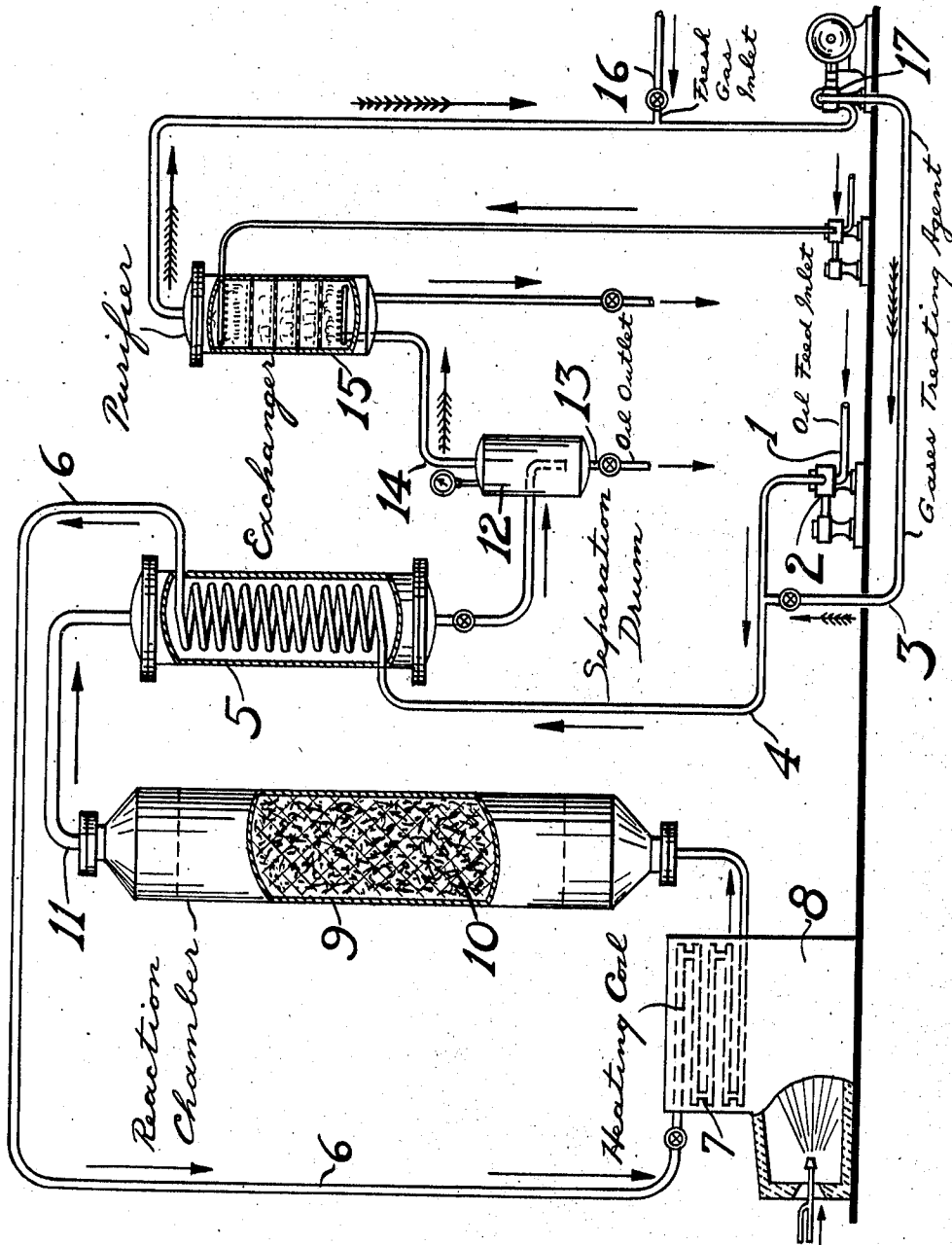


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PROCESS OF RECONSTITUTING AND DEHYDROGENATING HEAVIER
HYDROCARBONS AND MAKING AN ANTIKNOCK GASOLINE
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PROCESS OF RECONSTITUTING AND DE-HYDROGENATING HEAVIER HYDROCARBONS AND MAKING AN ANTIKNOCK GASOLINE

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This invention relates to a process of reconstituting and dehydrogenating heavier hydrocarbons and making anti-knock gasoline and relates specifically to the heating of liquid normally and preferably relatively heavy hydrocarbons preferably in vapor phase and preferably above critical temperature in a compressed atmosphere or vehicle of a hydrocarbon fixed gas, with or without small proportions of other gases such as nitrogen, carbon monoxide, carbon dioxide, ammonia, and the like, preferably in the absence of hydrogen in essential predominating and hydrogenating proportions.

