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(54) PROCESS FOR TREATING THE OIL-RICH PHASE OF SYNTHESIS PRODUCT

(54) PROCÉDE POUR LE TRAITEMENT DE PHASE D'HUILE GRASSE DE PRODUIT SYNTHETIQUE

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ABSTRACT:

CLAIMS: [Show all claims](#)

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This invention relates to a process for treating synthesis product obtained by the catalytic conversion of hydrogen and carbon monoxide into synthetic fuel. More specifically this invention discloses a process for treating the synthesis product so as to substantially free it from the oxygenated compounds produced as by-products.

Vapor phase treatment of the oil-rich phase of synthesis product with surface active contact materials for octane improvement is well known in the art. The octane rating of the gasoline fraction of synthesis product is substantially improved by treating the oil-rich phase with contact materials such as bauxite and Fullers earth. Treatment of the oil-rich phase with such adsorptive materials not only deoxygenates the oxygen-containing organic compounds, but also effects olefin isomerization of the product material with accompanying octane improvement. The treatment of the synthesis product with such contact materials converts product olefins which are mainly alpha in nature to olefins containing the double bond nearer the center of the molecule; which latter olefins are substantially higher in octane rating than alpha olefins.

This invention provides a method for deoxygenating the oxygen-containing by-products of synthetic fuel without effecting substantial isomerization of either the olefins initially present in synthesis product or those olefins formed by the deoxygenation process. The process of the invention is particularly useful in treating the gas oil fraction of synthesis product. It is advantageous to deoxygenate the gas oil fraction, but the olefin isomerization which normally accom-

panies the deoxygenation process decreases the value of the gas oil fraction as diesel fuel because the cetane rating of the gas oil fraction is substantially lowered. This invention provides a method for effecting deoxygenation of the gas oil fraction without concomitant substantial olefin isomerization. As a consequence the cetane rating of the gas oil fraction is maintained at a high level.

In accordance with this invention the oil-rich phase of synthesis product is contacted at elevated temperature with a base-promoted oxide of aluminum, titanium or thorium or alkali-promoted mixtures thereof. Contact of the oil-rich phase of synthesis product or a fraction thereof with base-promoted alumina, titania or thoria deoxygenates the oxygen-containing organic compounds contained therein without causing substantial isomerization of the olefinic components of synthesis product. Alumina is the preferred treating agent and will be mainly employed to illustrate the process of the invention. Alkali metal oxides are the preferred promoters, but alkaline earth metal oxides may also be employed. The treating agent may be maintained alkaline by the continuous introduction of ammonia together with the oil-rich phase.

Catalytic conversion of carbon monoxide and hydrogen into synthetic fuel by contact with a fluidized iron catalyst at an elevated temperature of 500 to 750° F. and at a pressure of 100 to 500 pounds per square inch results in the formation of a product comprising a gas phase and liquid phase, the latter consisting of approximately one part oil phase and two

parts water phase. Oxygen-containing organic compounds such as alcohols, acids, esters, ketones and aldehydes are distributed throughout the two-phase liquid product; the molecular weight of the oxygen-containing organic compounds determines whether they are primarily found in the water-rich phase or in the oil-rich phase. The oxygen-containing organic compounds ordinarily found in the water-rich phase comprise lower molecular weight compounds such as C<sub>1</sub> to C<sub>6</sub> alcohols, esters containing up to about four carbon atoms and C<sub>2</sub> to C<sub>6</sub> organic acids with traces of higher molecular weight compounds. The oxygen-containing organic compounds ordinarily found in the oil-rich phase comprise higher molecular weight compounds such as C<sub>4</sub> and higher alcohols, esters containing more than three carbon atoms, C<sub>3</sub> and higher organic acids and traces of lower molecular weight compounds. The considerable overlapping in the distribution of the oxygen-containing compounds between the oil-rich and water-rich phase is due to the fact that the compounds of intermediate molecular weight such as C<sub>5</sub> alcohols are found in substantial proportion in both the oil-rich phase and the water-rich phase.

