

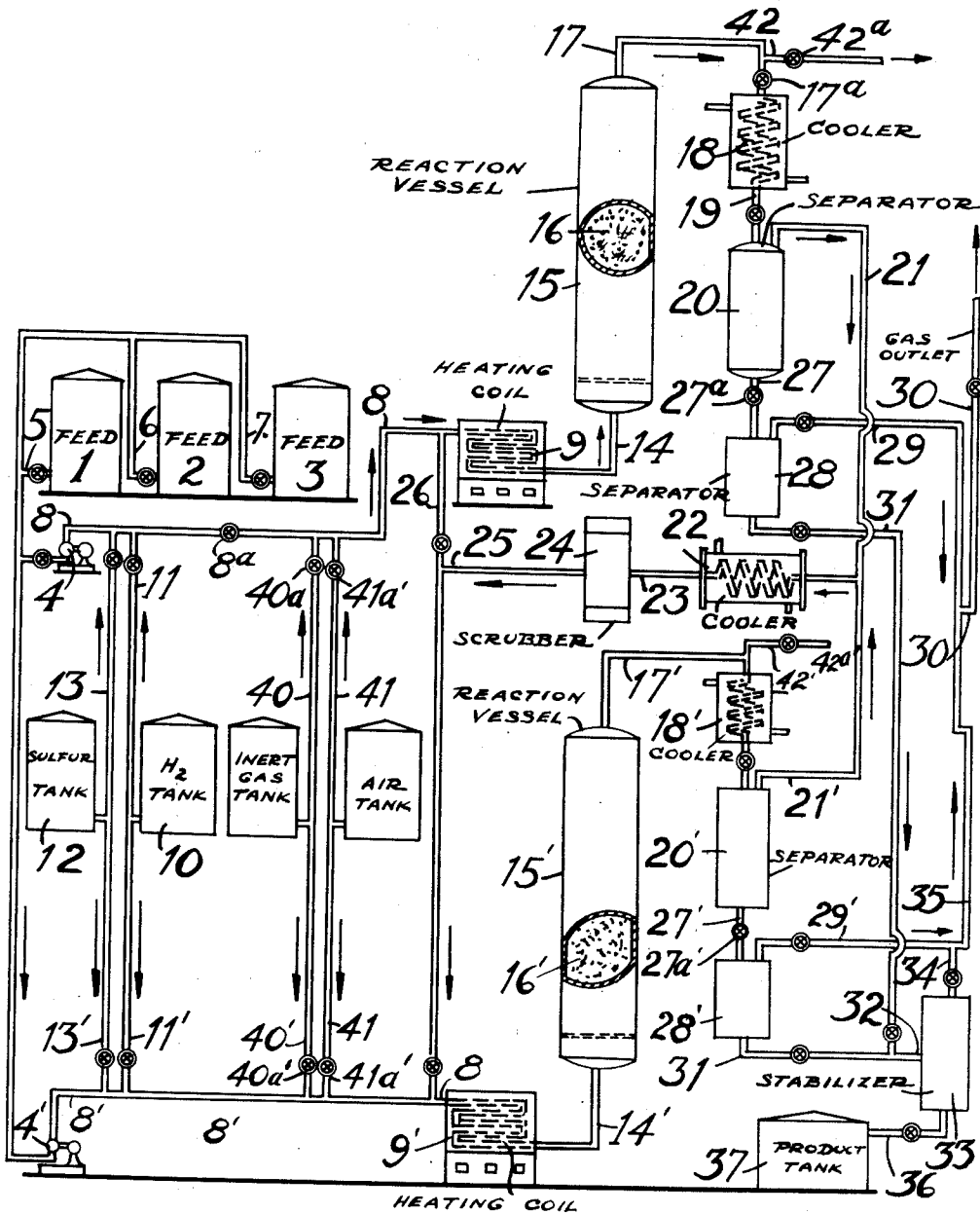
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CATALYTIC REFORMING OF NAPHTHAS

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CATALYTIC REFORMING OF NAPHTHAS

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This invention relates to certain improvements in the catalytic reforming of heavy naphthas.

