

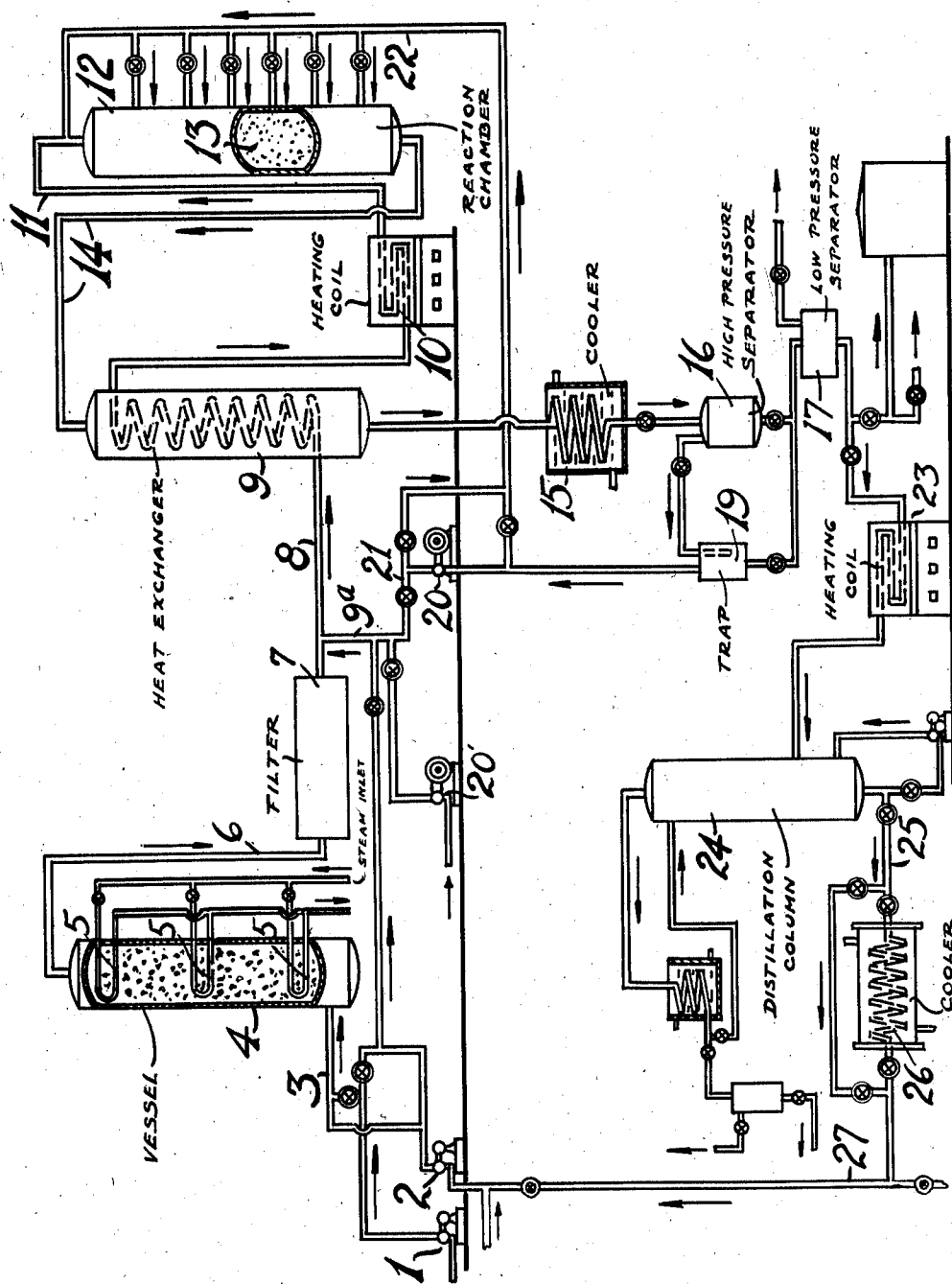
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HYDROGENATION PROCESS

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HYDROGENATION PROCESS

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This invention relates to the treatment of vaporized carbonaceous materials with hydrogenating gases in the presence of catalysts containing sulfur, and is directed particularly to methods for regulating the activity of such catalysts.