While it is true that the oxygen-containing by-products of synthesis conversion are valuable chemicals, it is often desirable to obtain a maximum yield of fuel, particularly gasoline and diesel fractions, from synthesis gas conversion. Deoxygenation of the oxygen-containing organic compounds present in synthesis product offers a simple procedure for obtaining a maximum yield of synthesis fuel. The subject

invention provides a method for effecting such deoxygenation without causing substantial olefin isomerization. As indicated previously, deoxygenation without olefin isomerization is particularly advantageous in treatment of the gas oil fraction of synthesis product since thereby a diesel oil of good cetane rating can be obtained. The process of the invention is advantageously applied to the treatment of the gasoline fraction when it is desirable to obtain a gasoline fraction rich in alpha olefins. Alpha olefins boiling within the gasoline fraction are excellent starting materials for the manufacture of chemical specialty products by processes such as the carbonylation reaction, that is, the reaction of olefins with CO and H<sub>2</sub> to produce carbonyl compounds.

The treating agents used in this invention contain base measured as alkali metal oxide or as alkaline earth metal oxide of at least 0.1 to 3.0 per cent. The base can be incorporated in the alumina, thoria or titania during their preparation. Alkaline solutions may be employed to precipitate the treating agents from solution of the soluble salts of aluminum, titanium and thorium. The hydroxides, carbonates, and bicarbonates of alkali metals such as sodium, potassium, lithium, etc., are advantageously employed as precipitating agents. However, a basic substance such as alkali metal oxides or alkaline earth metal carbonates may be added to the catalyst after its preparation. It is also possible to maintain the alumina, titania or thoria treating agent on the alkaline side by continuously incorporating ammonia or an

ammonia compound such as ammonium hydroxide into the oil-rich phase subjected to the deoxygenating treatment. The addition of as little as 1 per cent ammonia to the oil-rich phase maintains the treating agent on the alkaline side during the vapor phase deoxygenation treatment.

The oil-rich phase of synthesis product is contacted in the vapor phase with base-promoted treating agent at a temperature between 500 and 1000°F. It is possible to employ diluent gases such as gaseous by-product of synthesis conversion, flue gas and gaseous hydrocarbons such as methane, to aid in the maintenance of the synthesis product in the vapor phase during the contact of the oil-rich phase with treating agent such as base-promoted alumina. Advantageously, the oil-rich phase is fractionated into a gasoline fraction and gas oil fraction prior to deoxygenation. The gas oil fraction is preferably contacted in the vapor phase with a base-containing treating agent of the described type at a temperature between 650 and 950°F. whereas contact of the gasoline fraction is advantageously effected at a temperature between 500 and 700°F. When the total oil-rich phase of synthesis product is treated in accordance with the process of this invention, the temperature is advantageously maintained between 600 and 850°F.

It is possible to employ pressures from atmospheric to 500 pounds per square inch for contacting the oil-rich phase of synthesis product with base-promoted alumina, but atmospheric pressure is ordinarily employed since it is easier to maintain vapor phase operation thereat. However, an attractive modification of the invention involves contacting the

oil-rich phase of synthesis product in the vapor phase with base-containing alumina at a pressure equivalent to that prevailing in the synthesis reaction zone, namely, a pressure of 200 to 400 pounds per square inch.

5 The oil-rich phase is contacted with base-promoted treating agent at a space velocity between about 1 and 10 volumes of liquid product per volume of treating agent per hour. Space velocities between about 2 and 5 are preferred and are most often employed in the process of this invention.

10 Advantageously, the deoxygenation of the oil-rich phase by contact with base-promoted alumina, titania, thoria is effected in the presence of a small quantity of steam of the order of 10 weight per cent or less. The catalyst is kept clean during the process by the addition of steam with the re-  
15 sult that the catalyst life is substantially increased. A portion of the water phase separated from synthesis product is advantageously used to provide the diluent steam. The oxygen-containing organic compounds present in the portion of the water phase employed as diluent steam are deoxygenated by  
20 contact with the base-promoted alumina, so that the water, after separation from the treated oil-rich phase, can be rejected without contaminating the stream into which it is emptied.