The term "catalytic reforming" wherever used in the specification and claims shall be understood to mean any process of subjecting materials consisting essentially of hydrocarbons substantially boiling in the gasoline range to heat treatment at a temperature in excess of 500° F. and in the presence of catalysts to produce a dehydrogenated or otherwise chemically reconstructed product, for example, of anti-knock characteristics superior to those of the starting material, with or without an accompanying change of volatility and with or without an accompanying change in molecular weight. By the term "chemically reconstructed" is meant something more than the mere removal of impurities or ordinary finishing treatments. The term catalytic reforming shall be understood to include reactions such as dehydrogenation, aromatization or cyclization, desulfurization and isomerization, all or some of which may occur to a greater or lesser extent during the process.

One of the principal purposes of a catalytic reforming process is to convert hydrocarbons boiling in the motor fuel range into hydrocarbons suitable for motor fuels, aviation fuels and other purposes for which a gasoline of high octane number, high aromaticity, and increased stability may be desired. A number of processes for catalytic reforming has been proposed recently. In general, these processes consist in subjecting a heavy naphtha to a temperature between 850 and 1000° F. under substantially atmospheric or slightly elevated pressures and in the presence of catalysts such as natural clays of the Attapulugus type or activated clays such as Super Filtrol or other materials containing substantial proportions of alumina and silica. One of the chief difficulties with processes of this type is that after relatively short periods of operation, the catalyst becomes coated with contaminants, chiefly carbonaceous deposits, which gradually destroy the activity of the catalyst for reforming purposes. The activity of the catalyst can be regenerated by burning off the carbonaceous deposits by means of inert gases containing relatively small amounts of oxygen. The catalytic reforming process as carried out commercially therefore consists of alternate periods of reforming and regeneration. It can readily be seen that it is desirable to prolong the reforming period and to shorten the regeneration period.

More recently it has been found that by conducting the catalytic reforming process in the presence of hydrogen and under moderate pressures, for example between 100 and 500 pounds per square inch, the tendency for the deposition of contaminants on the catalyst is greatly re-

duced and hence the activity of the catalyst is preserved for a substantially longer period. The necessity for regeneration is therefore less frequent. It has also been found that catalytic reforming in the presence of hydrogen may be carried out under conditions such that there is no net consumption of hydrogen in the process. The gases evolved in the process may therefore be continuously recycled without having to add fresh hydrogen. In this way, the catalytic reforming process becomes much more economical from a commercial standpoint because the activity of the catalyst is preserved for longer periods and it is not necessary continuously to add fresh hydrogen. In addition to lengthening the period over which the catalyst maintains its activity, it is also observed that by conducting the catalytic reforming process in the presence of hydrogen, the yields and characteristics of the product obtained are noticeably better than those which would be obtained by conducting the process under conditions otherwise the same but in the absence of hydrogen.

Catalytic reforming in the presence of hydrogen is carried out essentially as follows: A heavy naphtha is introduced into a reaction vessel at a temperature of about 950° F. under pressure of about 200 to 400 pounds per square inch at a rate of about one to two 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 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 much longer, there will be a net consumption of hydrogen. If the reforming period is continued, it would be necessary to add fresh hydrogen to make up for this consumption. It is preferable, however, to discontinue the reforming period 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 period may be carried out fol-

lowed by another regeneration period and so on. It should be understood that this description of the process is merely given for illustrative purposes. The nature of the catalyst which may be used and the other operating conditions will be more fully discussed below.

It has now been found that the boiling range and distillation characteristics of the hydrocarbon oil subjected to catalytic reforming in the presence of hydrogen have an important effect on the net quantity of free hydrogen either produced or consumed during the process. For example, it is observed that hydrocarbon oils rich in low boiling fractions produce greater net quantities of hydrogen or show less net consumption of hydrogen than hydrocarbon oils poorer in low boiling fractions. Thus, if two naphthas A and B, having 86% off @ 302° F. and 41.5% off @ 302° F. respectively, are both subjected to catalytic reforming in the presence of hydrogen under substantially the same conditions, there will be a markedly greater net production of hydrogen from naphtha A than from naphtha B. Moreover, there will continue to be a net production of hydrogen from the treatment of naphtha A for a substantially longer period than from the treatment of naphtha B. The following data may illustrate the point more clearly:

Naphtha A is an East Texas light virgin naphtha, and naphtha B is a West Texas heavy virgin naphtha. The respective distillation characteristics are as follows:

	Naphtha A	Naphtha B
Initial boiling point, °F.....	111	248
Per cent at—		
140° F.....	3.0	
158° F.....	6.0	
167° F.....		
203° F.....		
212° F.....	28.0	
257° F.....	58.0	1.5
302° F.....	86.0	41.5
356° F.....		85.0
Final boiling point, °F.....	342	401

Each naphtha is subjected to catalytic reforming in the presence of hydrogen under the following approximate conditions:

Pressure, lbs./sq. in.....	400
Temperature, °F.....	950
Oil feed rate v./v./hr.....	1.0
Hydrogen cu. ft./bl. oil.....	1800-2000
Mol per cent hydrogen.....	70
Catalyst.....	Aluminum and chromium oxides

The net production of hydrogen during the operation from each naphtha is as follows (a minus sign indicates a net consumption):

Hours of run	Net H ₂ production cu. ft./bbl. of naphtha	
	Naphtha A	Naphtha B
6-12.....		244
12-36.....	330	
36-48.....		0
36-72.....	261	
48-120.....		-90
84-108.....	118	
108-120.....	-44	

It will be noted that in the case of naphtha A, the one rich in low boiling hydrocarbons, there is a net production of hydrogen until some time after the 108th hour of the run whereas in the case of naphtha B, the one poorer in low boiling hydrocarbons, there is no net production of hy-

drogen after the 36th hour of the run. Further, the quantity of net hydrogen produced in the early hours of the runs is much greater in the case of naphtha A than in the case of naphtha B.

Under the best operating conditions and in the presence of the most active catalysts known at the present time, it is found that hydrocarbon oils boiling above the range of naphthas, say above 400 or 450° F., will produce little, if any, net hydrogen even in the early hours of a run when the catalyst is presumably most active for reforming purposes. It should be understood, however, that if improved catalysts are found it is quite possible that hydrocarbon oils boiling in the range above heavy naphthas may be treated with a resultant net production of hydrogen. The important point is that the net production of hydrogen increases markedly as the proportion of lower boiling hydrocarbons in the feed stock increases, all other conditions being substantially the same.

As pointed out above, it is desirable from an economic standpoint to operate the process of catalytic reforming in the presence of hydrogen in such a manner that there will be no net consumption but rather a net production of free hydrogen. The present invention provides a new and convenient method of ensuring not only (1) that there will be a net production of hydrogen but also (2) that the length of time the catalyst can be used before the net production of hydrogen ceases will be as long as possible, under given conditions and with a given catalyst.

In accordance with the invention, the boiling range and the distillation characteristics of the feed stock are initially selected and thereafter adjusted so that there will be a sufficient proportion of low boiling hydrocarbons to give under the particular conditions of operation and catalyst age a net production of free hydrogen. A convenient index of the proportion of lower boiling hydrocarbons is the percent boiling off at a certain temperature which in the case of naphthas may be a temperature between say 250 and 310° F. Thus, by increasing the percent off @ 300° F. the feed stock will contain more lower boiling hydrocarbons and by decreasing the percent off @ 300° F. it will contain less lower boiling hydrocarbons, and as a result the net production of hydrogen can be expected to increase and decrease respectively. In general it may be said that the percent off @ 300° F. may vary between 35 to 40 as a minimum and 60 to 90 as a maximum. Between these limits a wide variation in net hydrogen production may be obtained.

It will be recalled that the net production of hydrogen tends to decrease as the reforming period continues, that is, at the beginning of the reforming period there may be a substantial net production of hydrogen, as much as 300-500 cubic feet of hydrogen per barrel of naphtha, whereas after 12 to 100 hours or more the net production of hydrogen may have dropped to almost nothing. According to one modification of the present invention, a feed stock containing a relatively small amount of low boiling hydrocarbons may be used during the early hours of the reforming cycle and then as the net production of hydrogen decreases as a result of the decreasing activity of the catalyst the proportion of the lower boiling hydrocarbons in the feed stock may be progressively increased whereby the net production of hydrogen is maintained.

