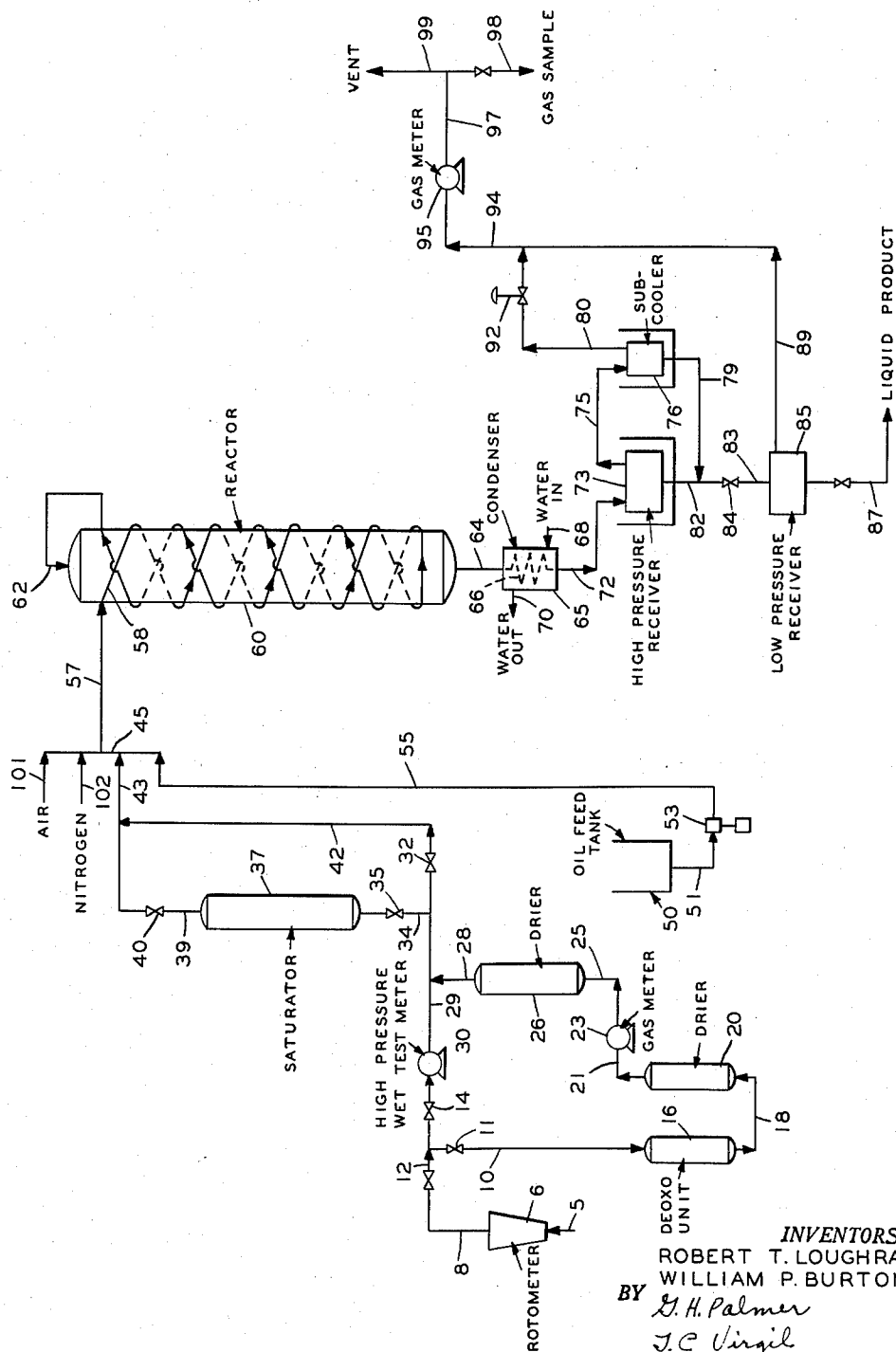


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 IN THE REFORMING OF HYDROCARBONS
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PRETREATMENT OF MOLYBDENUM OXIDE CATALYST EMPLOYED IN THE REFORMING OF HYDROCARBONS

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This invention relates to an improved reforming process, and more particularly pertains to an improved hydroforming process for naphtha fractions whereby high yields of high anti-knock gasolines are produced.

It is an object of this invention to provide an improved reforming process for light hydrocarbon oils.

Another object of this invention is to provide an improved hydroforming process for naphtha fractions, which is especially effective for producing unusually high yields of high anti-knock gasoline.

Still another object of this invention is to provide an improved reforming process for light hydrocarbon oils which utilizes a molybdenum oxide catalyst.

Other objects and advantages will become apparent from the following description and explanation thereof.

In accordance with the present invention, light hydrocarbon oils are reformed by the process which comprises first treating a molybdenum oxide type catalyst with a hydrogen-containing gas substantially free of water at an elevated temperature before contacting the catalyst with the light hydrocarbon oil under reforming conditions including the use of a small amount of water.