It has already been proposed to carry out the hydrogenation of carbonaceous materials with catalysts which are immune to sulfur poisoning and which are in fact rendered more active when sulfur is present, particularly when the sulfur is combined chemically with the catalyst. The use of such catalysts in the hydrogenation of carbonaceous materials is described in U. S. Patents 1,890,434 and 2,115,336 to Krauch and Pier and 2,123,623 to Cecil L. Brown.

It has also been proposed to activate such catalysts and to regulate their activity during use by introducing sulfur into the hydrogenation zone during operation. Elemental sulfur is preferred for this use on account of its cheapness, ease of handling and safety. However, it has been observed that in the treatment of carbonaceous materials in the vapor phase, such as the treatment of distillate oil fractions under conditions at which they are substantially completely vaporized, considerable difficulty has been experienced due to the plugging up of heat exchanger and preheater tubes and in the building up of pressure drop across the reaction zones in continuous operation.

An improved process has now been devised whereby these objections to the use of elemental sulfur are avoided. A heavy liquid carbonaceous material, which is vaporized to only a slight extent, if at all, in the preheaters and the hydrogenation reaction zone, is supplied in a minor proportion of the total charge of carbonaceous material. The heavy oil is preferably such that at least the major portion of it is unvaporized in the preheaters and the inlet portion of the reaction zone, and it may be so involatile and refractory that at least a substantial portion of it remains in liquid phase even to the exit from the reaction zone. It is offered in explanation that this heavier, relatively involatile liquid fraction maintains a small amount of a continuous liquid phase which serves as a solvent for the elemental sulfur being supplied to the reaction zone and thereby prevents its deposition and also aids in its uniform distribution over the catalyst.

The drawing is a diagrammatic illustration in partial sectional elevation of an apparatus suitable for carrying out one embodiment of this invention, and indicates the flow of materials.

A readily vaporizable oil fraction, preferably a

petroleum distillate oil boiling within the range of about 200° to 500° F. is supplied as the major portion of the charge stock by pump 1. A heavier oil fraction, preferably boiling substantially completely above 500° F., is supplied by pump 2. A portion of either or both of these oils is passed through line 3 into vessel 4 which is filled with lumps of sulfur and which is provided with suitable heating means, such as the steam coils 5. The heated oil solution of sulfur is then passed by line 6 through filter 7 and by line 8 into heat exchanger 9, being mixed either in this exchanger or just prior to entry thereto with the remainder of the oil charge and with hydrogenating gases supplied by line 10. Lines 6 and 8 and filter 7 are suitably heated or lagged in order to avoid precipitation of sulfur from the hot oil solution.

The mixture of charge stocks and hydrogen passes from the heat exchanger 9 through a heating coil 10, preferably a direct fired coil, in which they are heated to a temperature approximating or somewhat below the desired reaction temperature. The heated charge materials are then passed by line 11 into a reaction chamber 12 which is preferably designed to provide an elongated substantially vertical reaction zone into which the charge materials are supplied at or near the top, the reaction vessel being suitably heated or lagged to prevent loss of heat should this be desired, and being constructed to withstand the pressure and corrosive effects of the reagents and catalytic materials used. Vessel 12 also contains the catalyst, which is preferably provided in the form of pills, tablets or lumps which are either packed directly into the reaction vessel or are disposed therein upon suitable trays or baffles. The treated materials leave the reaction vessel by line 14, pass through heat exchanger 9 and cooler 15 into a high pressure separator 16, from which the liquid fraction is withdrawn to low pressure separator 17 and liquid products are then passed by line 18 to suitable storage or distillation equipment. The gases leaving separator 16 may be passed through trap 19 and returned to the reaction zone as recycle gas by compressor 20 and line 21. The temperatures in the reaction zone may also be controlled by supplying a cooling gas to any desired point therein from the manifold 22. This cooling gas may be the recycle gas or an inert gas.

The total liquid products in line 18 may be passed through distillation equipment, such as the heater 23 and distillation column 24, and the heavy liquid fraction withdrawn as bottoms in

line 25 may be returned with or without cooling in cooler 26 to the feed pump 2 by line 27. This recycling of the heavy oil fraction is preferred as in many types of hydrogenation operations the heavy recycle oil becomes saturated and does not thereafter require as much hydrogen as the fresh feed.