According to another modification of the in-

vention, a feed stock may be separated by distillation into two fractions, one rich in the lower boiling hydrocarbons and the other rich in the higher boiling hydrocarbons. The two fractions may then be reformed simultaneously in two separate reaction vessels under conditions best adapted for the respective fractions, with a common recycle gas recovery system for the two reactors. In this way, there will be a substantial net production of hydrogen from the reactor in which the fraction containing the lower boiling hydrocarbons is treated, and there will be a relatively small net production of hydrogen or even a net consumption of hydrogen from the reactor in which the fraction containing the higher boiling hydrocarbons is treated. However, because of the fact that there is a common recycle gas recovery system an overall net production of hydrogen may be maintained even in the event that there is a net consumption of hydrogen in the reactor in which the higher boiling hydrocarbons are treated.

According to still another modification of the invention, a reforming period may be continued for 12 to 20 hours or more until the net production of hydrogen becomes very small and then instead of discontinuing the reforming period, a feed stock consisting primarily of relatively lower boiling hydrocarbons may be substituted with the result that the reforming cycle may be continued for another 2 to 5 hours before the lack of a net production of hydrogen makes it economically expedient to stop the reforming and regenerate the catalyst.

It will be understood that there are other modifications and adaptations of the present invention, for example, a sudden and unexplained drop in the net production of hydrogen during the reforming period may be compensated for by introduction of a substantial quantity of low boiling hydrocarbons into the reaction vessel, or the quantity of hydrogen produced in the reaction may be maintained substantially constant by regulating the ratio of low boiling to high boiling hydrocarbons in the feed stock.

The method of carrying out the process will be fully understood from the following description read with reference to the accompanying drawing which is a semi-diagrammatic view in sectional elevation of one type of apparatus which may be used.

Referring to the drawing, numerals 1, 2 and 3 designate supply tanks of feedstocks of different boiling ranges. Pump 4 draws feedstock from these tanks through lines 5, 6 and 7 respectively and forces it through line 8 into and through a heating means 9. Hydrogen or a gas rich in free hydrogen is supplied to line 8 from tank 10 through line 11. If sulfur or sulfur compounds are to be used to increase the activity of the catalyst, these may be supplied from tank 12 through line 13. The mixture of feedstock, hydrogen and sulfur compounds is brought to reaction temperature in heating means 9 and thence it flows through line 14 into reaction vessel 15 which contains a suitable catalyst 16. The catalyst may be disposed on trays or shelves spaced within the reaction vessel, or the entire reaction vessel may be filled with lumps of the catalytic material.

The products of reaction leave reaction vessel 15 through line 17 and flow first through a cooling means 18 and thence through line 19 into a high pressure separator 20 in which the liquid

and gaseous products are separated. The gaseous products which are rich in hydrogen are removed from separator 20 through line 21 and pass thence through a cooling means 22, line 23 and a scrubbing means 24 and finally are returned to the process through lines 25 and 26. The scrubbing means 24 is provided to remove normally gaseous hydrocarbons such as methane, ethane and propane from the recycle gases. These hydrocarbons are evolved during the process in addition to hydrogen, and if allowed to accumulate would tend to decrease the concentration of hydrogen in the recycle gases.

The liquid products are removed from separator 20 through line 27, pressure release valve 27a and thence discharge into low pressure separator 28.

Gases are removed from separator 28 through line 29 and passed thence through line 30 to a gas absorption system or otherwise disposed of.

Liquids are removed from separator 28 through line 31 and are introduced through line 32 into a stabilizer 33 in which the too volatile constituents of the product are removed. The gases from stabilizer 33 leave through line 34 and may be carried through lines 35 and 36 to the gas absorption system or otherwise disposed of.

The final product is removed from stabilizer 33 through line 36 and collected in storage tank 37.