The raw hydrocarbon material employed preferably is of the mineral oil type, that is petroleum oil, shale oil, and the like, and their various distillates, also distillates obtained from coal and even in some cases coal itself used in a powdered state preferably in suspension in one of the oils mentioned above.

The fixed gas vehicle may be a hydrocarbon gas such as natural gas and so forth, but preferably is refinery gas especially cracking still gas, that containing gaseous unsaturates being preferred. In this case hydrogen also may be present in various proportions, but usually as a minor constituent frequently in an amount represented by only a few percent, the effect of such hydrogen being overcome in carrying out the present invention by causing suitable dehydrogenation to obtain volatile liquid products of the gasoline type having high anti-knock values.

In some cases the gas obtained from cracking stills may be sufficiently impure so that washing is required to remove oxygen, hydrogen sulphide and other unneeded gases. Cracking still gas which has been washed with alkali and then passed through fairly concentrated sulphuric acid to remove higher unsaturates for the purpose of hydrolyzing them to alcohols may be used appropriately in some cases. Gas of this character will contain ethylene but the major part of the higher unsaturates will be removed. In other cases the spent gases of hydrogenation plant used for treating petroleum oils may be used.

The fixed gas used is substantially non-reactive under the operating conditions, that is, it is an inert gas which does not enter into the reaction appreciably. Other inert gases such as nitrogen may also be used.

The ratio of the fixed gas vehicle to oil usually is rather high, preferably in the neighborhood of 100 up to 300 cubic feet (calculated at atmospheric pressure) to 1 gallon of oil to be treated.

The temperature preferably is between 900 and

1000° F. although higher or lower temperatures may be used in some cases. For example, temperatures of the order of 860° F. (460° C.) and as low as 662° F. (350° C.) may be used. Time and temperature may vary in the present process just as they do in ordinary cracking process and adequate time should of course be provided for the splitting reaction just as in cracking under similar temperature conditions.

The pressure should be elevated well above atmospheric, preferably operating in the neighborhood of 200 to 300 atmospheres or higher, e. g., 500 to 1000 atmospheres.

The temperature and pressure preferably are above the critical points of the oil used, or at least above the critical points of the major portion of the constituents thereof.

When coal is to be treated a modification of the process is required involving liquid phase operation.

Preferably a catalyst is employed which has the property of accelerating the reconstitution of the oil, such catalyst preferably being resistant to sulphur, or sulphactive. The oxides or oxysulphides of chromium, molybdenum, tungsten and cobalt may be employed, especially mixtures of these such as a mixture in which a chromium compound forms the major part, the balance being made up of compounds of molybdenum and/or tungsten. Sulphactive catalysts of this character may be employed in finely divided state in suspension in the oil and removed therefrom after their catalytic action has been sufficiently exerted on the oil. Preferably, however, the catalyst is employed in the form of lumps and for this purpose may be formed into shaped masses such as briquettes or cubes using magnesium oxide or aluminum oxide or mixtures of these as the supporting and promoting agent.

To facilitate dehydrogenation I preferably use as the raw material an oil which is rich in sulphur or I may add free sulphur to the oil. Sulphur has the advantage of being a volatile catalyst, travelling with the oil through the zone of reconstitution where contact is reached with the reconstituting catalysts and then by the reactions which take place may be eliminated from the volatile liquid products desired.

Other dehydrogenating catalysts may be used, including selenium, tellurium, and the like, but sulphur is cheap and readily available as well as volatilizing readily. In some cases an oil will be found in the natural state rich enough in sulphur to be used in admixture with another raw oil stock which is low in sulphur.