The pretreatment of the molybdenum oxide catalyst is conducted by means of a hydrogen-containing gas at an elevated temperature. The pretreatment can be conducted at atmospheric or elevated pressures. It was noted, however, that the use of an elevated pressure, generally in the range of about 50 to about 1000 p.s.i.g., preferably about 100 to about 500 p.s.i.g., resulted in yields of C₅+gasolines in a reforming operation which are significantly higher than those obtained by treating the catalyst with a hydrogen-containing gas at atmospheric pressure. An elevated temperature is used for the pretreatment falling in the range of about 750 to about 1200° F., more usually, about 900° to about 975° F. It is noted that in the initial stages of the pretreatment a temperature rise is experienced, indicating that the molybdenum oxide catalyst is reduced from a higher to a lower level of oxidation.

The pretreating step can be accomplished in various ways at elevated temperatures. One method of pretreatment involves maintaining a continuous flow of hydrogen through the zone containing the molybdenum oxide catalyst. The flow of hydrogen is maintained at a low rate, e.g., about 20 to 50 standard cubic feet per hour (measured at 60° F. and 760 mm.) per pound of molybdenum oxide during the initial part of the treatment, e.g., about 0.1 to 1.0 hour. This type of pretreatment is readily adapted to a fluid operation wherein the finely divided solids are maintained fluidized for intimate contact between gas and solid particles. Accordingly, during the initial part of the treatment the net flow of hydrogen-containing gas can provide a superficial linear gas velocity of about 0.1 to 1.0 feet per second, hence, maintaining a fluidized system. Following the initial part of the operation, the net rate of hydrogen gas can be increased to about 50 to 400 standard cubic feet of hydrogen per pound of molybdenum oxide, thus providing a gas velocity of

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about 0.5 to 5.0 feet per second for the remainder of the operation, e.g., for about 0.1 to 2 hours. It is desirable to maintain the water of reduction formed during the initial stage of pretreatment in contact with the catalyst in order that it might desorb impurities contained in the catalyst, which adversely influence the activity and/or reduction thereof.

Another method of pretreatment involves the static condition, i.e., wherein no net flow of hydrogen gas is permitted over the catalytic material. This method is readily applicable to a fixed bed-non-fluid system, and it produces good results. The pretreatment of molybdenum oxide catalyst can also involve first using a static condition or a low net rate of hydrogen flowing through the zone containing the catalyst, followed by a depressuring or purging operation whereby the contents of the pretreatment zone are substantially removed, and then the system is recharged again with fresh hydrogen gas. This is conveniently carried out by operating at an elevated pressure, although atmospheric pressure is a useful operation, then depressuring from the elevated pressure level of about 50 to 500 p.s.i.g. to a lower level of about atmospheric pressure to 50 p.s.i.g. and then repressuring to a higher level of about 50 to 750 p.s.i.g. Still another method of pretreating the catalyst involves first having no net flow of hydrogen-containing gas through the zone containing the catalyst, and then, completing the pretreatment by employing the elevated pressure with a high net flow of hydrogen through the catalyst zone. A high net rate is, for example, about 50 to 500 s.c.f. of hydrogen gas per pound of molybdenum oxide, on an hourly basis.

The pretreatment operation can involve the use of pure hydrogen or a hydrogen-containing gas having about 35 to about 80% by volume of hydrogen. In this regard, the normally gaseous product which is produced from the reforming operation, and which contains about 50 to about 70% of hydrogen by volume can be used for the purpose of pretreating the molybdenum oxide catalyst. The quantity of hydrogen-containing gas employed for the pretreatment will be determined by the pressure at which the operation is conducted. In the event that a hydrogen-containing gas has a relatively small concentration of hydrogen, it may be desirable to employ a higher pressure for pretreatment than would ordinarily be used in the case of pure hydrogen. The hydrogen is substantially free of water. However, generally, about 50 to about 500 standard cubic feet of hydrogen per hour (measured at 60° F. and 760 mm.) per pound of molybdenum oxide are employed for the entire pretreating operation. The entire period of time involved in the pretreatment of catalyst can vary considerably, however, usually about 0.1 to about 3 hours, preferably about 0.5 to about 2 hours are employed.

The pretreatment of catalyst with a net flow of hydrogen or suitable purging of gas from the system is preferably conducted at a temperature of at least about 930° F. and this temperature can be less than about 975° F., or usually up to about 962° F. The preferred temperature is about 950° F. The pretreatment can involve an elevated pressure under static or flow conditions, or combinations of first having either a static or flow condition at elevated pressures followed by one or the other type of condition, viz., static or flow, depending upon which was used first. In the case of using the pretreatment of first an elevated pressure under static or flow conditions followed by depressuring, and then repressuring the system again, it is preferred to employ a temperature of about 850° to about 975° F., or more usually about 900° to about 930° F.