When the catalyst in reaction vessel 15 is to be regenerated valves 8a in line 8 and 17a in line 17 are closed, and valves 40a in line 40, 41a in line 41, and 42a in line 42 are opened. A mixture of inert gas and regulated quantities of air or oxygen then flows through line 8 and heating coil 9 into the reaction vessel 15. The effluent gases leave the reactor through line 17 and are vented through line 42. It will be understood that the usual methods of heat exchange may be used to prevent undue heat losses. For example, the gases entering the reaction vessel may first be partially heated by heat exchange with the hot gases leaving the reaction vessel.

In the event it is desired to operate two separate reaction vessels with a common recycle gas recovery system the drawing illustrates how this may be done. In the drawing similar pieces of apparatus are designated by the same numbers, but the second unit is designated by numbers marked prime ('). For example, the reaction vessel of the second unit is 15', the heating coil is 9', the high pressure separator is 20', the low pressure separator is 28' and so forth. Certain pieces of equipment such as the feed tanks 1, 2 and 3, the stabilizer 33, and the gas scrubber 24 need not be duplicated, one item serving both units.

It will be understood also that more than two units may be operated with a common recycle gas recovery system, the essential purpose being to combine units operating on different feed stocks so that there will be an over-all net production of free hydrogen even though one or more units may show a net consumption of hydrogen.

In the operation of the process the temperature is maintained between about 850 and 1000° F., preferably between 900 and 1000° F. The pressure is maintained between 50 and 500 pounds per square inch, preferably between 150 and 400 pounds per square inch.

The feed rate may be varied over relatively wide limits, for example between 0.3 and 3 volumes of liquid naphtha per volume of catalyst

per hour, preferably between 1 and 2 v./v. per hour.

The recycle gas rate is maintained between 1500 and 4000 cubic feet per barrel of naphtha, preferably between 2000 and 3500 cubic feet per barrel of naphtha. At the start of the process, the concentration of hydrogen should be between 60 and 90 mol percent, conveniently about 70%. As the operation proceeds and the gas is recycled, the concentration of hydrogen will gradually diminish because hydrocarbon gases are also evolved in the reaction. If the rate at which the hydrocarbon gases such as methane, ethane and propane are evolved is greater than the rate at which hydrogen is evolved, the concentration of hydrogen will continually decrease until it may be too low to have any beneficial effect. Therefore, it is generally desirable to pass the recycle gases through a scrubbing means prior to their return to the process in order to remove at least a portion of the hydrocarbon constituents. This may be accomplished by scrubbing the gases while still under reaction pressure with a hydrocarbon oil such as kerosene or gas oil which will absorb the hydrocarbon constituents but very little of the hydrogen, or by passing the gases through relatively small quantities of water at temperatures close to the freezing point thereof whereby solid hydrates of the hydrocarbons are formed and the hydrogen remains unaffected, or by any other means of separating hydrocarbon gases from hydrogen. By scrubbing the recycle gases to remove hydrocarbon gases, the concentration of hydrogen may be maintained at between 40 and 60% which in most cases will be sufficient. Fresh hydrogen may, of course, always be added to compensate for any sudden drop in the concentration of hydrogen in the recycle gases or to counteract any temporary decrease in the activity of the catalyst. It should be understood also that the process may be operated with equally satisfactory results on a once-through gas basis, that is the gas containing hydrogen is passed once through the reaction vessel and the effluent or recovered gases are not recycled. While operation on a once-through gas basis has the advantage of maintaining a constant high concentration of hydrogen, it can be seen that it requires a constant input of extraneous hydrogen and therefore it may not be as desirable from a commercial and economic standpoint.

The regenerating gases may consist of inert gases such as steam, flue gases, nitrogen, carbon dioxide, and the like containing about 4 to 10% of oxygen. The rate at which the regenerating gases are passed through the catalyst may be between 1500 and 3000 volumes per volume per hour. The temperature during regeneration should be maintained between 600 and 1000° F. Care should be taken to prevent the temperature from rising, say above about 1200° F. At the start of the regeneration period, the quantity of oxygen should be relatively small and as the carbonaceous material is gradually burned off, the quantity of oxygen may be increased until near the end of the regeneration period, the maximum amount of oxygen is used.