The process is preferably carried out in a continuous or non-cumulative manner as, for example, by passing the oil and gas vehicle through a heating zone in which a reconstituting catalyst may or may not be present. In actual operation it is preferable to pass the oil and gas vehicle through a preheater or heat exchanger where heat is derived from products leaving the reaction zone. From the preheater the mixture then may be passed to a heating coil heated by externally applied heat and then enters the reactor or reaction chamber through coming in contact with the reconstituting catalyst present or if these are absent then being subjected to a temperature where cleavage or splitting occurs, this change taking place in the presence of the sulphur bodies acting as dehydrogenating catalysts, thereby tending towards the formation of unsaturated compounds and cyclic bodies of lower hydrogen content and of improved anti-knock qualities.

On leaving the reactor the current of gas and vaporous liquid products are preferably passed through a heat exchanger as indicated and through suitable condensing means the liquid products being separated from the gas and the latter preferably recycled in order that they may be again available for use in the operation. Any part of such gases not needed for the purpose may be discarded, used as a fuel or otherwise employed. The light liquid products of the condensate are especially desired, the heavy liquid residues as a rule being returned to the reaction zone or passed into another reaction zone where temperatures, pressures, catalysts, and so forth, may be differently adjusted to meet special conditions desired.

In the present invention it is an object to carry out the cleavage of the heavy hydrocarbon from which useful volatile liquid products are to be obtained, in such a manner that polymerization will be greatly reduced or eliminated, thereby overcoming the formation of coke and the like which offers great difficulties in ordinary cracking operations. In order to prevent polymerization of an objectionable character each of the molecules of the heavy oil are separated as far as feasible by the employment of a spacing proportion of the fixed hydrocarbon gas; this spacing proportion being adequate to prevent molecular collision during cleavage in a manner such that unsaturated radicals or fragments of the oil have no opportunity to combine to relatively heavy products before the current of oil and gas has passed from the reactor into the condensing chamber.

Referring to the drawing, numeral 1 denotes the feed line through which the oil is forced by pump 2. The oil is mixed with a gaseous treating agent which is supplied under high pressure from line 3, the composition of which is disclosed above, and the mixture flows through a pipe 4 and a heat exchanger 5, thence by line 6 to a fired coil 7 mounted in the furnace setting 8. The preheated mixture then flows through a reaction chamber 9 which may be supplied with a suitable catalytic agent indicated at 10, the composition of which is disclosed above.

The products leaving the reaction chamber by line 11 flow to the heat exchanger 5 mentioned above, and then pass into a separation drum 12, from which condensed oils flow to storage, not shown, by line 13 and gaseous products are drawn off by pipe 14 to a purifier 15 which is in the form of a scrubbing tower. By proper adjust-

ment of the quantity of scrubber oil, temperature and other conditions, a large portion of the hydrogen sulfide may be removed from the gas. A considerable quantity of methane and other hydrocarbon gas is generally removed with the hydrogen sulfide and is lost in this manner. Fresh gas is added by line 16 and this composition is so adjusted as to control the composition of the total mixture in accordance with the principles outlined above. The gas mixture is compressed by a pump 17 and forced through the pipe 3 mentioned above for circulation through the system. Flow meters (not shown), or other control means, should be placed on the various gas lines and on the liquid oil feed pipe so as to properly adjust the volume of oil and gas in accordance with the present invention.

In the following examples the proportions of oil to gas are expressed in gallons and cubic feet respectively, this being a simple and easily understood ratio. For example, oil:gas is equivalent to 1:500 signifies that 1 gallon of oil is used to 500 cubic feet of the gas vehicle.

Example 1.—Pass sour burning oil distillate and gas, ratio 1:100 at 960° F. and 200 atmospheres through a catalytic mass composed of chromium oxide 60 parts, molybdenum and tungsten oxides each 20 parts on a magnesium oxide support. Collect the light liquid products and recycle the gas with a fresh supply of distillate. Any heavy liquid ends likewise are to be recycled.

Example 2.—Mix sweet gasoline (e. g., low sulphur straight run) with the gas vehicle, ratio 1:150, and pass over an oxysulphide catalyst at 210 atmospheres and at 990° F. Collect the products as aforesaid.

Example 3.—Pass a mixture of low-sulphur gas-oil, gas vehicle and water vapor in a ratio of 1:100:100 (the latter figure being water vapor figured as saturated steam at its condensation point) through a reaction zone at 300 atmospheres and at a temperature of 1000° F. and separate the liquid products from the gas, including recovery of any hydroxylated bodies and the like which may be formed.

