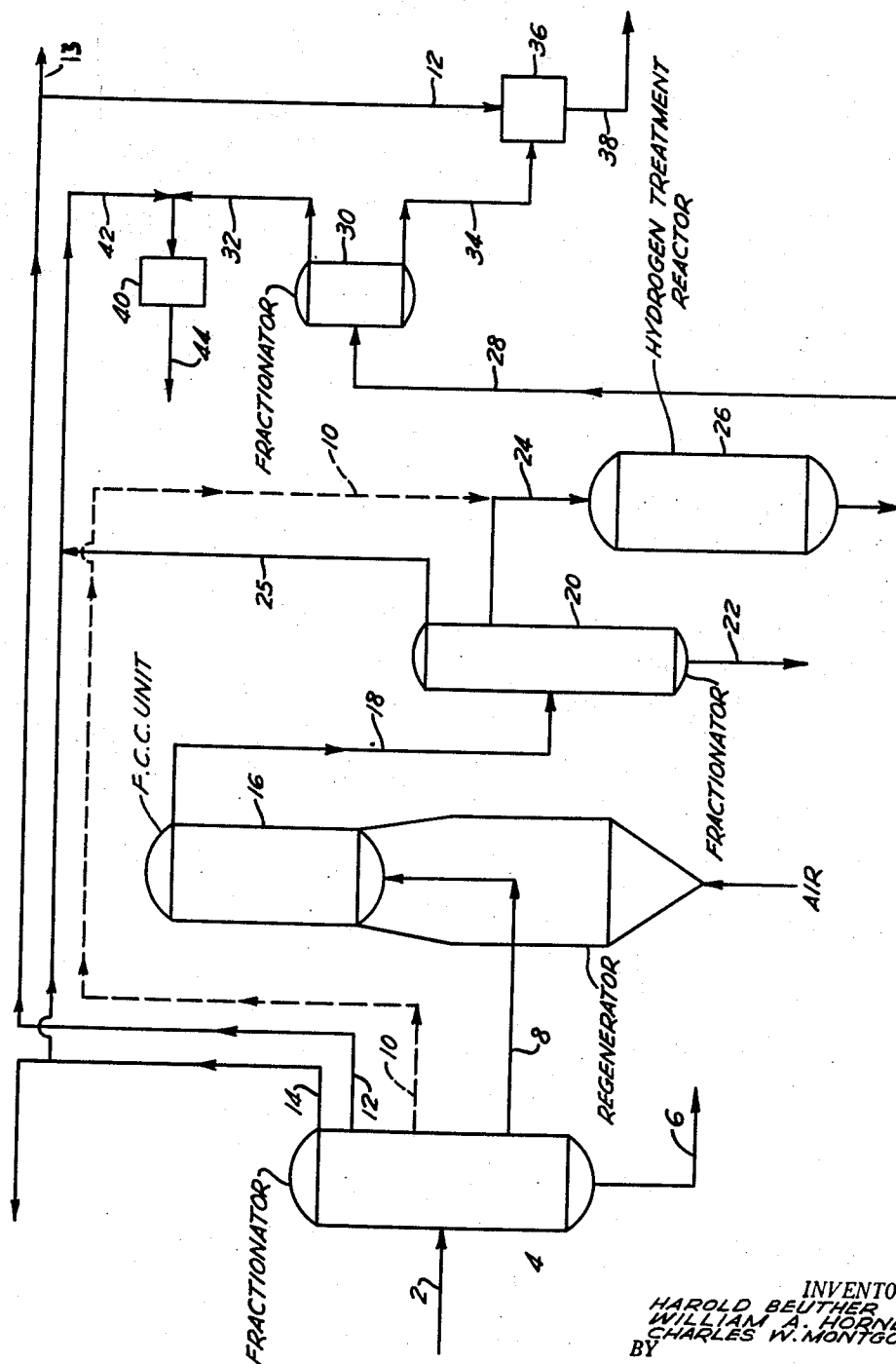


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HYDROGEN TREATMENT OF HYDROCARBONS

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HYDROGEN TREATMENT OF HYDROCARBONS

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This invention relates to improved procedure for hydrogen treatment of hydrocarbons and especially for simultaneous improvement in octane number of certain hydrocarbon fractions and improvement of stability, color and/or sulfur content of other fractions.

It is well known to subject hydrocarbons of various types to treatment with hydrogen under elevated temperature and pressure in the presence of a hydrogenation catalyst to effect an improvement in sulfur content, stability, etc. This procedure when applied to gasolines of various types has been recognized to result in decrease in octane number although the sulfur content may be greatly reduced. When applied to fuel oils, it has been recognized to improve the color and stability and also to result in decreased sulfur content.