The length of the reforming period will be determined largely by the point at which the net production of hydrogen approaches zero and a slight net consumption of hydrogen is observed. This period may be anywhere from 10 to 100 hours or more, depending on the nature of the catalyst, the type of feed stock, and the general

conditions of operation. The length of the regeneration period may be varied over rather wide limits. In commercial operation two or more reaction chambers filled with catalyst will be used so that while one chamber is on a reforming period, the other may be on a regenerating period. As a practical matter therefore, the length of the regeneration period will be substantially the same as the length of the reforming period. Of course, if there is only one reaction chamber or if suspended or moving catalyst is used, it will be advantageous to keep the regeneration time as short as possible.

The catalysts used in this process may be selected from a wide variety of different materials. The preferred catalysts are compounds such as the oxides or sulfides of metals of the VI group of the periodic system, especially molybdenum, chromium, tungsten and uranium. These VI group metal compounds may be used alone or in combination with other substances which may serve as supports or carriers and may also have some catalytic activity. As examples of such supporting materials may be mentioned bentonite clays, montmorillonite clays, kieselguhr, Super Filtrol, crushed firebrick, crushed silica, zeolites either acid washer or base-exchanged, bauxite, glauconite, calcined dawsonite, aluminum oxide, magnesium oxide, aluminum phosphate, aluminum silicate, alumina gels, silica gels, "activated alumina," activated silica. The catalyst compositions may be prepared in different ways. For example, finely powdered support and catalyst may be mechanically mixed in the wet or dry state and then pressed or moulded into lumps of suitable size and shape; or the support may first be prepared in suitable porous form and then impregnated with a solution of the catalytic metal compound; or the support and catalytic metal hydroxides may be co-precipitated either as gelatinous precipitates or as gels and the mass then dried and calcined. Mixtures of alumina and chromium oxide or alumina and molybdenum oxides are especially effective. These mixtures may be prepared by impregnating "activated alumina" with solutions of chromium or molybdenum compounds, or by co-precipitating aluminum hydroxide with chromium hydroxide or molybdenum hydroxide. Gels of alumina and chromium oxide or molybdenum oxide are also suitable. In most cases it is desirable to have the chromium or molybdenum oxide constitute between 6 and 40% by weight of the catalyst mixture, although in the case of molybdenum oxide it has been found that a mixture comprising as little as 3 to 10% of molybdenum oxide and the balance aluminum oxide is very effective. Compounds of metals of the IV group of the periodic system may also be used. Among these are oxides or sulfides of titanium, zirconium, cerium, hafnium and thorium. These may be used either alone, in admixture with one another or in admixture with alumina, silica or other materials. Compounds of metals of the V group of the periodic system may also be used. Among these are oxides or sulfides of vanadium, columbium or tantalum which may be used either alone, in admixture with each other, or in admixture with alumina, silica or other materials. These catalysts may be used in a variety of different forms. When the reaction vessel is packed with catalyst and is used in what is called a stationary form, the catalytic material is preferably prepared in small sized lumps, tablets, pills, pellets, granules or other shapes of approxi-

mately 4 to 10 millimeters diameter. These lumps may be supported in the reaction vessel on a number of trays or the entire reaction vessel may be filled with the lumps. The catalyst may also be used in finely divided or powdered form in which case it may be suspended in the naphtha to be treated or it may be introduced separately in powdered form into the reaction vessel or it may be introduced along with the hydrogen or recycle gases. The catalyst may also be granulated and placed on a moving conveyor or belt within the reaction vessel so that it is constantly moving into and out of the reaction vessel. It will be understood that when suspended or moving catalyst is used, the regeneration will not be accomplished in situ as described above, but in a separate vessel. The method of regeneration, however, may be substantially the same.

It is frequently found that sulfur or sulfur compounds have a decidedly beneficial effect on the activity of these catalysts, particularly those comprising compounds of metals of the VI group of the periodic system, and it is therefore advantageous to carry out the process in the presence of small quantities of added sulfur, say between 0.1 and about 2% by weight on the naphtha. Free sulfur may be used for this purpose, although it is generally preferable to use sulfur compounds such as hydrogen sulfide, carbon disulfide or ammonium polysulfide, or organic sulfides such as carbonyl sulfide, alkyl sulfides, alkyl hydrosulfides, alkyl disulfides, alkyl trisulfides, aryl sulfides, thiophene and the like which under the conditions of the reaction will decompose to produce sulfur or hydrogen sulfide. Selenium or tellurium or compounds thereof such as hydrogen selenide and hydrogen telluride may be used in place of or in conjunction with sulfur or sulfur compounds.

