydrogenation-dehydrogenation catalyst, supplying heat to said reaction zone and maintaining it at a temperature of about 400–800° F. and at a pressure of about 50–500 p.s.i.g. to vaporize said naphtha in said reaction zone and at least a portion of the gas oil, passing naphtha vapors upwardly through the upper portion of said reaction zone, supplying hydrogen-containing treat gas to the bottom of said reaction zone and passing said gas upwardly through said reaction zone countercurrently to the descending gas oil in the lower portion of the zone and concurrently with the naphtha vapors in the upper portion of said reaction zone, removing hydrofined naphtha product overhead from the said reaction zone, removing liquid gas oil as bottoms from said reaction zone, condensing hydrofined naphtha product and returning a portion of said liquid hydrofined naphtha product to the top of said reaction zone to maintain liquid oil in contact with catalyst in the upper portion of said reaction zone.

2. The method of catalytically hydrogenating heat sensitive naphtha feed stocks that tend to form a deposit upon a heat transfer surface when heated to temperatures above about 250–350° F. and which tend to form an excessive amount of a carbonaceous deposit upon the hydrogenating catalysts which comprises mixing the said naphtha feed stock with a higher boiling gas oil, introducing the resultant mixture at about the mid-section of a vertical reaction zone containing a hydrogenation-dehydrogenation catalyst, maintaining said reaction zone at a temperature of about 400–800° F. and a pressure of about 50–500 p.s.i.g. by supplying heat to the bottom of said zone to vaporize the naphtha in said reaction zone and at least a portion of the gas oil in said reaction zone, supplying hydrogen-containing treat gas to the bottom of said reaction zone and passing said treat gas upwardly through the reaction zone countercurrently to the descending gas oil in the lower portion of said reaction zone and concurrently with the naphtha vapors in the upper portion of said reaction zone, removing hydrofined naphtha product overhead from the said reaction zone, condensing the hydrofined naphtha product, recycling a portion of the liquid naphtha product to the top of said reaction zone to maintain liquid oil in contact with the catalyst in the upper portion of said reaction zone and removing hydrofined liquid gas oil as bottoms from said reaction zone.

3. The method of catalytically hydrogenating heat sensitive naphtha feed stocks that tend to form a fouling deposit upon a heat transfer surface when preheated to a temperature above about 250–350° F. and which tend to form an excessive amount of a carbonaceous deposit upon a hydrogenating catalyst in a reaction zone, which comprises mixing the said naphtha feed stock with a higher boiling gas oil, introducing the resultant mixture

below said fouling temperature of 250–350° at about the mid-section of a vertical reaction zone containing hydrogenation-dehydrogenation catalyst and maintained at a temperature of about 400–800° F. and a pressure of about 50–500 p.s.i.g., supplying heat to the bottom of said reaction zone in sufficient amount to vaporize the naphtha and at least a portion of the gas oil, supplying hydrogen-containing treat gas to the bottom of said reaction zone, recycling a portion of the condensed hydrofined naphtha product referred to hereinafter, to the upper portion of said reaction zone to maintain liquid oil in contact with the catalyst within the upper portion of said reaction zone, removing hydrofined naphtha product overhead from the said reaction zone, condensing the hydrofined naphtha product, removing hydrofined liquid gas oil as bottoms from said reaction zone, and recycling a portion of said hydrofined liquid gas oil to the inlet of said reaction zone for mixing with fresh feed naphtha.

4. The method of catalytically hydrogenating heat sensitive naphtha feed stocks that tend to form a deposit upon a heat transfer surface when heated to a temperature above about 250–350° F. and which tend to form an excessive amount of carbonaceous deposit upon a hydrogenating catalyst in a reaction zone which comprises mixing the said naphtha feed stock with a higher boiling gas oil, introducing the resultant mixture at a temperature of about 250–350° F. about the mid-section of a vertical reaction zone containing a hydrogenation-dehydrogenation catalyst and maintained at a temperature of about 490–650° F. and a pressure of about 50–500 p.s.i.g., supplying heat to the bottom of said zone in sufficient amount to vaporize the naphtha and at least a portion of the gas oil, supplying hydrogen-containing treat gas to the bottom of said reaction zone and passing the treat gas upwardly through said reaction zone countercurrently to the descending gas oil in the lower portion of said reaction zone and concurrently with the naphtha vapors in the upper portion of said reaction zone, removing hydrofined naphtha product overhead from the said reaction zone, condensing the hydrofined naptha product, recycling a portion of the liquid naphtha product as reflux to the top of said reaction zone to maintain liquid oil in contact with the catalyst in said reaction zone, removing hydrofined liquid gas oil as bottoms from said zone, and recycling a portion of said hydrofined liquid gas oil for admixture with fresh feed naphtha to be introduced into said reaction zone.

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