This invention has for its object to provide improved procedure for hydrogen treatment of fuel oil and heavy catalytically cracked gasoline. Another object is to provide improved procedure for hydrosulfurizing a mixture of fuel oil and heavy catalytically cracked gasoline whereby the sulfur content of both components of the mixture is reduced and whereby the octane number of the heavy catalytically cracked gasoline is improved. A still further object is to provide improved procedure for hydrogen treatment and subsequent utilization of a mixture of fuel oil, heavy catalytically cracked gasoline and light gasoline. Other objects will appear hereinafter.

These and other objects are accomplished by our invention which includes subjecting a mixture of a distillate fuel oil and a catalytically cracked gasoline boiling predominantly in the range between about 310° and about 430° F. to treatment with hydrogen in the presence of a hydrogenation catalyst at a temperature between about 650° and 850° F. at a pressure between about 300 and 1000 p.s.i.g. at a space velocity between about 1 and 18 liquid volumes of the mixed charge stock per hour per volume of hydrogenation catalyst and fractionating the resultant hydrocarbon mixture to separate improved fuel oil and gasoline having an improved octane number. It has been found that both components of the mixture are hydrosulfurized if they contain sulfur compounds. Also nitrogen is removed if present in either or both components. The stability and color of the fuel oil is improved and the octane number of the gasoline is improved. However, it has also been found that subjecting this same gasoline to the same hydrogen treatment alone results in a gasoline having a lower octane number than that of the initial gasoline.

Our invention also includes hydrogen treatment under

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the above specified conditions of a mixture of the fuel oil, catalytically cracked gasoline boiling predominantly between 310° and 430° F. and a third component which is a gasoline boiling below about 310° F. and being either a straight run gasoline, a thermally cracked gasoline, any other naptha which needs pretreatment before being sent to a reformer, or a mixture of the same. After hydrogen treatment the product is fractionated as before to separate the fuel oil, the heavy gasoline and the gasoline boiling below about 310° F. This lower boiling gasoline fraction is then subjected to reforming in the presence of hydrogen and a dehydrogenation catalyst.

In the following examples and description we have set forth several of the preferred embodiments of our invention, but it is to be understood that they are given by way of illustration and not in limitation thereof.

The fuel oil employed in our invention may be derived from any crude petroleum, by which term we include oils derived from shale, etc. Also it may be obtained from any catalytic cracking or thermal cracking of a heavy oil fraction of petroleum. In other words the fuel oil may be a straight run, thermally cracked or catalytically cracked fuel oil. It should distill predominantly between about 425° and 650° F. Fuel oils usually distill over a rather broad range. However, we may use either narrow boiling or full range fuel oils. Also fuel oils frequently contain small amounts of components boiling below 425° F. (to give lower flash points) or boiling above 650° F. and such fuel oils may be used. We prefer to employ a full range type fuel oil and also prefer to employ a light fuel oil such as #2 fuel oil distillate.

The high boiling catalytically cracked gasoline may be obtained by any catalytic cracking of a heavy fraction of petroleum. Thus a fluid catalytically cracked fraction may be employed. The product obtained by moving bed catalytic cracking using a pelleted catalyst may also be employed, or a product obtained by fixed bed catalytic cracking may be the source of the catalytically cracked heavy gasoline. This gasoline should preferably have an end point below about 430° F.; an initial boiling point of about 310° F. is ordinarily preferred. These gasoline distillates generally contain a larger amount of sulfur and also cause larger deposits of carbon and like materials in internal combustion engines than the lighter boiling catalytically cracked distillates. Therefore, these high boiling catalytically cracked gasolines are products of lower economic value. It has been found that by subjecting these distillates to the process of our invention they are not only desulfurized but converted into products having a higher octane number and less tendency to form carbon deposits in use. This high boiling gasoline is normally removed as a separate fraction in ordinary refinery operations; however, part of it may be left in the fuel oil fraction. It will be advantageous for this invention to separate a single fraction including both the heavy catalytically cracked gasoline and the fuel oil and subject this mixture to the process of our invention.

The fuel oil charge stocks discussed above frequently will contain sulfur and/or nitrogen compounds. In such event the procedure of our invention has the advantage that these deleterious compounds are, to a large extent,

removed. Therefore, the invention not only has the advantage of improving the stability and color of the fuel oil but also of substantially reducing the sulfur and/or nitrogen content.