25 It is possible to effect vapor phase contacting of the oil-rich phase or a fraction thereof with base-promoted treating agent in accordance with any of the usual techniques for catalytic vapor phase contact. Accordingly, the oil-rich phase in the vapor state can be passed through a fixed bed of

solid particulate base-promoted alumina maintained at a temperature of 500 to 1000° F. or can be contacted with a fluidized bed of base-promoted alumina. The vaporized oil-rich phase can also be contacted with a moving bed or with a stirred bed of base-promoted treating agent.

The oil-rich phase after treatment with alumina, titania or thoria having an alkali content of 0.1 to 3.0 weight per cent alkali metal oxide or alkaline earth metal oxide is substantially free from oxygen-containing organic compounds. The effect of contacting the oil-rich phase of synthesis product in the vapor state with an agent of the described type is illustrated by the results obtained when contacting the oil-rich phase at a temperature of 850° F. with alumina having a sodium oxide content of about 0.5 per cent. The oil-rich phase after separation from liquid product at atmospheric conditions had an alcohol content of 8 volume per cent, an ester content of 3 volume per cent, an acid content of 3 volume per cent as indicated by saponification, neutralization and hydroxyl numbers. After treatment under the aforescribed conditions with base-promoted alumina, the oil-rich phase had an alcohol content of 2 volume per cent and contained substantially no esters and acids. In Table I, there is shown the effect of contacting the oil-rich phase of synthesis product with alumina containing about 0.5 per cent Na<sub>2</sub>O; the changes in the saponification, neutralization and hydroxyl numbers are striking.



TABLE I

Effect of Base-Promoted Alumina on Oil-Rich Phase

|   | <u>Untreated Oil-Rich Phase of<br/>Synthesis Product</u> | <u>Oil-Rich Phase After Contact<br/>with Base-Promoted Alumina</u> |
|---|--|--|
| 5 | Sap. No. 40  | 1  |
|   | Neut. No. 15   | 1  |
|   | Br. No. 85   | 100  |
|   | OH No. 25  | 7  |

The effect of this treatment on olefin isomeriza-  
 10 tion is illustrated in Table II wherein there are shown the  
 cetane numbers of the diesel fraction and octane numbers of  
 the naphtha cut before and after contact with base-containing  
 alumina. For comparative purpose there are also included in  
 15 Table II the octane and cetane ratings of the gasoline and gas  
 oil fractions of an oil-rich phase which was contacted with a  
 conventional treating agent such as bauxite.

TABLE II

Effect of Base-Promoted Alumina on Olefin Isomerization

|    | <u>Cetane No. of Diesel Cut</u>                                  | <u>Clear Octane No. (CFRM) of Naphtha<br/>Cut</u> |
|----|--|---|
| 20 | Untreated Synthesis<br>Product 41.5                              | 60.0  |
|    | Synthesis Product<br>Treated with base-<br>promoted Alumina 37.0 | 67.1  |
| 25 | Synthesis Product<br>Treated with<br>Bauxite 31.3                | 75.9  |

It is apparent from Table II that contact of the  
 oil-rich phase with base-promoted alumina has substantially  
 30 less effect on the cetane number of the diesel fraction and  
 the octane number of the naphtha fraction than contact with  
 a conventional treating agent such as bauxite. The cetane

rating of the diesel fraction is lowered from 41.5 to 37.0 by treating with alkali-promoted alumina, whereas it is lowered to 31.3 by bauxite treatment; the octane number is raised from 60 to 67.1 by treating with alkali-promoted alumina, and to 75.9 by bauxite treatment. It is readily apparent that olefin isomerization is substantially minimized by treatment of the synthesis product with base-promoted alumina. The production of olefins from the oxygen-containing organic compounds accounts for a substantial portion of the cetane lowering and octane improvement effected by contact with the base-promoted alumina.

The primary advantage of the process of the subject application resides in the fact that the gas oil fraction is deoxygenated without suffering too great a loss in cetane rating.

Another advantage of the subject invention is that it anticipates the time when oxygen-containing organic compounds normally present in synthesis product, which are at present in demand as chemicals of commerce, have become a glut on the market because of the huge supplies available from a plurality of synthetic fuel plants. In such instance this invention provides a method for converting a major portion of oxygen-containing organic by-products into fuel by deoxygenation without olefin isomerization.