Numerous modifications in the above illustrated process will be readily apparent. The amount of sulfur supplied with the charge stock is regulated both by the temperature maintained in vessel 4 and the quantity of oil passed there-through. This may represent the total charge stock or any desired proportion of the light and the heavy stocks. While the process is preferably conducted in a continuous manner, and indeed the reaction chamber 12 is usually operated continuously, it is not necessary to supply either the sulfur or the heavy oil continuously in such a process. Sulfur may be supplied as desired in order to regulate the activity of the catalyst 13. The heavy oil is supplied throughout the time that sulfur is being supplied and the heavy oil charge is preferably continued for a sufficient time after the completion of the period of sulfur supply in order to prevent any deposition of sulfur in the preheaters. The sulfur used in this invention may be wholly or partly replaced with elemental selenium or tellurium, or with a mixture of these materials.

While the materials charged are preferably passed downwardly over the catalyst in the reaction zone in order to prevent accumulation of liquid therein, the materials may be passed horizontally and even upwardly through the catalyst bed in the event that such accumulating liquid is not objectionable, as in the relatively low temperature hydrofining treatments in which oils are treated with hydrogen at temperatures at which no substantial cracking occurs.

The process of this invention is applicable to the treatment of volatile and even normally gaseous carbonaceous materials in the presence of catalysts whose activity is enhanced or prolonged by the presence of sulfur or hydrogen sulfide with hydrogenating gases over a wide range of temperatures and pressures. Such catalysts include the compounds of metals of group 6 of the periodic system, particularly the oxides and sulfides. The expression "treatment with hydrogenating gases" is intended to comprise processes conducted with either a net consumption or a net production of hydrogen. These processes include hydrogenation treatments involving partial or complete saturation of unsaturated carbonaceous materials with hydrogen, for example, the conversion of aromatic hydrocarbons into hydroaromatic hydrocarbons. Such processes also include the destructive hydrogenation of carbonaceous materials with hydrogenating gases under high pressures, preferably above about 20 atmospheres, for conversion into relatively lower boiling products; also hydrofining treatments for the removal of non-hydrocarbon impurities such as sulfur, oxygen or nitrogen compounds, from crude carbonaceous materials, for example, the refining of crude benzene or of crude motor fuels, illuminating oils, etc., by treatment with hydrogen; also, the conversion of oxygen- or sulfur-containing organic compounds to produce the corresponding hydrocarbons or hydrogenated hydrocarbons, for example the conversion of phenols or cresols into the corresponding aromatic hydrocarbons. Such processes also include isomerization and dehydrogenation treatments such

as the catalytic reforming treatments, and the hydrocyclization treatments of naphthas. Such catalytic reforming treatments comprise the conversion of hydrocarbons boiling in or slightly above the motor fuel range into hydrocarbons of higher octane number, suitable for motor fuel, conducted at temperatures between about 850° and 1000° F. and under moderate pressures, for example about 100 to 500 pounds per square inch, in the presence of catalysts of the type described above, particularly the oxides and sulfides, of metals of group 6 of the periodic system which may also be used in admixture with natural clays of the Attapulugus type or activated clays such as Super-filtrol or other materials containing substantial proportions of alumina and silica. In operation under these conditions the catalyst usually becomes coated with contaminants, chiefly carbonaceous deposits which gradually destroy the activity of the catalyst for reforming purposes after relatively short periods of operation. The activity of the catalyst is regenerated by burning off the carbonaceous deposits by means of inert gases containing relatively small amounts of inert gases containing relatively small amounts of oxygen, usually not more than a few percent. The catalytic reforming process as carried out commercially therefore consists of alternate periods of reforming and regeneration. Advantages of the present process are that gasoline of higher octane number is obtained with reforming periods of equal length, and that gasoline of equal octane number is obtained during longer reforming periods, as compared to operation without the addition of sulfur. An example of suitable conditions of catalytic reforming in the presence of hydrogen according to the present invention is as follows:

A heavy naphtha, admixed with about 10% of a relatively heavier petroleum oil boiling above about 600° F. having elemental sulfur dissolved therein in a proportion of about ½% of the total charge, is introduced into a reaction vessel at a temperature of about 950° F. under a pressure of about 200 to 400 pounds per square inch at a rate of about 1 to 2 volumes of naphtha per volume of reaction space per hour. At the start of the process, fresh hydrogen is introduced into the reactor so that the quantity of hydrogen is about 70 mol percent. As the reaction proceeds, the gases evolved in the process, which contain substantial quantities of hydrogen, are continuously recycled at a rate of about 2000 to 3000 cubic feet per barrel of naphtha. The reaction vessel is packed with lumps of a sulfactive catalytic material such as a mixture of aluminum oxide and chromium oxide. At the beginning of the process there is a net production of hydrogen of about 100 to 400 cubic feet per barrel of naphtha. As the reaction proceeds, the net production of hydrogen decreases gradually until finally after 16 to 24 hours or more, the net production of hydrogen approaches zero and if the process is continued further, there will be a net consumption of hydrogen. If the reforming cycle is continued, it would be necessary to add fresh hydrogen to make up for this consumption. It is preferable, however, to discontinue the reforming cycle at this point and to regenerate the catalyst even though its activity may not have been substantially destroyed. The regeneration may be accomplished by passing inert gases or steam containing 4 to 10% of oxygen through the catalyst mass at a rate of several thousand volumes per volume of reaction

space per hour. After the regeneration, another reforming cycle may be carried out followed by another regeneration cycle and so on. It should be understood that this description of the process is merely given for illustrative purposes.

The "treatment with hydrogenating gases" according to the process of this invention also includes isomerization and dehydrogenation treatments conducted in the presence of hydrogen, and various combinations of the treatments described above.

The process of this invention is particularly suitable for the conversion of relatively low boiling petroleum distillation fractions into motor fuels high in naphthenic constituents and of high knock rating. Suitable conditions for carrying out this modification of the present invention are described in the following example:

The characteristics of a suitable light petroleum oil charging stock and of a heavy petroleum oil suitable for use therewith in accordance with this process are presented in the following table:

	Light oil	Heavy oil
A. P. I.	49.3	37.1
Color	+8	-----
Aniline point, °F.	120.3	192
Lamp sulfur, percent.	0.036	0.19
Gum:		
Copper bowl..... milligrams ..	2	-----
Glass bowl..... do.....	1	-----
I. B. P., °F.	244	590
5% off at., °F.	258	600
10% off at., °F.	260	605
20% off at., °F.	264	610
30% off at., °F.	268	615
40% off at., °F.	271	618
50% off at., °F.	274	620
60% off at., °F.	277	625
70% off at., °F.	281	632
80% off at., °F.	286	640
90% off at., °F.	294	650
95% off at., °F.	304	-----
E. P., °F.	338	700+

The hydrocyclization of this light oil is preferably conducted by passing the oil with about 2,000 to 15,000 cubic feet of hydrogen per barrel of charge through a reaction zone maintained at a temperature between about 600 and 950° F. and preferably between about 650 and 850° F. and at a pressure of about 20 to 300 atmospheres, or at even higher pressures. The reaction chamber is packed with lumps of a hydrogenation catalyst, such as the oxygen and sulfur compounds of metals of group 6 of the periodic table, which require the presence of sulfur in order to maintain optimum activity, particularly the polysulfides (disulfides and trisulfides) of tungsten and of molybdenum, such as the catalysts described in U. S. Patent 2,123,623. With such catalysts the oil feed rate may be from one to three volumes of oil charge per volume of catalyst-filled reaction space per hour. The concentration of heavy oil may be in the range of 10 to 50% on the basis of the total charge of oil to the hydrogenation unit in this process, and is preferably below about 25%. The quantity of sulfur added to the total feed is adjusted in relation to the extent of use and the activity of the catalyst. The addition of about 0.5 to 2% or more of elemental sulfur by solution in the feed stock will generally be found sufficient. This sulfur is preferably dissolved in the heavy oil, because of the greater solubility of sulfur in such oils than in the lighter oils used as a major portion of the charge stock.

Under such conditions of operation about 40 to 70% of the light charge stock is converted per pass to products boiling in the motor fuel

range, and the motor fuel distillate fraction of the products (boiling below about 400° F.) has a knock rating generally above 70 and often to 75 or even higher. It is also characterized by low acid heat, below 3° F., low gum and sulfur content and is highly suitable for use in aviation fuels. The term "acid heat" wherever used in the specification and claims shall be understood to mean acid heat of gasoline as determined in accordance with A. S. T. M. test D-481-39. The acid heat of gasoline is an indication of the content of unsaturated and aromatic hydrocarbons and has a high value for a gasoline rich in these types of hydrocarbons and a low value for a gasoline relatively free from such types of hydrocarbons.

