

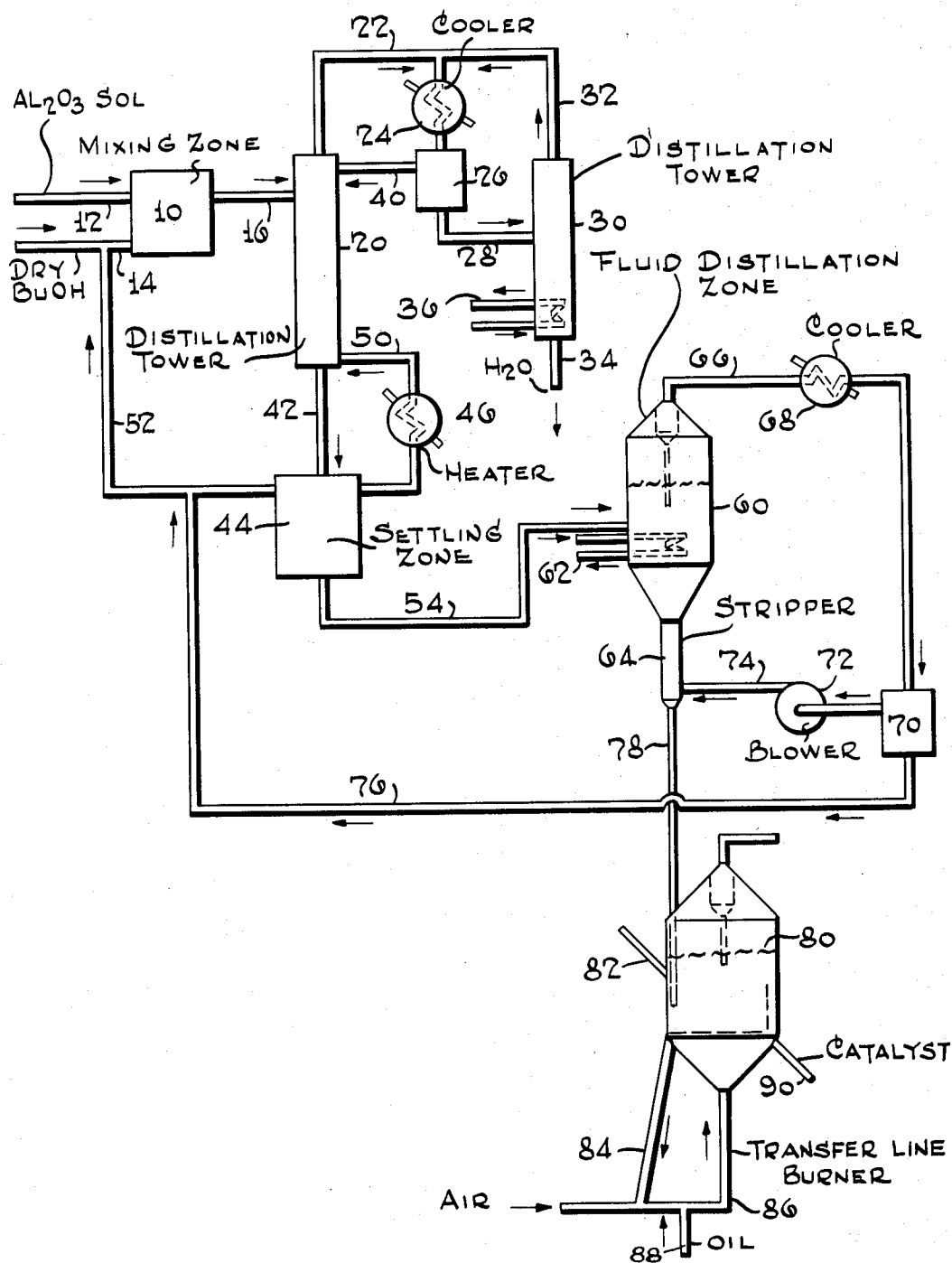
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HYDROFORMING PROCESS

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HYDROFORMING PROCESS

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6 Claims. (Cl. 196—50)

This invention relates to the catalytic conversion of hydrocarbons and particularly to the hydroforming of hydrocarbon fractions boiling within the motor fuel range of low knock rating into high octane number fuels rich in aromatics by contacting these fractions with metal oxide containing catalysts prepared in a certain way.