The physical form of the catalyst involved in the pretreatment operation will usually be determined by the

type of system which is being used for the reforming operation. Accordingly, the catalyst may be used in the form of lumps, granules, pellets or finely divided material, depending upon the type of catalyst used in reforming the light hydrocarbon oil. In the case of a fixed bed reforming system, it is desirable to pretreat the catalyst after it has been regenerated by means of an oxygen-containing gas, without transferring the catalyst from the processing vessel. In effect, the cycles of operation would involve a reaction phase, regeneration phase and then a pretreatment phase, with or without suitable purging at appropriate intervals during the complete operation. In a moving bed system, it is preferred to employ a separate pretreating vessel for the purpose of conditioning the catalyst, before use in the reaction zone. This involves transferring the catalyst from the regeneration zone to a pretreating zone, and then circulating the catalyst to the reaction zone. The use of a separate vessel for pretreating applies to a fluid or non-fluid system, involving the moving bed system.

The catalyst to be preconditioned in accordance with this invention involves molybdenum oxide supported on a carrier material. The carrier material can include, for example, alumina, silica, silica-alumina, magnesia, silica-magnesia, alumina-magnesia, pumice, kieselguhr, fuller's earth, "Superfiltrol," bentonite clays, etc. A particularly effective catalyst is molybdenum trioxide supported on alumina. Generally, the catalytic agent, namely, molybdenum oxide, comprises about 0.5 to about 24% by weight of the total catalyst, more usually, it constitutes about 1 to about 10% by weight of the catalyst. In some cases, it is preferred to employ small amounts of silica in combination with molybdenum trioxide on alumina. The silica is employed in proportions of about 0.5 to about 12%, more usually, about 2 to about 8% by weight, based on the total catalyst. The silica serves to enhance the stability of the catalyst at elevated temperatures, and further, it can, in some instances, increase the activity and/or selectivity of the catalyst after continued use.

As previously indicated, the pretreatment of molybdenum oxide catalyst results in higher yields of reformed liquid of high octane quality. The material to be reformed is a light hydrocarbon oil and includes, for example, gasoline, naphtha and kerosene. The light hydrocarbon oil has an initial boiling point of about 85° to about 325° F., and an end point of about 350° to about 500° F. In the case of reforming a naphtha fraction, it is preferred to employ a naphtha having an initial boiling point of about 85° to about 250° F., and an end point of about 300° to about 450° F. Generally, the light hydrocarbon oils to be reformed have a Watson characterization factor of about 11.50 to about 12.00. The feed material can be one which is a straight run or virgin stock, a cracked stock derived from a thermal or catalytic cracking operation or a mixture or blend of straight run and cracked stocks. Accordingly, the octane number of the feed material can range from about 20 to about 70 CFRR clear, and have an olefin content of about 0 to about 30 mol percent. The light hydrocarbon oil can be derived from any type of crude, and thus it can contain sulfur in the amount of 0 to about 3.0% by weight.

The light hydrocarbon oil is reformed under conditions which can involve the net consumption or net production of hydrogen. A system involving the net production of hydrogen is commonly referred to as hydroforming, and it is operated under such conditions that the quantity of hydrogen produced is sufficient to sustain the process without need for extraneous hydrogen. Generally, for the reforming of light hydrocarbon oils, a temperature of about 750° to about 1100° F. is employed. At this temperature, the pressure of the operation is generally maintained at about 50 to about 1000 p.s.i.g. The quantity of oil processed relative to the amount of catalyst em-

ployed is measured in terms of the weight space velocity, that is, the pounds of oil feed on an hourly basis charged to the reaction zone per pound of catalyst which is present therein. The weight space velocity can vary from about 0.05 to about 10. The quantity of hydrogen which is added to the process is usually measured in terms of the standard cubic feet of hydrogen (measured at 60° F. and 760 mm.) per barrel of oil feed charged to the reforming operation (one barrel equals 42 gallons). On this basis, the hydrogen rate is about 500 to about 20,000 s.c.f.b., preferably about 1500 to 6000 s.c.f.b. Another method of indicating the quantity of hydrogen which can be present during the hydroforming operation is by means of hydrogen partial pressure. In this regard, the hydrogen partial pressure is about 25 to about 950 p.s.i.a.

In a hydroforming operation, the reaction conditions fall within the ranges specified hereinabove, however, they are selected on the basis of obtaining a net production of hydrogen. Accordingly, a preferred hydroforming process involves a temperature of about 850° to about 1050° F.; a pressure of about 50 to about 500 p.s.i.g.; a weight space velocity of about 0.1 to about 2; a hydrogen rate of about 1000 to 7500 s.c.f.b. and a hydrogen partial pressure of at least about 25 p.s.i.a. and up to the point at which hydrogen is consumed.

For the foregoing operation, a small amount of water is used in order to obtain the beneficial effect of increasing the yield of reformed liquid product of high anti-knock quality. Generally, the water can be introduced as a vapor with the hydrogen-containing gas, and/or as a liquid in the oil feed in the appropriate quantity, and/or it can be injected into the pretreated catalyst stream flowing to the reaction zone, and/or it can be injected directly into the catalyst bed of the reaction zone at a distant point to or in proximity to the point of introduction of oil feed. Generally, about 0.1 to about 10 mol percent of water, preferably about 0.25 to about 2 mol percent, based on the amount of hydrogen which is added to the reaction zone, is employed in this process. The optimum quantity of water used for the reforming process increases with the reforming temperature.

