

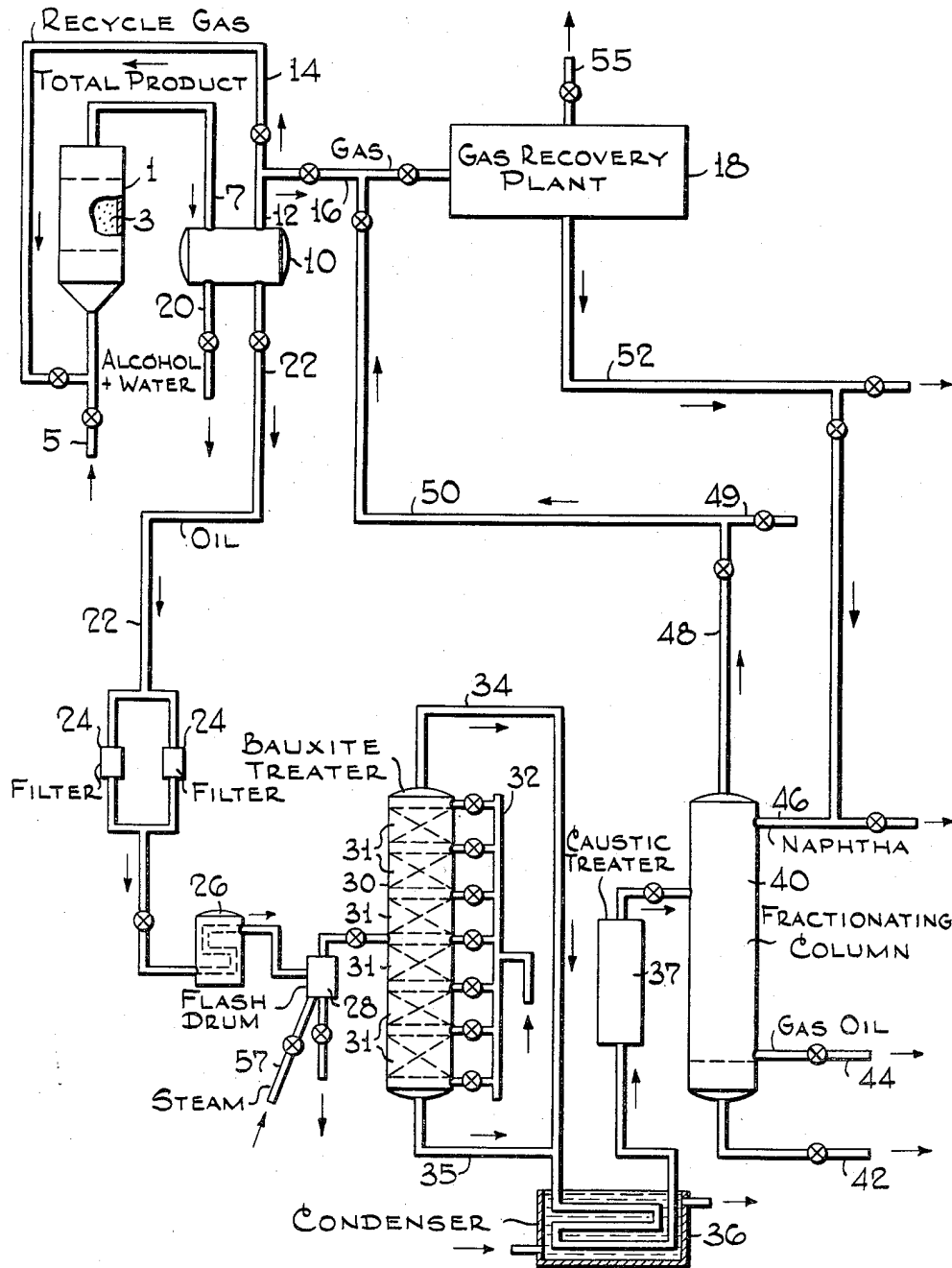
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HYDROCARBON SYNTHESIS

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HYDROCARBON SYNTHESIS

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5 Claims. (Cl. 260-450)

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This invention relates to the catalytic conversion of carbon oxides with hydrogen to form valuable synthetic products. The invention is particularly concerned with a method of improving the yields and properties of gasoline range hydrocarbons obtainable from the catalytic conversion of carbon monoxide with hydrogen.