It is well known that petroleum naphthas can be subjected to reforming operations to yield liquid products boiling within the gasoline range and possessing improved octane numbers. Reforming operations employing catalysts, especially hydroforming and aromatization processes are widely used in the petroleum industry. By hydroforming is ordinarily meant a process wherein hydrocarbon fractions boiling within the motor fuel or naphtha range are treated at elevated temperatures and pressures in the presence of certain solid catalysts and hydrogen whereby the hydrocarbon fraction is increased in aromaticity with no net consumption of hydrogen. The term "aromatization" when used broadly refers to conversions which increase the aromaticity of the hydrocarbon fractions treated. As generally used in the petroleum industry, aromatization is a process in which hydrocarbon fractions are treated at elevated temperatures in the presence of solid catalysts and in the presence or absence of hydrogen, usually at pressures lower than those employed in hydroforming, for the purpose of increasing the aromaticity of the hydrocarbon fraction.

Catalytic reforming processes are usually carried out at temperatures of about 750–1150° F. in the pressure range of about 0 to 3000 lbs. per square inch and in the presence of such catalysts as molybdenum oxide, chromium oxide, nickel oxide or sulfide or any of a number of oxides or sulfides of metal of groups IV, V, VI, VII and VIII of the periodic system. These catalytic materials are usually dispersed or supported on a base or spacing agent. A commonly used spacing agent for this type of catalyst is alumina either precipitated or of the gel type. Catalysts which give favorable yields of aromatic gasoline components, particularly with certain feeds and at relatively low pressures, have been prepared upon zinc aluminate spinel supports.

Hydroforming and aromatization are the most promising methods available for upgrading motor fuel or naphtha fractions because of the high yield-octane number relationships and because the products obtained tend to give less engine deposits than thermally reformed naphthas. In view of the increasing demands for larger amounts of motor fuel of higher anti-knock characteristics, this field has been the subject for intensive investigation by many groups in an effort to find improved catalysts and techniques which will give larger yields and/or higher octane number products.

It is the object of this invention to provide the art with an improved method for hydroforming motor fuel fractions.

It is also the object of this invention to provide the art with an improved method for hydroforming motor

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fuel fractions with high yield-octane number relationships.

It is a further object of this invention to provide the art with a method for hydroforming motor fuel fractions which permits high throughputs of fresh feed and still yields high octane number products.

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

It has now been found that hydrocarbon fractions boiling within the motor fuel or naphtha range can be advantageously reformed or hydroformed by contacting the hydrocarbon vapors under reforming or hydroforming conditions with a hydroforming catalyst supported upon an alumina or zinc aluminate spinel base, the pore size and pore size distribution of which is controlled and adjusted by dehydrating the same in the presence of an at most partially water-miscible organic liquid. Normal butanol is preferred; however, isobutyl alcohol, secondary butyl alcohol, isoamyl alcohol, secondary amyl alcohols, and the like or mixtures of these may also be useful. In the preferred embodiment an alumina hydrosol is dispersed in the organic liquid, maintained dispersed therein until it has set to a hydrogel and is then dried in contact with the organic liquid to form dry, spherical, alumina particles that are characterized by possessing a low density and a high surface area with a preponderance of large pores, i. e. larger than 50 and preferably larger than 100 Angstrom units in diameter. A group VI metal oxide, preferably molybdenum oxide is incorporated before or after the alumina gel is formed and dried.

The catalyst base material or support is preferably alumina. The alumina may be obtained from an alumina sol prepared by treatment of aluminum metal with a dilute acid such as 1% acetic acid solution in the presence of mercury or a mercury compound or by hydrolysis under peptizing conditions of an aluminum alcoholate such as aluminum ethylate, propylate or preferably aluminum amylate in view of the ease of recovery of amyl alcohol from the hydrolysis reaction mixture.

The alumina sol may be converted to the hydrogel and then dried in contact with the partially water-miscible organic liquids named above. It is preferred, however, to disperse sol droplets in the partially water-miscible organic liquid whereupon sufficient water is removed to form spherical gel particles which, upon further drying in contact with the organic liquid, are converted to the low density, high surface area catalyst supports which are used in accordance with the present invention.