As indicated above, we may also include in the mixture being treated a straight run, thermally cracked, and/or any other gasoline needing pretreatment before going to a reformer and having a lower boiling point, i.e. below about 310° F. These gasolines may contain sulfur or nitrogen compounds which are advantageously removed before reforming. Also the thermally cracked gasoline contains olefins which are not suitable for reforming. However, by passage through the hydrogen treating operation, the sulfur and nitrogen compounds are removed or reduced in amount and the olefins are hydrogenated so that a high grade reforming charge stock is obtained. The heavy catalytically cracked gasoline is not a suitable reforming charge stock either before or after the hydrogen treatment. However, by utilizing the particular fractions described, simple fractionation after the hydrogen treatment will enable separation of the heavy catalytically cracked gasoline from the lower boiling gasoline. Therefore these reforming charge stocks may be easily separated and partly or entirely utilized in a hydro-reforming operation. Mixtures containing about 5 to about 50 percent gasoline and about 95 to about 50 percent fuel oil may be treated in accordance with our invention.

The catalyst employed in the first stage of our improved process may be any type of hydrogenation catalyst. For instance, sulfide or oxide catalysts such as sulfides or oxides of tungsten, molybdenum, chromium, vanadium, etc. may be employed. A preferred type of catalyst is a mixture or chemical combination of an oxide or sulfide of an iron group metal with the oxide or sulfide of a metal of Group VI, left-hand column of the periodic table, such as a mixture of the oxide or sulfide of nickel or cobalt with the oxide or sulfide of tungsten or molybdenum. We prefer to use a catalyst comprising a mixture or chemical combination of an oxide or sulfide of cobalt with molybdenum oxide or sulfide. It is preferred to employ the catalyst on a porous carrier such as activated alumina, alumina stabilized with a small amount of silica or a silica-alumina cracking catalyst type carrier. It is preferred to employ a carrier which contains only a small amount of silica since the objective is to avoid substantial cracking of the fuel oil or the gasoline or naphtha. If a carrier containing a large amount of silica, such as a silica-alumina cracking catalyst, is used, it is preferred that the cracking activity be reduced by steam treatment. The hydrogenating component usually will be about 2 to 20 percent and preferably about 5 to 15 percent of the catalyst.

Temperatures below 650° F. give an insufficient rate of desulfurization and hydrogenation whereas temperatures above 850° F. result in a fuel oil having poorer characteristics and in thermal decomposition of both the fuel oil and naphtha. A temperature of 675° to 750° F. is preferred. The use of pressures below 300 pounds gives insufficient rates of desulfurization or incomplete desulfurization within reasonable reaction times and also shorter catalyst life due to less hydrogenation of polymers on the catalyst. Pressures above 1000 p.s.i.g. may be employed, but it is a distinct advantage of the present invention that moderate pressures below about 1000 pounds can be used to obtain rapid desulfurization and hydrogenation. By using these moderate pressures it is possible to avoid the utilization of expensive high pressure equipment and excessive consumption of hydrogen. Also the reforming characteristics of the gasoline are improved. A pressure of about 500 to 700 p.s.i.g. is preferred.

The space velocity employed will depend upon the character of the charge stock such as the amount of olefins and sulfur present in the charge stocks and the

degree of desulfurization desired. As the space velocity increases, desulfurization decreases. The same is largely true with respect to the saturation of the olefins present in the thermally cracked gasoline or naphtha. A space velocity between about 1 and 18 may be used. A space velocity of between about 2 and 8 will be found to be most satisfactory for mixtures commonly treated.

The throughput between regenerations does not affect desulfurization or hydrogenation to a marked extent and the throughput used will depend upon the nature of the charge stocks, especially the boiling point of the distillate fuel oil. Also the temperature of treatment has an important effect on throughput. The limiting factor is the amount of carbon deposited upon the catalyst, and of course the higher the boiling point of the fuel oil and the higher the temperature, the greater will be the amount of carbon deposited and therefore the more frequent the regeneration. When treating a mixture of light fuel oil having an end point of about 650° F. and catalytically cracked heavy naphtha with a cobalt molybdate catalyst on an alumina carrier, a throughput of 3400 volumes or more of the mixed charge stock per volume of catalyst has been obtained before regeneration was required. A throughput of about 8 to as much as 40,000 or more will generally be satisfactory. The regeneration is accomplished in conventional fashion by subjecting the catalyst to combustion with an oxygen-containing gas such as air to burn off the deposited carbon. When a molybdenum-containing catalyst is used, it is best to avoid regeneration temperatures that are above about 1100° F.