Due to the reforming operation, the molybdenum oxide catalyst becomes contaminated with carbonaceous material which lowers its catalytic activity undesirably. Hence, the catalyst is subjected to a regeneration treatment which involves contacting same with an oxygen-containing gas, e.g., oxygen, air, diluted air having about 1 to about 10% oxygen by volume, etc., at a temperature of about 600° to about 1250° F., preferably about 950° to about 1150° F. The regeneration is effected at atmospheric pressure or an elevated pressure of about atmospheric pressure to about 1000 p.s.i.g. Prior to regeneration the catalyst contains about 0.1 to about 5.0% by weight of carbonaceous material, and due to regeneration the carbonaceous material content is reduced to zero content or up to about 0.5% by weight. It is desirable to remove as much carbonaceous material as is economical, because possibly such material deposited on the catalyst undesirably may tend to cover the active molybdenum oxide centers, and thus render less effective the pretreatment operation. In such case, the ideal situation may be to burn off all the carbonaceous material deposited on the catalyst, insofar as the efficiency of pretreatment is concerned.

The reforming operation can be accomplished using a fluid or non-fluid technique, involving either a fixed bed or a moving bed system. In the case of a fixed bed operation, at least two processing vessels are employed in order that while one vessel is under regeneration and/or pretreatment, the other vessel is processing the light hydrocarbon oil to be reformed. In the commercial operations of present day, usually four processing vessels are employed. This is also suitable in the present invention, because it provides for larger quantities of material to be reformed. Normally, in the fixed bed system, the

reaction cycle takes about 0.25 to about 8 hours, the regeneration takes about 0.25 to about 8 hours and the pretreating operation can require about 0.1 to about 2.0 hours. In a fluid moving bed system, a finely divided catalytic material having a particle size in the range of about 5 to about 250 microns, more usually, about 10 to about 100 microns, is employed. A mass of the finely divided material is fluidized by the upward flow of gaseous or vapor materials which have a superficial linear velocity by about 0.1 to about 50 feet per second, more usually, about 0.1 to about 6 feet per second. In commercial operations, it is preferred to employ a superficial linear gas velocity of about 0.75 to about 2 feet per second. These linear gas velocities can exist in any of the processing vessels, namely, the reactor, the regenerator, the pretreating vessel and the transfer lines between vessels. Furthermore, the specified linear gas velocities can provide either a lean or dense phase of fluid mass. Usually, it is preferred to employ a dense phase because it provides a more intimate contact between the gas and/or vapor and the catalyst particles. The relative rates of catalyst being circulated and the oil being charged to the reaction zone is usually termed the catalyst to oil ratio, on a weight basis. Generally, in a moving bed system, the catalyst to oil ratio is about 0.05 to about 20. For commercial operations, it is preferred to employ a catalyst to oil ratio of about 0.5 to about 5.0.

Having thus provided a general description of the present invention, reference will be had to the accompanying drawing which illustrates a test unit which was employed for the purpose of evaluating the present invention.

In the accompanying drawing, hydrogen was supplied from source 5 and it passed into a rotometer 6 wherein the rate of hydrogen was measured. The measured hydrogen flowed from the rotometer to a valved line 8 and thereafter it passed to one of two circuits, namely, a circuit involving the removal of oxygen and water from the hydrogen gas stream and the other circuit which bypassed the oxygen removal system was going directly to a wet test meter. Water was added to either stream of hydrogen gas in the desired quantity. When it was desired to produce dry hydrogen, the hydrogen flowed into line 10 which contained a valve 11 in an open position. The processing of the hydrogen through the other circuit involved passing the hydrogen through a line 12 which contained a valve 14. The hydrogen in line 10 flowed into a Deoxo unit 16 comprised of palladium on aluminum oxide wherein oxygen removal was effected. Following the deoxygenation step in vessel 16, the hydrogen passed from the bottom thereof into a line 18 which was connected to the bottom end of a dryer 20 having present therein anhydrous calcium sulfate for the removal of moisture in the hydrogen gas. The dried hydrogen gas passed overhead from dryer 20 into an overhead line 21 and then it was measured by means of a wet test gas meter 23. A hydrocarbon mixture similar to the charge naphtha was used in the wet test gas meter instead of water. Since the hydrogen gas might absorb a small amount of water which might be present in the hydrocarbon mixture in the gas meter, it was passed through a line 25 which was connected to a second dryer 26 containing anhydrous calcium sulfate for the removal of water. The hydrogen gas stream was discharged from the top of dryer 26 through a line 28 which joined with a line 29. The deoxygenated gas was then passed through line 34 to the water saturator 37, where the desired concentration of water vapor was supplied. If no water was desired the dry deoxygenated hydrogen bypassed the saturator through line 42. In the event that it was desired to incorporate a predetermined quantity of water vapor into the hydrogen gas stream, without removing traces of oxygen beforehand, valve 11 in line 10 was kept in a closed position and valve 14 in line 12 was open. In this case, the measured hydrogen from