In the accompanying figure there is presented a flow diagram wherein a preferred modification of the subject invention is described in detail. In the modification described hereafter only the diesel fraction of synthesis product will be subject to contact with base-promoted alumina.

Hydrogen and carbon monoxide are introduced through a pipe 1 into a synthesis reactor 2 wherein conversion of carbon monoxide and hydrogen into liquid hydrocarbons is effected by contact with an iron catalyst maintained in a fluidized state at a temperature between 500 and 700° F. and at a pressure between 150 and 500 pounds per square inch.

An effluent comprising unconverted hydrogen and carbon monoxide, products of reaction comprising water, gaseous and liquid hydrocarbons, and oxygen-containing organic compounds issues from the synthesis reactor 2 through a pipe 3 and is introduced into a heat exchanger 4 wherein the product is cooled to a temperature between 150 and 400° F., preferably 200 to 300° F., without any reduction in pressure. Thereafter the effluent is introduced through pipe 5 into a separator 8 maintained at a temperature between 150 and 400° F. and at a pressure between 150 and 500 pounds per square inch. In the separator 8 the synthesis effluent is separated into a gas phase, an oil-rich phase, and a water-rich phase.

It is advantageous to effect separation of synthesis product into a gas phase, an oil-rich phase, and a water-rich phase at temperature between 150 and 400° F. and at a pressure equivalent to that prevailing in the synthesis reactor. Separation of the synthesis product into a gas, a water-rich, and an oil-rich phase at an elevated temperature and pressure effects displacement of normally water-soluble, oxygen-containing organic compounds from the water-rich phase to the oil-rich phase. Subsequent vapor phase treatment of the oil-rich phase with basic alumina gives a greater yield

of synthetic fuel when normally water-soluble organic compounds have been displaced from the water-rich phase to the oil-rich phase prior to the deoxygenation treatment.

5 However, it must be understood that this invention is not limited to a process wherein the synthesis product is separated into gas, oil and water phases at elevated temperature and pressure prior to treatment with base-promoted alumina, titania and thoria. The deoxygenating treatment of this invention is applied with excellent results to a synthesis product which has been separated into gas, oil-rich and  
10 water-rich phases at atmospheric conditions.

The gas phase is removed from the separator 8 through a pipe 9, through which it is recycled to the synthesis reactor 2 so that a recycle ratio of recycle gas to fresh  
15 feed between about 1:1 and 5:1 is maintained. A draw-off pipe 10 affords a means of withdrawing a portion of the non-recycled gas phase. Advantageously a portion of the gas phase is employed as a gaseous diluent for the contact of the oil-rich phase in the vapor state with alkali-promoted alumina.  
20 To this end a pipe 11 connects with pipe 9 and serves as a conduit for introducing a portion of the gas phase into the treating zone wherein the oil-rich phase contacts treating agent.

The water-rich phase is withdrawn from the separator 8 through a pipe 14. This water phase may contain from  
25 5 to 20 per cent oxygen-containing organic compounds depending on the temperature prevailing in separator 8. The oxygen-containing organic compounds present in the water phase

comprise low molecular weight organic acids, such as acetic and propionic acids, low boiling aliphatic alcohols, such as ethyl and propyl alcohols, and minor quantities of low-boiling aldehydes, ketones and esters. The non-acidic, oxygen-containing organic compound content of the water phase is substantially reduced by separation of the synthesis product into gas, water and oil phases at elevated temperature and pressure.

The water-rich phase is advantageously introduced through pipe 14 into a stabilizer 38 wherein alcohol-water azeotropes are flashed from the water phase and are taken off overhead from the stabilizer 38 through a pipe 39. The bulk of the water phase is withdrawn from stabilizer 38 through pipe 40. A portion of this water phase is advantageously used as steam diluent for the vapor phase contacting of the oil-rich phase with base-promoted treating agent. A pipe 41 connects with a pipe 40 and serves as a means of withdrawing a portion of the water-rich phase to serve as diluent steam in the vapor phase contacting. The bulk of the water-phase is made suitable for disposal by processes which are disclosed in co-pending applications.