The hydrogen employed in our process may contain considerable amounts of impurities such as gaseous hydrocarbons. It is preferred to employ as make-up hydrogen the off-gas from a hydro-reforming operation. Such a gas contains about 65 to 85 percent hydrogen, and such a hydrogen mixture may be employed although purer or pure hydrogen may be utilized. The hydrogen is preferably recycled at a rate of between about 1000 and 4000 standard cubic feet per barrel. A higher or somewhat lower hydrogen recycle rate may be employed without materially affecting the desulfurization and hydrogenation. However, recycling is expensive and the increased benefits are ordinarily not sufficient to justify recycle rates above 4000. The recycled hydrogen should have a purity such that when mixed with make-up hydrogen, the mixture will be above about 50 percent hydrogen.

After subjecting the mixture of fuel oil and gasoline to the above described treatment, the reaction mixture is separated from the hydrogen and is fractionated to separate the fuel oil from the catalytically cracked gasoline. This can be accomplished by conventional fractionation. The gasoline is preferably blended with lower boiling gasoline to obtain a product having the desired vapor pressure and octane number. If the fuel oil is to be used for certain purposes, such as furnace oil or diesel fuel, it is desirable to blend it with a small amount of straight run or other low octane naphtha in order to obtain the desired flash point.

When a mixture of fuel oil, catalytically cracked gasoline plus lower boiling gasoline is treated, the products also may be separated by simple fractionation. Thus the lower boiling gasoline after treatment will distill at a temperature below about 310° F. while the catalytically cracked gasoline will be separated as a separate fraction between about 310° and 430° F. while the fuel oil will distill at a higher temperature.

The lower boiling gasoline product then may be subjected to a reforming operation in the presence of hydrogen. Hydro-reforming is well known in the art, and the process per se forms no part of this invention. Reference is made to "Progress for Petroleum Technology," August 7, 1951, pages 39 to 76 (A.C.S. edition of 1951) for a more complete description of several conventional reforming processes which may be employed for im-

proving the octane number of the hydrogen treated light gasoline or naphtha. It is known that in certain types of hydro-reforming operations, it is desirable to utilize a charge stock which is free of sulfur and nitrogen. The process of our invention provides an admirable charge stock for this purpose in that the light gasoline is substantially free of sulfur and nitrogen. Furthermore, it is desirable that the charge stock for a hydro-reforming process should be relatively free of aromatics and olefins. A thermally cracked naphtha contains only small amounts of aromatics, and the olefins are largely saturated in the first step of our invention.

In the accompanying drawing we have illustrated diagrammatically apparatus in which one embodiment of our invention may be carried out. Referring to the drawing, numeral 2 designates a conduit through which a crude is introduced into fractionator 4 where a heavy bottoms fraction is removed through conduit 6, a gas oil fraction through conduit 8, a furnace oil fraction through conduit 10, a heavy gasoline fraction through conduit 12 and a light gasoline fraction through conduit 14. The light gasoline fraction removed through conduit 14 may be subjected to reforming in the presence of hydrogen or used for blending as described below. The heavy gasoline removed through conduit 12 may be subjected to reforming in the presence of hydrogen in which case it would be removed through conduit 13, or it may be used for blending as described below.

The gas oil fraction flows through conduit 8 into fluid catalytic cracking unit 16 and the products therefrom flow through conduit 18 into fractionator 20. Here heavy gas oil is separated as a bottoms fraction through conduit 22 while furnace oil and heavy gasoline boiling between 310° and 430° F. are removed through conduit 24 and light gasoline through conduit 25. The furnace oil plus heavy gasoline may be mixed with straight run furnace oil removed in crude fractionator 4 through conduit 10. This mixture of furnace oil and heavy gasoline is then subjected to hydrogen treatment in reactor 26. The treated products flow through conduit 28 into fractionator 30 where heavy gasoline boiling between 310° and 430° F. is separated as overhead through conduit 32 while a furnace oil is separated as bottoms through conduit 34. This furnace oil may be blended in blender 36 with straight run heavy gasoline removed from crude fractionator 4 through conduit 12 and the furnace oil blend is removed through conduit 38. The gasoline fraction removed from fractionator 30 through conduit 32 is blended with straight run gasoline derived from fractionator 4 and cracked gasoline derived from fractionator 20 and introduced into blender 40 by way of conduits 14 and 25 respectively. The blended gasoline is removed through conduit 44.

This apparatus may also be utilized to carry out the above described modification of our invention by introducing the lower boiling straight run gasoline removed through conduit 14 into conduit 24 where the straight run gasoline would become mixed with the the furnace oil and heavy gasoline charge to the hydrogen treating unit. In this modification the subsequent fractionation in fractionator 30 would be modified to separate the light gasoline as a separate fraction which would then be sent to a hydro-reforming operation.