The feed stocks to which the present process may be applied are hydrocarbon oils boiling substantially in the motor fuel range, that is, from about 90 to 450° F. or somewhat higher. These hydrocarbon oils may have been derived from any source. For example, they may be obtained by the distillation, destructive distillation, cracking, hydrogenation or destructive hydrogenation of coals, tars, mineral oils, shales, peats, lignites, brown coals, bitumens and other solid or semi-solid carbonaceous materials, or by synthetic processes such as the Fischer Synthesis in which carbon oxides are hydrogenated, or by polymerization of normally gaseous hydrocarbons, or by gas reversion. The hydrocarbon oils may also be obtained by solvent extraction and similar processes.

The products of this process may be suitable without further treatment for use as motor fuel. However, the usual finishing treatments may be applied, if necessary. Among these are rerunning to a predetermined endpoint, caustic and acid treating, clay treating and the like. Tetraethyl lead or other anti-knock agents may be added to the finished and rerun products still further to improve the anti-knock characteristics thereof. Similarly, blending agents such as isooctane, isopentane, alkylated isobutane or other isoparaffins, iso-propyl ether or hydrogenated polymers of isobutylene may be mixed with the product to produce gasolines of 90 to 100 octane number or more which are especially suitable for use in aviation engines.

This process of catalytic reforming in the pres-

ence of hydrogen may be operated either alone or in combination with other processes. For example, it may be especially convenient in some cases to operate the reforming process in combination with a preliminary cracking or destructive hydrogenation process by which the feed stock for the reforming operation may be prepared. It will be understood also that various combinations of distillation, cracking, destructive hydrogenation, solvent extraction and reforming may be made.

This invention is not limited by any theories of the mechanism of the reactions nor by any details which have been given merely for purposes of illustration, but is limited only in and by the following claims in which it is intended to claim all novelty inherent in the invention.

We claim:

1. In the catalytic reforming of naphthas in the presence of hydrogen under conditions such that there is no net consumption of free hydrogen, the method of increasing the net quantity of free hydrogen produced in the process under given conditions of operation which comprises increasing the percentage of lower boiling hydrocarbons in the naphtha feed.

2. In the catalytic reforming of naphthas in the presence of hydrogen under conditions such that there will be no net consumption of free hydrogen in the process and in the presence of a catalyst comprising aluminum oxide and a compound of a metal of the VI group of the periodic system, the method of maintaining a substantially constant net production of free hydrogen in the process for a period of at least 12 hours which comprises progressively increasing the percentage of lower boiling hydrocarbons in the naphtha feed as the reforming period proceeds.

3. In the catalytic reforming of naphthas in the presence of hydrogen and in the presence of a catalyst comprising aluminum oxide and an oxide of a metal of the VI group of the periodic system, in which a reforming period and a regenerating period are continuously alternated and in which each reforming period is continued until the net production of hydrogen is insufficient to maintain a high enough concentration of hydrogen, the method of prolonging the reforming period which comprises increasing the percentage of lower boiling hydrocarbons in the naphtha feed when it is observed that the net quantity of hydrogen produced decreases.

4. In the catalytic reforming of naphthas in the presence of hydrogen and in the presence of a catalyst comprising a metal of the VI group of the periodic system in which a reforming period and a regenerating period are continuously alternated and each reforming period is continued until the net production of hydrogen is insufficient to maintain a high enough concentration of hydrogen, the improved method of operation which consists in separating the naphtha feed into two fractions, one containing the relatively lower boiling hydrocarbon constituents of the naphtha and the other containing the relatively higher boiling constituents of the naphtha, subjecting the fraction containing the relatively higher boiling constituents to treatment in the early stages of the reforming period and subjecting the fraction containing the relatively lower boiling constituents to treatment in the later stages of the reforming period.

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