Example 4.—Pass sour gas-oil and gas vehicle in the ratio 1:300 over an oxysulphide catalyst at 920° F. and 200 atmospheres, collecting and separating the light liquid products from the heavier part. Reheat the latter and subject to a similar treatment but at 1000° F. and 400 atmospheres pressure.

Example 5.—Have present in the gas vehicle from 3 to 4 percent of carbon monoxide to assist in maintaining the temperature of the reaction chamber. Use gas from cracking stills containing from 10 to 15 percent hydrogen. To a low-sulphur gas-oil add 3 percent of sulphur and pass through the reaction chamber at a pressure of 300 atmospheres and at a temperature of about 1000° F. using an oil and gas ratio of 1:200.

In producing anti-knock motor fuel by the methods described above, it should be noted that I aim to have present such a ratio of hydrocarbon gas molecules to oil molecules which are undergoing cleavage that a spaced proportion exists enabling each oil molecule to undergo cleavage and reformation substantially without objectionable contact with other oil molecules in like condition, in other words, the preferred form of the process involves the employment of the fixed gas hydrocarbon spacing agent in substantially polymerization inhibiting proportion.

tion. Furthermore, such spacing agent is preferably largely at least of extrinsic origin.

The present application is a continuation-in-part of copending application Ser. No. 483,382 filed September 20th, 1930.

What I claim is:

1. An improved process for converting petroleum distillates rich in paraffinic constituents into lower boiling oils rich in naphthenic constituents which comprises passing the oil in vapor form through a reaction zone at a temperature in excess of 900° F. and at a rate adapted to permit thermal decomposition of the initial material to said lower boiling hydrocarbons while under total pressure of the order of 200 atmospheres in the presence of a gaseous hydrocarbon diluent which is substantially non-reactive under the conditions, in proportion of at least 100 cubic feet per gallon of oil and adjusted to effect splitting without excessive polymerization.

2. An improved process for converting petroleum distillates rich in paraffinic constituents into lower boiling oils rich in naphthenic constituents which comprises passing the oil in vapor phase through a reaction zone at a rate permitting thermal decomposition of said petroleum distillate to lower boiling products, under pressure of the order of 200 to 1,000 atmospheres while in the presence of a gaseous hydrocarbon diluent containing only small amounts of reactive constituents and in proportion of at least 100 cubic feet per gallon of oil, and also in the presence of a catalytic material consisting of dehydrogenating and reconstituting constituents.

3. Process according to claim 2 in which one constituent of the catalyst is selected from the group of oxides and sulfides of 6th group metals and the other is a sulfur bearing substance.

4. Process according to claim 2 in which one constituent of the catalyst is selected from the

group of oxides and sulfides of 6th group metals and the other is sulfur.

5. An improved process for converting petroleum distillates rich in paraffinic constituents to lower boiling products rich in naphthene constituents, which comprises passing the oil in vapor phase through a reaction zone at a rate to permit thermal decomposition of the oil to said lower boiling products while under pressure of the order of 200 to 1000 atmospheres, and in the presence of gaseous hydrocarbon diluent containing substantially unreactive concentrations of free hydrogen and unsaturated hydrocarbons, and in proportion of the order of 100 to 500 cubic feet per gallon of oil, and also in the presence of a catalyst comprising a compound selected from the 6th group oxides and sulfides and a volatile sulfur bearing catalyst.

6. A process for the conversion of heavy hydrocarbons with limited formation of free hydrogen, which comprises bringing together the hydrocarbons and only an inert gas which does not enter into the reaction appreciably, and treating the mixture at a temperature in excess of 350° C. and at a pressure of the order of three hundred atmospheres, the inert gas being a substantial portion of the gaseous material present during the treatment.

7. A process for the conversion of heavy hydrocarbons with limited formation of free hydrogen, which comprises bringing together the hydrocarbons and only an inert gas which does not enter into the reaction appreciably and treating the mixture at a temperature of the order of 460° C., and at a pressure of the order of three hundred atmospheres, the inert gas being a substantial portion of the gaseous material present during the treatment.

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