EXAMPLE

A gas oil derived from a mixed West Texas crude was subjected to fluid catalytic cracking and a fraction constituting 15.1 percent of heavy naphtha 365°-430° F. and 84.9 percent of fuel oil 430°-650° F. was separated. This mixture was subjected to hydrogen treatment by contacting with about 2000 s.c.f./bbl. hydrogen at a temperature of 750° F., at a pressure of 500 p.s.i.g., in the presence of a catalyst composed of cobalt and molybdenum oxides supported on activated alumina. The space velocity was 8 vol./vol./hr. The results are given

in column 2 of Table I. The same heavy naphtha fraction (365°-430° F.) was also subjected alone to the same hydrogen treatment. The results are given in column 3 of Table I. Column 1 of Table I gives the characteristics of the naphtha fraction (365°-430° F.) prior to treatment.

Table I

	Charge naphtha (Col. 1)	Naphtha from treated blend (Col. 2)	Naphtha treated alone (Col. 3)
15 Gravity, ° API.....	32.7	32.1	32.4
Sulfur, L, percent.....	0.385	0.063	0.127
Olefins, percent by vol., ASTM D875.....	19.8	12.1	2.5
Bromine number, ASTM D1159.....	24.8	12.6	4.8
Aromatic content, percent by vol., ASTM D875.....	62.9	64.8	63.1
Knock ratings, ASTM D857:			
Micro motor method, octane num- ber—			
Clear.....	78.8	81.0	75.8
+3.0 cc. TEL, ASTM D958.....	84.1	86.0	80.4
Micro research method, octane number—			
Clear.....	90.0	90.5	86.5
+3.0 cc. TEL.....	95.2	97.3	92.2
25 Distillation, gasoline, ASTM D86:			
Overpoint, ° F.....	366	368	345
Endpoint, ° F.....	432	432	507
10% at ° F.....	380	384	382
30%.....	389	392	391
50%.....	395	396	400
70%.....	402	404	409
90%.....	413	414	424
30 Recovery, percent.....	99.1	99.0	97.2
Residue, percent.....	0.9	1.0	2.4

We claim:

1. The process for hydrogen treatment of a straight run fuel oil distillate and a catalytically cracked gasoline boiling between about 310° and about 430° F. and for simultaneously improving the octane number of the catalytically cracked gasoline which comprises contacting a mixture of hydrogen, said fuel oil distillate and said catalytically cracked gasoline boiling between about 310° and about 430° F. with a cobalt-molybdenum oxide catalyst composited with an activated alumina carrier at a temperature between about 675° F. and about 750° F., at a pressure between about 500 and about 700 p.s.i.g., at a space velocity between about 2 and about 8 liquid volumes of mixed charge stock per hour per volume of hydrogenation catalyst, fractionating the resultant hydrocarbon mixture to separate an improved fuel oil fraction and a gasoline fraction having a higher octane number and boiling between about 310° and 430° F. and blending this last mentioned gasoline fraction with a lower boiling point gasoline to obtain a finished gasoline product.

2. The process which comprises in combination contacting a mixture of hydrogen and the following components: (1) catalytically cracked gasoline boiling predominantly in the range between about 310° and about 430° F.; (2) a straight run fuel oil distillate boiling predominantly in the range between about 430° and about 650° F.; (3) a member of the group consisting of straight run gasoline, thermally cracked gasoline and other gasolines requiring pretreatment prior to reforming and boiling predominantly below about 310° F.; with a hydrogenation catalyst composited with a porous carrier at a temperature between about 650° F. and about 850° F., at a pressure between about 300 and about 1000 p.s.i.g., at a space velocity between about 1 and about 18 liquid volumes of mixed charge stock per hour per volume of hydrogenation catalyst, said reaction conditions being selected so that substantially no thermal decomposition takes place during said contacting, subjecting the resulting hydrocarbon mixture to fractionation to separate a fuel oil fraction boiling predominantly between 430° F. and 650° F., a heavy gasoline fraction boiling predominantly in the range between 310° and 430° F. and

having a higher octane number than the corresponding material in the charge stock and a member of the group consisting of straight run, thermally cracked or other gasoline boiling below about 310° F., subjecting at least part of this last mentioned gasoline to a catalytic reforming process in the presence of hydrogen at elevated temperature and pressure and blending the gasoline fraction boiling predominantly in the range between 310°

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and 430° F. with a lower boiling gasoline to obtain a finished gasoline product.

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