The synthetic production of normally liquid hydrocarbons from gas mixtures containing various proportions of carbon monoxide and hydrogen is already known and numerous catalysts, usually containing an iron group metal, have been described which are specifically active in promoting the desired reactions at certain preferred operating conditions. For example, cobalt supported on an inert carrier and promoted with small proportions of thorium compounds or other promoters is used at relatively low pressures (atmospheric to about 5 atmospheres) and low temperatures (about 375° to 425° F.) to manufacture a substantially saturated hydrocarbon product yielding valuable Diesel fuels and paraffin wax but a gasoline of relatively low octane rating. A substantially unsaturated product containing some branched-chain constituents may be manufactured when iron-type catalysts are employed at relatively higher temperatures (about 450° to 750° F.) and higher pressures (about 5 to 50 atmospheres and higher). The gasoline obtainable from the latter product has a superior octane rating which may fall anywhere between 60 and 75 Research octane number.

However, even the gasoline produced in the presence of iron catalysts does not comply with the octane rating requirements of modern high compression automotive and aviation engines. This gasoline must, therefore, be blended with high octane constituent or subjected to refining treatments in order to raise its octane rating to Research octane numbers of at least 85. The unsatisfactory octane number of the gasoline results mainly from the fact that the olefins produced in the hydrocarbon synthesis are almost exclusively α -olefins; that is, unsaturated hydrocarbons in which the double bond is located at the end of a relatively long hydrocarbon chain. This type of olefins is known to have a lower octane rating than olefins in which the double bond is in a more central location.

It is known in the art of petroleum oil refining that the octane rating of gasolines rich in α -olefins may be considerably improved by a refining treatment with bauxite under non-cracking conditions and it has been suggested prior to the present invention to apply this treatment to

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synthetic gasolines. These non-cracking bauxite reforming conditions include temperatures of about 700° to 900° F., pressures of about 1 to 10 atmospheres and throughputs of about 0.5 to 2 v./v./hr., so correlated as to prevent substantial cracking. While in this manner substantial improvements of the octane rating were obtained, the yields of high octane gasoline remained relatively low.

It is also known in the refining of petroleum oils as well as of synthetic oils to subject the gas oil cut to catalytic cracking in the presence of siliceous catalysts such as various natural or synthetic clays and siliceous gels in order to improve the total gasoline yield by the addition of the cracked gasoline of usually improved octane rating.

While it has been thus possible to produce gasoline of satisfactory octane rating by combining treatments of the two types mentioned above, such a procedure has required a two-stage operation, the individual stages of which had to be adapted to the different character of the different feeds involved.

The present invention has for its principal object to provide an improved process permitting the production of improved yields of synthetic gasoline range hydrocarbons having Research octane numbers substantially above 80 in a single stage procedure.

It has been found that this object and other advantages may be accomplished, quite generally, by treating the total oil including gasoline and gas oil range hydrocarbons produced from carbon monoxide and hydrogen under synthesis conditions conducive to the formation of unsaturated hydrocarbons, with bauxite at conditions of temperature, pressure and throughput which are conducive to substantial cracking of the gas oil constituents. These conditions include temperatures of 800°-1000° F., pressures of 1-10 atmospheres abs., and throughputs of .5 to 2 volumes of liquid feed per volume of bauxite, which in accordance with the present invention are so correlated that substantial cracking of the gas oil range hydrocarbons is accomplished. In order to enhance the cracking activity of the bauxite at the conditions specified, it is desirable to regenerate the bauxite either continuously or at intervals considerably more frequent than those employed in conventional bauxite reforming of gasoline range hydrocarbons. The cracking activity of the bauxite may also be prolonged by adding steam to the feed in amounts which will prevent excessive carbon deposition on the baux-

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ite without reducing the effective contact time below levels conducive to substantial cracking. Steam concentrations of about 20 to 70 mol per cent are suitable for this purpose.

Any conventional apparatus known in the art of bauxite treating natural or synthetic gasoline may be used for the purposes of the present invention. A typical example for the type of equipment suitable to carry out the process of the present invention is illustrated schematically in a simplified manner in the accompanying drawing which will be referred to in the following more detailed description of the invention.

Referring now to the drawing, chamber 1 is a conventional type synthesis reactor containing a catalyst mass 3 of a catalyst suitable for the production of predominantly unsaturated liquid hydrocarbons from carbon monoxide and hydrogen. Iron catalysts such as reduced sintered pyrites ash or reduced precipitated iron oxide, promoted with conventional promoters such as the oxides, hydroxides, carbonates, chlorides or fluorides of sodium or potassium, or the iron catalysts used in the production of synthetic ammonia from nitrogen and hydrogen and containing about 1.5% of alumina, or others may be used for this purpose. Synthesis reactor 1 may be operated as a fixed or moving bed or fluid reactor in any conventional manner.