The oil-rich phase is withdrawn from the separator 8 through a pipe 16 and is thereby introduced into a fractionating tower 17 wherein it is separated into a gasoline fraction and a gas oil fraction by fractional distillation. The gasoline fraction is taken off overhead from the fractionating tower 17 through a pipe 18. The gasoline fraction is ordinarily contacted with an adsorbent, such as Fullers earth and bauxite at a temperature between 700 and 850° F. whereby

oxygen-containing organic compounds present therein are de-oxygenated, and the octane rating of the gasoline is substantially increased as a result of olefin isomerization. It is also possible to extract oxygen-containing organic compounds from the gasoline fraction by solvent extraction with sol-  
5 vents such as ethanol, glycol and aqueous methanol prior to contacting with an adsorbent at elevated temperature for octane improvement.

It is also feasible to contact the gasoline frac-  
10 tion with base-promoted alumina, thoria or titania in accordance with this invention in order to provide a gasoline fraction rich in alpha olefins. However, in order to simplify this detailed description of the invention, only the gas oil fraction will be contacted with base-promoted alumina.

A gas oil fraction is withdrawn from the fractiona-  
15 ting column 17 through a pipe 20. This gas-oil fraction may contain from 5 to 25 per cent oxygen-containing organic compounds which are distributed between acids, alcohols, esters, aldehydes and ketones. This gas oil fraction has a cetane  
20 rating of approximately 41. The gas oil fraction is introduced through pipe 20 into a heat exchanger 21 wherein it is vaporized and raised to a temperature between 650 and 900° F. and preferably to about 750° F. A portion of the water phase combines with the gas oil fraction in pipe 20 and is vaporized  
25 therewith in exchanger 21. This added water phase ordinarily constitutes 10 or less weight per cent of total gas oil fraction.

The gas oil fraction and added water phase at a temperature of about 750° F. leaves the heat exchanger 21

through a pipe 22. A portion of the gas phase separated from synthesis product in separator 8 flows through the pipe 11 and combines with the vaporized gas oil fraction in the pipe 22. Prior to combination with the vaporized gas oil fraction, the diluent gas phase is raised to a temperature of about 700° F. in a heat exchanger 24.

The vaporized gas oil fraction, gaseous diluent and diluent steam are introduced to a treating zone 26 wherein it contacts alumina containing about 0.5 per cent sodium oxide at a temperature between 650 and 900° F. Treatment of the gas oil fraction in the vapor state with base-promoted alumina results in substantially complete deoxygenation of the gas-oil fraction. However, olefin isomerization is substantially minimized by the treatment.

The deoxygenated gas oil fraction issues from the treating zone 26 through a pipe 27 and is introduced into a heat exchanger 28 wherein it is cooled to atmospheric conditions. Thereafter the condensed gas oil fraction is introduced through a pipe 29 into a separator 30 wherein diluent water is separated from the condensed gas oil fraction. The separated water is substantially free from oxygen-containing compounds as a result of the deoxygenation treatment and may be rejected through pipe 34 without fear of polluting a river. The gas oil fraction is then introduced through pipe 31 into a fractionating tower 32 wherein the treated gas oil fraction is separated into a high-boiling residue, a diesel fraction, and small gaseous fraction formed by contact of the gas oil fraction with base-promoted alumina.

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The gaseous fraction is taken off overhead from the fractionating tower 32 through a pipe 33 and is recycled there-  
through to the synthesis reactor 2. The pipe 33 leads into  
the pipe 9 through which the gas phase separated from synthe-  
sis product is recycled to the synthesis reactor. This gaseous  
fraction comprises mainly gaseous olefinic hydrocarbons, such  
as ethylene, propylene, butene and amylene. This gaseous  
fraction constitutes about 0.5 to 10.0 per cent of the gas  
oil fraction contacted with alumina and is approximately 90  
per cent olefinic in nature. This gaseous fraction is an ex-  
cellent recycle gas to the synthesis reactor, since it sub-  
stantially increases the yield of condensable hydrocarbons  
formed during the synthesis reaction.