rotometer 6 was first measured in a high pressure wet test gas meter 30. The measured hydrogen gas stream flowed first through line 29 in which there was situated a valve 32. In this type of an operation, valve 32 was maintained in a closed position and the hydrogen gas stream flowed through a line 34 in which there was installed a valve 35 in an open position. The hydrogen gas stream was then passed into the bottom of a saturator 37 which contained water and was surrounded by an electric jacket to maintain the temperature at a desired level for obtaining the appropriate quantity of water vapor in the hydrogen gas stream. The moisture-laden hydrogen gas passed overhead from saturator 37 into a line 39 in which there was installed a valve 40 in an open position. When a dry gas was employed for the pretreating operation, valves 35 and 39 were maintained closed in order to avoid moisture from getting into the hydrogen gas. Likewise, in such an operation, valve 32 in line 29 was kept open in order that the hydrogen gas by-passed saturator 37 by means of a line 42. The hydrogen-containing gas then flowed through a line 43 which was connected to a main header 45 by which processing materials were charged to the reaction zone containing the catalytic material.

During the reaction cycle, the oil being processed was supplied from an oil feed tank 50 through a line 51 connected to the bottom thereof and thence transported by means of pump 53 through a line 55 which was connected to the main header 45. The mixture of hydrogen-containing gas and oil flowed from header 45 into a line 57 which was connected to a coil 58 surrounding the reactor vessel 60. The coil 58 was wound downwardly over the length of the reactor for a coil length of 10 feet, and then upwardly across the same area of the reactor, before entering the top of the reactor as line 62. The reactor was a cylindrical vessel having an internal diameter of 1.5 inches and a length of 1.5 feet. The catalytic material, being present in the form of $\frac{3}{16}$ inch pellets, occupied about 550 cc. of the reactor capacity. The reactant materials flowed downwardly over the catalytic material, and thence passed from the reaction zone through a bottom line 64 which was connected to a condenser 65. The reaction product passed through an internal coil 66, which was surrounded by cooling water introduced via line 68 and then leaving the condenser via line 70. The condensed liquid product flowed from the bottom of the condenser through a line 72 which was connected to the top of a high pressure receiver 73. Any gaseous material which was combined with the liquid product passed from receiver 73 into an overhead line 75 which was connected to a secondary cooler 76. In the secondary cooler any gaseous material which was condensable accumulated therein and was removed from the bottom thereof through a line 79. The normally gaseous material in the secondary cooler 76 passed overhead through a line 80. The liquid product in high pressure receiver 73 was discharged through the bottom thereof by means of a line 82 and it combined with the liquid product flowing through line 79, in line 83, in which there was installed a valve 84 for the purpose of maintaining the desired high pressure within receiver 73. The combined liquid product in line 83 flowed into a low pressure receiver 85. The liquid product was then discharged from receiver 85 through a bottom valved line 87. Any gaseous material which was present with the liquid product was removed from the top of receiver 85 and it flowed through a line 89. The normally gaseous product from the secondary cooler 76 is passed through a pressure control valve 92 which is installed in the overhead line 80. The normally gaseous products in lines 80 and 89 were combined in line 94 before passing through a gas meter 95. The measured gaseous product then flowed through a line 97 before a portion thereof was taken as a gas sample through a valved line 98 and the remainder was vented through a line 99.

The temperature of the reaction zone was maintained by submerging the reactor with coil 58 into a molten lead bath maintained at a desired temperature. The molten lead bath is not shown in the schematic diagram. After the reaction cycle had run for the prescribed period of time, the catalytic material was regenerated by employing a regeneration gas constituting a mixture of nitrogen and air. Air was introduced through a line 101 and nitrogen was supplied through a line 102, and both of these lines were connected to the main header 45, from which the material passed into line 57 prior to flowing through coil 58 circumscribing the reaction vessel. Following the reaction cycle, the stream of nitrogen was passed through the reactor in order to remove as much of the reaction product wetting the catalyst as was possible. This was carried out at a temperature of about 875° to 1050° F. and for a period of 45 minutes. Following the purging cycle, air was introduced along with the nitrogen in a quantity appropriate to obtain 2% by volume of oxygen. The temperature of the catalyst during this cycle of the operation was maintained at about 950 to about 1150° F. The concentration of air was increased during the regeneration until the oxygen concentration was about 8% by volume. The concentration of air was controlled at the lower level to prevent the temperature from exceeding 1150° F. When it appeared that all combustible materials had been removed 100% air was passed through the catalyst bed for 30 minutes. The passage of the regeneration gas continued for a period of about 4 hours. Following the regeneration of the catalyst, nitrogen, without previous treatment as to water content or oxygen-containing compounds, was passed through the reactor 60 in order to purge the same of any air or flue gas which might be present. The purging cycle with nitrogen was conducted at a temperature of about 875° to about 1050° F. and for a period of about 15 minutes. Following the nitrogen purge of the reactor, operation was commenced in the desired manner in order to evaluate the various factors of pretreatment and reaction conditions.