Synthesis gas containing hydrogen and carbon monoxide in the approximate ratio of 0.5-3:1 is introduced into reactor 1 through line 5. The reaction conditions within reactor 1 are those known for iron catalysts and may include temperatures of about 550° to 800° F., and pressures of about 5-50 atmospheres.

The total synthetic product is withdrawn from reactor 1 through line 7 and passed through a separator 10 wherein the separation of liquids and gases and of a hydrocarbon layer from an aqueous layer is accomplished by cooling and settling. Gas is withdrawn overhead through line 12 to be either recycled through line 14 to synthesis feed gas line 5 or to be passed through line 16 to a gas recovery plant 18. The aqueous layer containing the water-soluble oxygenated products is withdrawn from the bottom of separator 10 through line 20.

The total liquid hydrocarbon oil product is withdrawn from an upper liquid layer within separator 10 and passed through line 22 to a filtering system 24 wherein entrained solids may be removed. The filtered oil may be vaporized in a coil heater 26 and passed through a flash drum 28 to bauxite treating tower 30 at a temperature of about 800°-1000° F. and a pressure of about 1-10 atmospheres abs.

Bauxite treating chamber 30 may contain a plurality of superimposed individual bauxite layers 31 through which the oil vapors may pass upwardly and downwardly in series or parallel flow as indicated in the drawing. The hydrocarbon vapor feed and the amount of bauxite are so chosen that a throughput of about 0.5 to 5 v./v./hr. may be maintained. Bauxite treating chamber 30 is also provided with a manifold 32 through which air may be introduced to regenerate the bauxite by burning off carbon at any desired intervals, preferably after purging with steam. The regenerating treatment may be carried out at temperatures of about 900° to 1400° F. During the hydrocarbon runs the pressure in chamber 30 is preferably maintained at about 5-30 p. s. i. g.

The cracked and reformed hydrocarbon vapors

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may be withdrawn from both ends of chamber 30 through lines 34 and 35, condensed in condenser 36 and passed to a caustic treater 37 wherein acid constituents are removed to sweeten the oil. The caustic-treated products are passed to fractionating column 40 from which bottoms are withdrawn through line 42, gas oil through line 44, gasoline range hydrocarbons through line 46 and gas through line 48.

The gasoline withdrawn through line 46 is ready for use, if desired after blending with other fuels or the addition of anti-knock agents such as tetraethyl lead. The bottoms and/or the gas oil withdrawn through lines 24 and 44, respectively, may be treated in any conventional manner, for example by thermal or catalytic cracking, to produce further amounts of gasoline or they may be used as fuels, Diesel oils or the like.

The gas withdrawn through line 48 may be either vented through line 49 or returned through line 50 to gas line 16 to be worked up together with the gas from separator 12 in the gas recovery plant 18. C₄ and C₅ hydrocarbons recovered in plant 18 may be added through line 52 to the gasoline in line 46. Gases of low molecular weight may be withdrawn through line 55 for any desired use.

Steam required for stripping or to be supplied together with the feed for reducing carbonization may be fed through line 57 to chamber 30.

It will be appreciated that the system illustrated by the drawing permits of many modifications obvious to those skilled in the art without deviating from the spirit of the invention. For example, chamber 30 may be a conventional fluid-type reactor permitting continuous operation of the hydrocarbon treatment and the bauxite regeneration, in a manner known per se.

The invention will be further illustrated by the following specific examples.

Example 1

A total liquid oil product (gasoline plus gas oil) was synthesized over a catalyst analyzing as follows:

	Parts by weight
Fe ₂ O ₃	93.2
SiO ₂	1.3
Al ₂ O ₃	2.5
MnO	0.8
K ₂ O	1.5
	<hr/>
	99.3

The synthesis conditions included an average catalyst temperature of 637° F., a synthesis pressure of 240 p. s. i. g., a H₂:CO ratio in the fresh feed of 2.14 and a recycle rate of 1.9 parts of gas from separator 12 per part of fresh feed gas. The synthesis reactor was a fluid bed reactor operated at a total gas throughput of 50 S. C. F. per hour of H₂+CO in fresh feed per pound of carbon- and oxygen-free catalyst.

A sample of the total liquid oil product was fractionated. It yielded a gasoline cut of the range C₄-430° F. amounting to 70.3% by volume of the liquid product, a gas oil cut having a 90% point of about 700° F. and amounting to 29.2% by volume of the total oil, and a gas cut of 0.5% by weight. The gasoline cut contained 15.0% by volume of hydrocarbons distilling up to 158° F., it had a Reid vapor pressure of 5.5 p. s. i. g. and an octane number of 65.0 by the Research method.