The catalytic metal oxides may be incorporated in a variety of ways. For example, the catalytic metal compound, for example ammonium molybdate can be incorporated in the alumina hydrosol or it may be incorporated in the set or dried alumina gel either by impregnation with a suitable solution or by dry mixing molybdc acid or a heat decomposable compound of molybdenum with the gel particles and heating to effect distribution of the molybdenum oxide upon the support.

Reference is made to the accompanying drawing illustrating a diagrammatic flow plan of a process for preparing microspherical catalysts that may be used in accordance with the present invention.

Referring to the drawing, into mixing zone 10 are introduced alumina sol by line 12 and dry normal butanol by line 14; the volume ratio of butanol to alumina sol is about 10 to 1 or more. In mixing zone 10 the Al_2O_3 sol is dispersed in the butanol in the form of small spherical droplets. The butanol extracts a part of the water from the sol droplets thus causing the droplets to harden into small spheres of hydrogel or semi-dry gel. The suspension of gel spheres in butanol is transferred by line 16 to distillation tower 20 where the water is distilled

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overhead in the form of the butanol-water azeotrope which passes through line 22 and condenser 24 into water-butanol separator 26. The lower layer of water containing a small amount of butanol is transferred from separator 26 by line 28 to distillation tower 30 where the butanol is distilled overhead through line 32 and condenser 24 into separator 26. Water freed of butanol is withdrawn from tower 30 by line 34. Tower 30 may be heated by coil 36. The upper layer of butanol containing some water is returned from settler 26 to tower 20 by line 40. The suspension of dehydrated gel microspheres in dry butanol is withdrawn by line 42 into settler 44 where it settles into an upper layer of clear, dry butanol and a lower layer of thickened slurry of gel microspheres in butanol. A part of the clear butanol may be vaporized in heater 46 and returned to tower 20 by line 50 in order to provide heat for tower 20. The remainder of the clear butanol is returned to line 14 by line 52. The thickened slurry of dehydrated gel microspheres is transferred from settler 44 through line 54 into fluidized solids distillation zone 60 which is heated by coil 62 and in which dried gel microspheres are fluidized by recirculated inert gas introduced into the bottom of stripping zone 64. The butanol associated with the gel microspheres is vaporized in distillation zone 60 and passes overhead with the fluidizing and stripping gas by line 66 through condenser 68 into gas-liquid separator 70 whence the gas is returned by blower 72 and line 74 into the lower section of stripping zone 64. The separated butanol is withdrawn from separator 70 and returned to line 14 by lines 76 and 52. The dried gel microspheres remaining in distillation zone 60 descend through stripper 64 where they are stripped of butanol by the ascending stripping gas. The dry gel microspheres freed of butanol are removed by line 78.

The dried gel microspheres may be discharged from line 78 into impregnation vessel 80. Molybdc acid, preferably in dry powder form, is introduced into vessel 80 through line 82. The resultant mixture is maintained as a dense fluidized mass and at temperatures of about 950° F. to 1500° F., preferably about 1250 to 1350° F. for a sufficient period, generally about 1 to 12 hours, preferably 2 to 4 hours, in order to permit the catalytic metal oxide to become uniformly distributed over the support. Catalyst descending through standpipe 84 is picked up by a stream of air entering transfer line burner 86. Oil, gas, or similar fuel introduced by line 88 is burned in transfer line burner 86 which discharges into the lower section of impregnation vessel 80, thus providing heat and fluidizing gas to the contents of vessel 80. It is important for best impregnation that an excess of air be employed in transfer line burner 86 over the amount needed to burn the fuel, in order to provide an oxidizing atmosphere in vessel 80 and thus prevent the reduction of the molybdc acid to a lower state of oxidation. Other means of heating vessel may be employed if desired. Finished catalyst is withdrawn from vessel 80 by line 90.

In place of the high temperature dry impregnation of the alumina microspheres, the latter may be impregnated by a wet technique with a solution of a molybdenum compound, if desired. For this purpose the microspheres from line 78 may be treated with a solution of ammonium molybdate containing the desired amount of molybdenum. The impregnated catalyst is then dried and, if desired, may be activated by high temperature treatment, for example, at 1200° F. to 1300° F. for about 6 hours. The finished catalyst may comprise from 5 to 20 wt. percent of molybdenum trioxide, preferably 8 to 15%. If desired, various stabilizers or promoters may be added such as the oxides of silicon, calcium, chromium, zirconium, titanium, zinc, or cobalt. When stabilizers or promoters are used, these may be added in amounts up to about 10 wt. percent of the finished catalyst, but are usually added in amounts of less than about 6 wt. percent.