A naphtha having the properties shown in Table I was evaluated in the test unit illustrated in the attached drawing.

Table I

Feed designation.....	A
Gravity, °API.....	55.4
ASTM distillation, °F.:	
IBP	206
5	256
10	264
20	274
30	282
40	290
50	299
60	306
70	316
80	328
90	346
95	360
E.P	381
Reid vapor pressure, p.s.i.....	0.7
K-characterization factor.....	12.00
Refractive index, n_D^{68}	1.4229
Aniline point, ° F.....	133
Octane No. CFRR clear.....	30.2
Aromatics, vol. percent (ASTM).....	12.5
Olefins, mol percent.....	0.6
Sulfur, wt. percent.....	0.073
Molecular weight.....	125

The catalyst employed for evaluation and the present invention is described in Table II below.

Table II

Catalyst Designation.....	I	II
5 Component, Wt. Percent:		
MoO ₃	9.3	9.3
SiO ₂	3.6	3.6
Fe ₂ O ₃	0.03	0.03
Cl ₂	0.4	0.4
Al ₂ O ₃	86.7	86.7

Several tests were performed in the test unit shown in the attached drawing and these are reported in Table III below.

Table III

Run No.	I	2	3	4
Catalyst.....	I	II	I	I
Feed.....	A			
20 Operating Conditions:				
Temperature, ° F.....	900	930	900	900
Pressure, p.s.i.g.....	250	250	250	250
Space Vel. W ₀ /hr./W _c	0.5	0.5	0.8	0.8
H ₂ rate, s.c.f.b.....	5,000	5,000	5,000	5,000
Oil Rate, gm./hr.....	284	285	432	423
Catalyst, gm.....	563	539	555	555
25 Mol Percent H ₂ O, (Basis H ₂).....	0	0.5	0.5	0.5
Period of Run, hrs.....	2	2	2	2
Pretreatment of Catalyst:				
Temperature.....	909	930	915	921
Hydrogen pressure, p.s.i.g.....	250	0	250	250
Static treatment.....	Yes		Yes	Yes
Flowing treatment.....	Yes	Yes	Yes	
30 Period of Treatment, hrs.....	0.50	4	1.25	1.25
Yields (Output Basis):				
Liquid Yield (100% C ₄), Vol. Percent.....	86.8	85.7	90.3	93.3
C ₄ free liquid, Vol. Percent.....	78.3	75.0	83.5	88.6
C ₄ free Gasoline, Vol. Percent.....	76.2			4.7
Butanes, Vol. Percent.....	8.5	10.7	6.8	
35 Polymers, Vol. Percent.....	2.1			
Dry Gas, Wt. Percent.....	13.5	14.4	9.0	6.0
Hydrogen, s.c.f.b.....	108	319	600	-3
Inspections:				
Octane No. (CFRR clear) C ₄ free Gasoline.....	85.2	93.0	82.0	76.1
Yield of C ₄ free-Gasoline of 85 O.N. (CFRR clear).....	78.5	80.8	81.9	84.3

¹ 400° F. (E.P.).

From Table III above, it is to be noted that Run 1 involves a hydroforming operation in which no water was added during the reforming step. In this run, the regeneration of catalyst was conducted at atmospheric pressure and immediately after the regeneration step, the catalyst was purged with dry nitrogen. Dry nitrogen was introduced to pressure the system to 275 p.s.i.g. A static pressure test was maintained for 15 minutes. The pressure was lowered to 250 p.s.i.g. and a flow of dry hydrogen at 12 s.c.f.h. was established. The flow of dry hydrogen was extended over 45 minutes after which time the naphtha flow was started to the reactor.

In Run No. 2, the hydroforming operation was conducted with the addition of a small amount of water; whereas the pretreatment step was effected by flowing dry hydrogen at the net rate of 0.6 s.c.f.h. over the catalyst at atmospheric pressure. By comparing Run No. 2 with Run No. 1, it is noted that the addition of water to the hydroforming operation effects a beneficial increase in the quantity of reformed liquid measured as the yield of C₄ free-gasoline having an octane number of 85 CFRR clear.

Run No. 3, in Table III, involves a pretreatment of the catalyst following regeneration, by using dry hydrogen at 250 p.s.i.g., and maintaining a continuous flow of hydrogen at a net rate of 18 s.c.f.h. over the catalyst. It is to be noted that the yield of C₄ free-gasoline of 85 octane no. is higher in Run No. 3 than that obtained in Run No. 2. This clearly indicates that pretreatment of the catalyst at an elevated pressure is desirable. Run No. 4 in the same table involves a pretreatment of catalyst with dry hydrogen, by employing a pressure of 250 p.s.i.g. under static conditions. It is to be noted by comparison with Run No. 3 that the

yield of C₄ free-gasoline having an 85 octane no. is higher when using an elevated pressure under static conditions for the pretreatment operation.

Other experiments were performed in which the pretreatment was modified. These results are reported in Table IV below. In the case of Runs 1 and 2 in Table IV, the pretreatment was effected by the following procedure:

(a) After normal regeneration at 950° F., the catalyst was cooled at 900° F. and the catalyst was flushed with nitrogen for 15 minutes at 900° F.