A diesel fraction substantially free of oxygen-  
containing organic compounds is withdrawn from the fractiona-  
ting tower 32 through a pipe 35. This diesel fraction consti-  
tutes approximately 75 to 95 per cent of the gas oil fraction  
fed to the treating zone 26. This diesel fraction contains  
less than 2 weight per cent oxygen-containing organic compounds  
and has a cetane rating of substantially the same as the un-  
treated gas oil fraction.

A high boiling residuum comprising approximately 5  
to 25 per cent of the gas oil fraction fed to the treating  
zone 26 is withdrawn from the fractionating column 32 through  
a pipe 36. This high-boiling residuum has a boiling point  
over 650° F.

The above detailed description presents only a pre-  
ferred modification of the subject invention. Another modi-



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5 fication comprises contacting the total oil-rich phase of synthesis product with base-promoted alumina, titania, thoria in the vapor phase at a temperature between 600 and 1000° F. It is also feasible to treat both the gasoline fraction and the gas-oil fraction separately with the base-promoted treating agent of the type described in this invention.

10 Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and, therefore, only such limitations should be imposed as are indicated in the appended claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for treating the oil-rich phase of the synthesis product obtained by catalytic conversion of carbon monoxide and hydrogen, which comprises separating an oil-rich phase from said synthesis product and contacting said oil-rich phase in the vapor state at a temperature between 500 and 1000°F. with a treating agent comprising a metal oxide selected from the group consisting of alumina, titania, thoria and mixtures thereof and 0.1 to 3.0 weight per cent of a promoter selected from the group consisting of alkali metal oxides, alkaline earth metal oxides and mixtures thereof.

2. A process according to Claim 1 in which the treating agent is alumina.

3. A process according to Claim 1 in which the treating agent comprises alumina and an alkali metal oxide.

4. A process according to Claim 1 in which the treating agent comprises alumina and an alkaline earth metal oxide.

5. A process according to Claim 1 in which the oil-rich phase is fractionated into a gas oil and gasoline fraction and the gas oil fraction is contacted with the treating agent.

6. A process for treating the oil-rich phase of the synthesis product obtained by catalytic conversion of carbon monoxide and hydrogen, which comprises separating an oil-rich phase from said synthesis product, adding ammonia to said oil-rich phase and contacting said ammonia-containing oil-rich phase in the vapor state at a temperature between

and 1000°F. with a treating agent comprising a metal oxide selected from the group consisting of alumina, titania, thoria and mixtures thereof and 0.1 to 3.0 weight per cent of a promoter selected from the group consisting of alkali metal oxides, alkaline earth metal oxides and mixtures thereof.

7. A process according to Claim 6 in which the added ammonia constitutes less than 2 weight per cent of the oil-rich phase.