This invention is not to be limited to any examples or explanations presented herein, all such being intended solely for purpose of illustration, as it is intended to claim all novelty in this invention as broadly as the prior art permits.

I claim:

1. In a process for the treatment of vaporizable carbonaceous materials with hydrogenating gases, in which said carbonaceous material is passed in vapor phase with hydrogen through a reaction zone packed with a solid sulfactive catalyst, an improved method of operation to regulate the activity of said catalyst comprising preparing a solution of elemental sulfur in a relatively small amount of an oil which is not substantially vaporized in said reaction zone and passing said sulfur solution into said reaction zone.

2. In a process for the treatment of distillate oil fractions with hydrogenating gases in which said oil fraction is passed with hydrogen through a preheating zone in which it is substantially completely vaporized, and the mixture of vapor and hydrogen is then passed through a reaction zone packed with solid sulfactive catalyst, an improved method of operation to regulate the activity of said catalyst comprising preparing a solution of elemental sulfur in a relatively small amount of a heavier oil which is not substantially vaporized in said preheating zone and in the inlet portion of said reaction zone and passing said sulfur solution into said reaction zone.

3. Process according to claim 2 in which said sulfur solution is passed through said preheating zone and into said reaction zone.

4. Process according to claim 2 in which said sulfur solution is mixed with said distillate oil fraction and the resulting mixture is passed with hydrogen through said preheating zone and into said reaction zone.

5. In a process for the treatment of distillate oil fractions with hydrogenating gases in which said oil fraction is passed with hydrogen through a preheating zone in which it is substantially completely vaporized, and the mixture of vapor and hydrogen is then passed through a reaction zone packed with solid sulfactive catalyst, an improved method of operation to regulate the activity of said catalyst comprising mixing said distillate oil fraction with a heavier oil which is not substantially vaporized in said preheating zone and in the inlet portion of said reaction zone, dissolving elemental sulfur in at least one of said oils, and passing the resulting mixed oil containing dissolved sulfur with hydrogen through said preheating zone and into said reaction zone.

6. Process according to claim 5 in which said

heavier oil is from 10 to 25% of the total oil charge.

7. Process according to claim 5 in which the amount of elemental sulfur dissolved is above about 0.5% by weight of the total charge.

8. Process according to claim 5 in which the amount of elemental sulfur dissolved is from about 0.5 to about 2% by weight of the total oil charge.

9. Process according to claim 5 in which said catalyst contains a compound of a metal of group 6 of the periodic table and sulfur.

10. Process according to claim 5 in which said catalyst contains a polysulfide of molybdenum.

11. In a process for the treatment of a distillate oil fraction boiling within the range of 200 to 500° F. with hydrogenating gases in which said oil fraction is passed with hydrogen through a preheating zone in which it is substantially completely vaporized and into a reaction zone maintained at a temperature of about 600 to 950° F., said zone being packed with a solid hydrogenation catalyst containing a sulfur compound of a metal of group 6 of the periodic table, whereby said distillate oil fraction is converted into a motor fuel of high knock rating and low acid heat, an improved method of operation to regulate the activity of said catalyst comprising preparing a solution of about 0.5 to about 2%

(based on the total oil charged) of elemental sulfur in about 10 to about 25% (based on the total oil charged) of a heavier oil which is not substantially vaporized in said preheating zone and in the inlet portion of said reaction zone and which boils substantially completely within the range of 500 to about 850° F., mixing the resulting sulfur solution with said distillate oil fraction and passing the resulting mixed oils with hydrogen through said preheating zone and into said reaction zone.

12. In a process for hydrogenating vaporizable carbonaceous materials in the vapor phase and in the presence of a solid sulfactive catalyst, the activity of which is increased by the addition of elemental sulfur to the carbonaceous material to be hydrogenated, the method of preventing the deposition of added elemental sulfur in the preheating apparatus and inlet lines to the reaction zone in which the vapor phase hydrogenation is carried out, which comprises introducing into the vaporizable material prior to its passage through the preheating and inlet lines to the reaction zone a relatively small quantity of a higher boiling hydrocarbon oil which remains substantially unvaporized under the conditions prevailing in the preheating and reaction zones.

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