(b) Dry hydrogen was then admitted to the reactor and the pressure was increased to 275 p.s.i.g. During this operation, a momentary increase in temperature to about 950° F. was observed. This indicates that the catalyst was undergoing reduction.

(c) The catalyst was maintained under a pressure of 275 p.s.i.g. for 1 hour without any flow of hydrogen over the catalyst.

(d) The hydrogen was released from the system and the pressure was allowed to decrease to atmospheric pressure over a period of 5 minutes.

(e) The catalyst remained under atmospheric pressure for 30 minutes.

(f) Dry hydrogen was admitted to the reactor to raise the pressure to 275 p.s.i.g.

(g) The hydrogen pressure of 275 p.s.i.g. was maintained for 15 minutes without any net flow of hydrogen over the catalyst.

(h) The pressure was reduced to 250 p.s.i.g. and a flow of wet hydrogen containing 0.5 mol percent by weight was established and maintained for 45 minutes after which time the naphtha was charged to the reactor.

In the case of Run No. 3 of Table IV, the procedure of pretreatment was as follows:

Steps a, b and c described above in connection with Runs 1 and 2 of Table IV were used in this procedure.

(d) Following step c, a flow of wet hydrogen containing 0.5 mol percent of water at the rate of 18 s.c.f.h. was established and maintained for 10 minutes, following which a flow of dry hydrogen at the same rate was maintained for a 10 minute period.

Following the flow treatment, steps g and h described above in Runs 1 and 2 in Table IV were followed.

Table IV

Run No.	1	2	3
Catalyst	I		
Feed	A		
Operating Conditions:			
Temperature, ° F.	900	900	900
Pressure, p.s.i.g.	250	250	250
Space Vel., W ₀ /hr./W _c	0.8	0.8	0.8
H ₂ rate, s.c.f.b.	5,000	5,000	5,000
Oil Rate, gm./hr.	0.80	0.77	0.77
Catalyst, gm.	555	555	555
Mol percent H ₂ O (Basis H ₂)	0.5	0.5	0.5
Period of Run, hrs.	2	2	2
Yields (Output Basis):			
Liquid Yield (100% C ₄), Vol. percent		93.1	92.4
C ₄ free Liquid, Vol. percent	86.5	88.3	87.3
C ₄ free-Gasoline, Vol. percent			
Butanes, Vol. percent		4.9	5.2
Polymer, Vol. percent			
Dry Gas, Wt. percent		5.9	6.5
Carbon, Wt. percent			
Hydrogen, s.c.f.b.		400	490
Inspections:			
Octane No. (CFRR clear) C ₄ free-Gasoline	81.4	80.3	79.3
Yield of C ₄ free-Gasoline of 85 O. N. (CFRR clear)	84.6	85.9	84.4

¹ 400° F. (E. P.).

It is to be noted from Runs 1, 2 and 3 in Table IV above, that various modifications of the technique of pretreatment at an elevated temperature can be resorted to for obtaining still better yields of the C₄ free-gasoline having an 85 octane no. By comparing Runs 1, 2 and 3 in Table IV, with Runs 3 and 4, in Table III, it is to be

noted that the modifications in the pretreatment step have resulted in still higher yields than those obtained by simply pretreating at an elevated pressure, with or without a net flow of hydrogen over the catalytic material.

Furthermore, it should be noted in the above runs that the system was pressured up with hydrogen rather than any other gas at the end of regeneration, and this is to be preferred, because gases, such as for example, nitrogen, carbon dioxide, etc., are in some instances detrimental to catalyst activity. Hence, one aspect of this invention involves pressuring up the system with a hydrogen-containing gas following the regeneration step.

Having thus described the present invention by reference to specific examples thereof, it should be understood that no undue limitations or restrictions are to be imposed by reason thereof, but that the present invention is defined by the appended claims.

We claim:

1. A process for reforming light hydrocarbon oils which comprises treating a molybdenum oxide catalyst which has been previously treated with an oxygen-containing gas with a hydrogen-containing gas substantially free of water under static conditions at an elevated pressure to convert the catalyst to a reduced form, and then contacting the reduced catalyst with a light hydrocarbon oil under suitable reforming conditions in the presence of added water in the amount of about 0.1 to about 10 mol percent.

2. A process for reforming light hydrocarbon oils which comprises treating a molybdenum oxide catalyst which has been previously treated with an oxygen-containing gas with a hydrogen-containing gas substantially free of water at a pressure of about 150 to about 400 p.s.i.g. at an elevated temperature and under static conditions to convert the catalyst to a reduced form, then lowering the pressure of the hydrogen-containing gas in contact with the catalyst to a level of about 1 atmosphere to about 50 p.s.i.g., then raising the pressure of the hydrogen-containing gas in contact with the catalyst to a level of about 150 to about 400 p.s.i.g. and then contacting the reduced catalyst with a light hydrocarbon oil under suitable reforming conditions in the presence of added water in the amount of about 0.1 to about 10 mol percent.