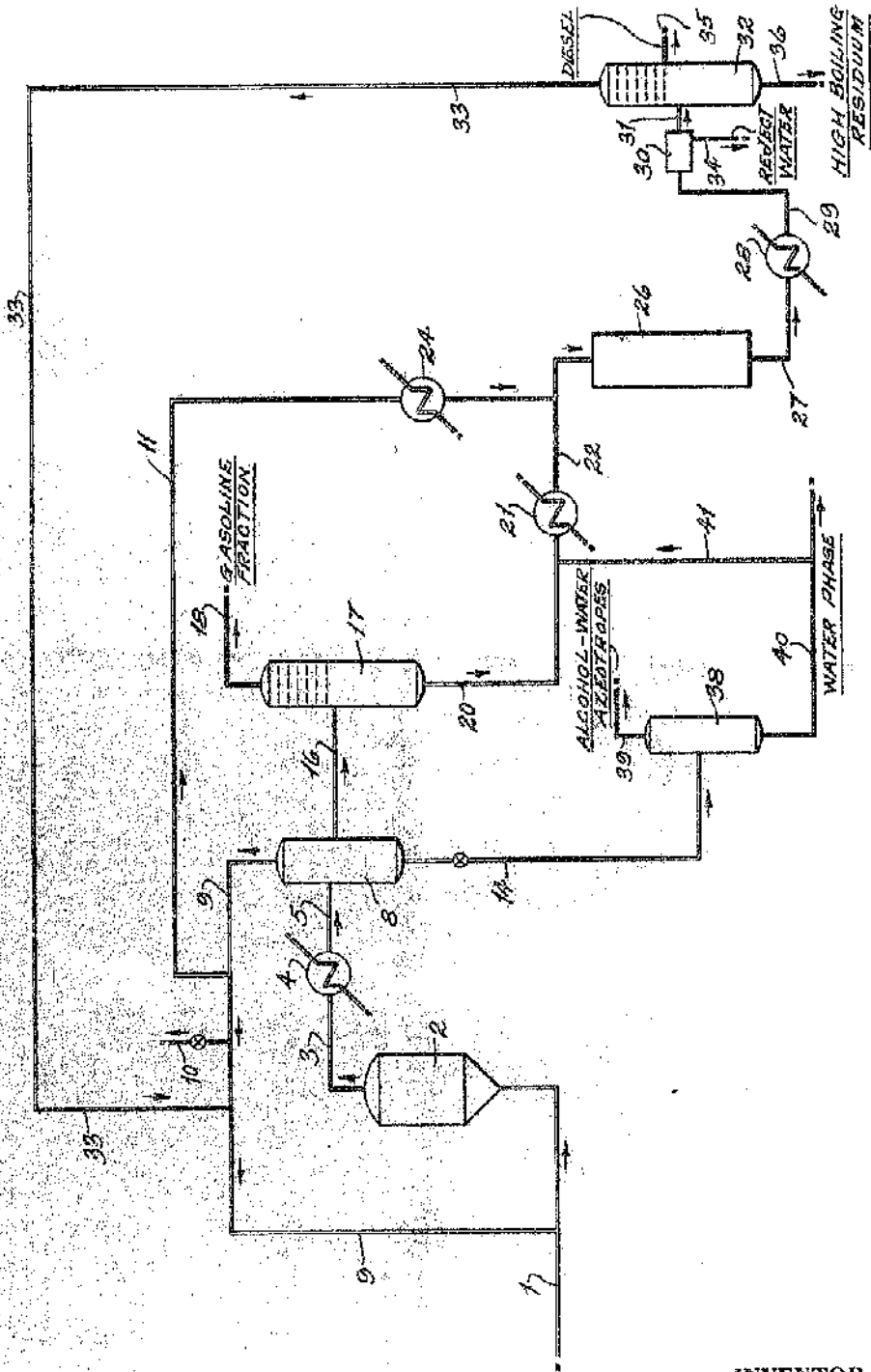
8. A process for treating the oil-rich phase of the synthesis product obtained by catalytic conversion of carbon monoxide and hydrogen, which comprises separating said synthesis product into an oil-rich phase and a water-rich phase, contacting said oil-rich phase in the vapor state in the presence of added steam at a temperature of 500 to 1000°F. with a treating agent comprising a metal oxide selected from the group consisting of alumina, titania, thoria and mixtures thereof and 0.1 to 3.0 weight per cent of a promoter selected from the group consisting of alkali metal oxides, alkaline earth metal oxides and mixtures thereof.

9. A process according to Claim 8 in which the added steam is obtained from a portion of the water-rich phase separated from the synthesis product.

10. A process for treating the oil-rich phase of the synthesis product obtained by catalytic conversion of carbon monoxide and hydrogen, which comprises separating said synthesis product into an oil-rich phase, a water-rich phase and a gaseous phase, contacting said oil-rich phase in the vapor state in the presence of a gaseous diluent at a temperature of 500 to 1000°F. with a treating agent comprising a metal oxide

lected from the group consisting of alumina, titania, thoria and mixtures thereof and 0.1 to 3.0 weight per cent of a promoter selected from the group consisting of alkali metal oxides, alkaline earth metal oxides and mixtures thereof.

11. A process according to Claim 10 in which the gaseous diluent is derived from the gas phase separated from the synthesis product.



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