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Catalysts prepared as described above are utilized in the hydroforming of motor fuel or naphtha fractions. The hydrocarbon feed stock may be a straight run or virgin naphtha, a cracked naphtha, a Fischer-Tropsch naphtha or the like. The feed stock is preheated alone, or in admixture with recycle gas to reaction temperature or to the maximum temperature possible while avoiding thermal degradation of the feed stock. Ordinarily, preheating of the feed stock is carried out to temperatures of about 800–1000° F., preferably about 950° F. The naphtha preheat should be as high as possible while avoiding thermal degradation thereof as by limiting the time of residence in the preheating coils as well as in the transfer or feed inlet lines. The preheated feed stock may be supplied to the reaction zone in admixture with hydrogen-rich recycle gas or it may be charged separately to the reaction zone. Contact of the reactants and catalyst may be effected in a fixed or a moving bed but is preferably effected in a dense fluidized bed of finely divided catalyst particles which are continuously circulated from the reaction zone to a regeneration zone and back into the reaction zone. The recycle gas, which contains from about 50 to 70 volume percent hydrogen is preheated to temperatures of about 1150 to 1200° F., preferably about 1185° F. The recycle gas should be circulated through the reactor at a rate of from about 1000 to 8000 cu. ft. per bbl. of naphtha feed. The amount of recycle gas added is preferably the minimum amount that will suffice to carry the necessary heat of reaction into the reaction zone and keep carbon formation at a satisfactory low level.

The hydroforming reaction zone should be operated at temperatures between about 850 and 950° F., preferably at about 900° F., and at pressures between about 50 and 500 lbs. per sq. inch. Temperatures above 900° F. result in increased carbon formation and lower selectivity to gasoline fractions while at temperatures below about 900° F. operating severity is low and would therefore require an excessively large reactor vessel. Lowering reaction pressure below 200 lbs. per sq. inch results in increased carbon formation which ordinarily becomes excessive at pressures below about 75 lbs. per sq. inch. Molybdenum oxide on zinc aluminate spinel catalysts appear to be somewhat of an exception in this regard since they give excellent results at pressures of about 50 lbs. per sq. inch. Above 200 lbs. per sq. inch, catalyst selectivity to light products (C₄'s and lighter) increases rapidly. The regeneration zone in a fluidized solids reactor system is operated at essentially the same pressure as the reaction zone and at temperatures of about 1100–1200° F. The time of residence of the catalyst in a fluidized solids system is of the order of about 3 to 4 hours in the reaction zone and of the order of from about 5 to 15 minutes in the regeneration zone.

The weight ratio of catalyst to oil introduced into the reactor in a fluidized solids system should be about 0.5 to 1.5. It is preferred to operate such systems at catalyst to oil ratios of about 1 since ratios above about 1 to 1.5 result in excessive carbon formation. Somewhat higher weight ratios can be used at higher pressures.

Space velocity or the weight in pounds of naphtha feed charged per hour per pound of catalyst in the reactor depends upon the age or activity level of the catalyst, the character of the feed stock and the desired octane number of the product. Space velocity for a molybdenum oxide on alumina gel catalyst prepared as described above may vary from about 0.8 wt./hr./wt. to about 3.0 wt./hr./wt.

The following example is illustrative of the results obtainable in accordance with the present invention.

EXAMPLE

Four samples of catalyst of essentially the same composition were tested in a fixed bed hydroforming unit to compare their activity.

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Catalyst A was a butanol dried alumina base hydroforming catalyst carrying 10 wt. percent MoO_3 . A nitrogen adsorption isotherm of this catalyst showed only a very small proportion of the pores, if any, to be less than 50–60 Angstrom units in diameter with the bulk of the pores being greater than 80 Angstrom units.

Catalyst B was prepared of the same materials in the same proportions as catalyst A except for the fact that the alumina was oven-dried at 250° F. instead of butanol dried.