3. A process for reforming light hydrocarbon oils which comprises treating a molybdenum oxide catalyst which has been previously treated with an oxygen-containing gas with a hydrogen-containing gas substantially free of water at a pressure between about 150 and about 400 p.s.i.g. under static conditions to convert the catalyst to a reduced form, then lowering the pressure of the hydrogen-containing gas in contact with the catalyst to between about 0 and about 50 p.s.i.g., then increasing the pressure of the hydrogen-containing gas in contact with the catalyst to between about 150 and about 400 p.s.i.g., and then contacting the reduced catalyst with a light hydrocarbon oil at a temperature of about 750 to about 1150° F., under a total pressure of about 50 to about 1000 p.s.i.g., at a weight space velocity of about 0.5 to about 10, at a hydrogen partial pressure of about 25 to about 950 p.s.i.a., and in the presence of about 0.1 to about 10 mol percent of water.

4. A process for reforming light hydrocarbon oils which comprises treating a molybdenum oxide catalyst which has been previously treated with an oxygen-containing gas with a hydrogen-containing gas substantially free of water at a pressure between about 150 and about 400 p.s.i.g. under static conditions to convert the catalyst to a reduced form, then lowering the pressure of the hydrogen containing gas in contact with the catalyst to between about 0 and about 50 p.s.i.g., then increasing the pressure of the hydrogen-containing gas in contact with the catalyst between about 150 and about 400 p.s.i.g. and then contacting the reduced catalyst with a light

hydrocarbon oil at a temperature of about 850 to about 1050° F., a total pressure of about 50 to about 500 p.s.i.g., and a weight space velocity of about 0.1 to about 2, using a hydrogen rate of about 1000 to about 7500 s.c.f.b., and in the presence of about 0.25 to about 2 mol percent of water.

5. A process for reforming light hydrocarbon oils which comprises treating a molybdenum oxide catalyst which has been previously treated with an oxygen containing gas with a hydrogen-containing gas substantially free of water at a pressure between about 150 and about 400 p.s.i.g. under static conditions to convert the catalyst to a reduced form, then contacting said catalyst with a flow of hydrogen-containing gas containing about 0.1 to about 10 mol percent of water, then contacting said catalyst with a flow of hydrogen-containing gas substantially free of water at a pressure between about 150 and about 400 p.s.i.g., then treating said catalyst with a hydrogen-containing gas substantially free of water at a pressure between about 150 and about 400 p.s.i.g. under static conditions, and then contacting the reduced catalyst with a light hydrocarbon oil under suitable reforming conditions in the presence of added water in the amount of about 0.1 to 10 mol percent.

6. A process for reforming light hydrocarbon oils which comprises treating a molybdenum oxide catalyst which has been previously treated with an oxygen-containing gas with a hydrogen-containing gas substantially free of water at a pressure of about 150 to about 400 p.s.i.g., at an elevated temperature and under static conditions to convert the catalyst to a reduced form, then contacting said catalyst with a flow of hydrogen-containing gas containing about 0.1 to about 10 mol percent water at a pressure between about 150 and about 400 p.s.i.g., then, treating said catalyst with a flow of hydrogen gas substantially free of water at a pressure of 150 and about 400 p.s.i.g., then treating said catalyst with a hydrogen-containing gas substantially free of water at a pressure of about 150 to about 400 p.s.i.g. at an elevated temperature and under static conditions, and then contacting the reduced catalyst with a light hydrocarbon oil under suitable reforming conditions in the presence of added water in the amount of 0.1 to about 10 mol percent.

7. A process for reforming naphtha fractions which comprises treating a molybdenum oxide catalyst which has been previously treated with an oxygen-containing gas with a hydrogen-containing gas substantially free of water at a pressure between about 150 and about 400 p.s.i.g. under static conditions to convert the catalyst to reduced form, then contacting said catalyst with a flow of a hydrogen-containing gas containing about 0.1 to about 10 mol percent of water at a pressure between about 150 and about 400 p.s.i.g., then contacting said catalyst with a flow of hydrogen-containing gas substantially free of water at a pressure of between about 150 and about 400 p.s.i.g. then treating said catalyst with a hydrogen-containing gas substantially free of water at a pressure between about 150 and about 400 p.s.i.g. under static conditions, and then contacting the reduced catalyst with a naphtha fraction at a temperature of about 850 to about 1050° F., under a total pressure of about 50 to about 500 p.s.i.g. at a weight space velocity of about 0.1 to about 2, using a hydrogen rate of about 1000 to 7500 s.c.f.b. and in the presence of about 0.25 to about 2 mol percent of water.

8. A process for reforming a light hydrocarbon oil which comprises treating a molybdenum oxide catalyst which has previously been treated with an oxygen-containing gas with a hydrogen-containing gas substantially free of water under static conditions at an elevated pressure to convert the catalyst to a reduced form and then contacting the reduced catalyst with a light hydrocarbon oil under suitable reforming conditions in the presence of dioxidized hydrogen and in the presence of added water in the amount of about 0.1 to about 10 mol percent.

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