Catalyst C has the same composition as catalysts A and B and was prepared by the impregnation of a pure, commercial activated alumina that was obtained as a product of the Bayer process.

Catalyst D has the same composition as catalysts A, B and C. It was a commercial gel type catalyst that was obtained by the co-precipitation of alumina and molybdenum oxide starting with a solution of an aluminum salt and a molybdenum compound such as ammonium molybdate.

The several samples of catalyst were heated for 6 hours at 1200° F. and the physical properties of the catalysts were then determined. The results of these tests are tabulated below in Table I.

Table I

Catalyst.....	A	B	C	D
Surface Area, M. ² /g.....	264	255	105	125
Pore Volume, cc./g.....	0.58	0.30	0.24	0.32
Alumina Phase.....	Eta	Eta	Gamma	Eta

The several samples of catalyst were used to hydroform a 200–330° F. virgin naphtha of 48.5 Research octane number in a fixed bed testing unit. The reaction zone was maintained at 900° F. and 200 lbs. per sq. inch with 1500 cu. ft. of hydrogen introduced per barrel of naphtha feed and was operated on a 4 hour cycle, i. e., naphtha feed and hydrogen gas were passed over the catalyst at hydroforming conditions for 4 hours, after which the coke deposit was burned from the catalyst with air, and the hydroforming process was resumed for another 4 hour period, and so on. The results obtained are summarized in Table II below, the comparison being made at 95 Research O. N. and 10# Reid Vapor Pressure Gasoline.

Table II

Catalyst.....	A	B	C	D
C ₄ -430° F. V. T. Gasoline, vol. percent yield on feed.....	86	86	87	87
Carbon, wt. percent on feed.....	0.2	0.5	0.4	0.4
W./Hr./w.* to give 95.0 O. N. Gasoline....	1.1–1.3	0.86	0.4	0.55

*Weight of naphtha feed per hour per weight of catalyst.

It appears from these data that the volume yield of C₄-430° F. gasoline at the 95 O. N. level is a standoff with the several catalysts tested. It should be noted, how-

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ever, that the catalyst A or butanol dried alumina base catalyst possessed much higher activity permitting feed rates of about 150 to 300% of those of the other catalysts tested. A further advantage of catalyst A is the low carbon make. Since carbon appears to be preferentially laid down in the minute pores of the catalyst, the low carbon make may be attributed to the substantial absence of small pores or pores smaller than about 50 Angstrom units.

The foregoing description contains a limited number of embodiments of the present invention. It will be understood, however, that the present invention is not limited thereto since numerous variations are possible without departing from the scope of this invention.

What is claimed is:

1. The method of hydroforming hydrocarbons which comprises subjecting the hydrocarbons at temperatures of 850–950° F., at pressures of from 50 to 500 lbs. per sq. inch and in the presence of hydrogen-rich gas to the action of a hydroforming catalyst consisting essentially of a group VI metal oxide supported upon a member of the group consisting of zinc aluminate and alumina gel that has been dried in the presence of a partially water-miscible alcohol to give a product with a high percentage of pores having diameters above 50 Angstrom units.
2. The method of hydroforming hydrocarbons which comprises subjecting the hydrocarbons at temperatures of 850–950° F., at pressures of from 50 to 500 lbs. per sq. inch and in the presence of hydrogen-rich gas to the action of a hydroforming catalyst consisting essentially of a group VI metal oxide supported upon alumina gel having a high percentage of pores above 50 Angstrom units obtained by dispersing an alumina hydrosol in butanol, converting the sol to gel and drying the resultant alumina gel particles in contact with butanol.
3. The method of hydroforming hydrocarbons which comprises subjecting the hydrocarbons at temperatures of 850–950° F., at pressures of from 50 to 500 lbs. per sq. inch and in the presence of hydrogen-rich gas to the action of a hydroforming catalyst consisting essentially of a group VI metal oxide supported upon alumina gel having a high percentage of pores above 50 Angstrom units obtained by drying alumina hydrogel in contact with butanol.
4. The process as defined in claim 1 in which the group VI metal oxide is molybdenum oxide.
5. The process as defined in claim 2 in which the group VI metal oxide is molybdenum oxide.
6. The process as defined in claim 3 in which the group VI metal oxide is molybdenum oxide.

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