Another sample of the total liquid was preheated and vaporized together with 20% by weight of water in a heating coil maintained at a temperature of 850° F. and the vapors were conducted upwardly through a bed of bauxite catalyst maintained at an average temperature of 850° F. by external electric heaters. The bauxite had been activated by dehydrating at a temperature of about 1000°-1200° F. Bauxites so dehydrated to a water content of less than 10%, preferably less than 3%, are particularly advantageous for the purposes of the invention. The reaction products were passed through a condenser and separator drum from which liquid and gaseous products were withdrawn separately. The oil feed rate to the bauxite was maintained at 1.0 volume of liquid per volume of bauxite per hour. The pressure on the reaction zone was substantially atmospheric. The bauxite was kept on-stream for 8 hours.

The above treatment produced yields of 70.2% by volume of gasoline and 25.2% by volume of gas oil, the remainder, amounting to about 2.7% by weight, being gas and coke. The gasoline contained 4.5% by volume of constituents distilling up to 158° F. and had a Reid vapor pressure of 6.3 lbs. per sq. in. and an octane number of 78.3 by the Research method.

Example 2

A third sample of the total liquid oil product was treated with bauxite by the same method as described in Example 1, however, at more severe treating conditions. The temperature remained at 850° F. and the feed rate at 1.0 v./v./hr., but the steam diluent was omitted and the pressure was increased to 10 lbs. per sq. in. gage so as to increase contact time. The on-stream periods were shortened to one hour in order to maintain catalyst activity at a high level.

This treatment produced yields of 77.0% by volume of gasoline and 15.0% by volume of gas oil, the remainder, amounting to about 7.1% by weight, being dry gas and coke. The gasoline contained 15.5% by volume of constituents distilling up to 158° F., and had a Reid vapor pressure of 7.7 p. s. i. g. and an octane number of 88.8 by the Research method.

The above example clearly indicates that the yield and octane number of synthesis gasoline are improved to a considerably greater extent when the bauxite treatment of the total oil product is carried out at more severe conditions which are conducive to substantial cracking as compared with the treatment under conditions at which the gas oil undergoes no significant change. The fact that these effects are the result of catalytic rather than thermal conversion has been established by blind runs carried out with the same type of feed in a reactor filled with inert quartz chips at otherwise similar reaction conditions which resulted in only insignificant changes of the feed.

Example 3

The gasoline cut and the gas oil cut obtained by fractionation of the total synthetic oil in accordance with Example 1 were separately treated with bauxite at the conditions specified in Example 2. The treatment of the gasoline cut produced yields based on gasoline feed of 90.2% by volume of gasoline and 3.8% by volume of gas oil formed by polymerization, the remainder, amounting to about 4.3% by weight, being gas

and coke. The gasoline contained 8.0% per volume of constituents distilling up to 158° F. and had a Reid vapor pressure of 5.9 lbs. per sq. in. and an octane number of 86.3 by the Research method.

The treatment of the gas oil cut produced yields based on gas oil feed, of 32.6% by volume of gasoline and 63.9% by volume of gas oil, the remainder, amounting to 5.9% by weight, being gas and coke. The gasoline contained 7.5% of constituents distilling up to 158° F., and had a Reid vapor pressure of 6.3 lbs. per sq. in. and an octane number of 84.9 by the Research method.

When comparing the results obtained by the separate bauxite treatments of the gasoline cut and the gas oil cut, it appears that the total yields amount to 73.3% by volume of gasoline and 20.9% by volume of gas oil and that the total gasoline has a blended octane number of 86.0 by the Research method. These yields and octane number are greatly inferior to the corresponding values obtained in Example 2, which shows that bauxite treatment of the total synthetic oil product including gasoline and gas oil at conditions conducive to a substantial cracking of the gas oil constituents is greatly superior to the separate bauxite treatment of the synthetic gasoline and gas oil cuts at similar conditions.

While the foregoing description and exemplary operations have served to illustrate specific applications and results of the invention, other modifications obvious to those skilled in the art are within the scope of the invention. Only such limitations should be imposed on the invention as are indicated in the appended claims.

I claim:

1. In the process of bauxite treating in a treating zone synthetic hydrocarbon oils produced by the catalytic conversion of CO with H₂ in the presence of an iron base catalyst, the improvement which comprises contacting a mixture of gasoline and gas oil constituents of said synthetic oil with bauxite at about 850° F., about 10 p. s. i. g. pressure and a throughput of about 1 v./v./hr. and on-stream periods of about 1 hour followed by catalyst regeneration periods.

2. The process of claim 1 in which said bauxite is regenerated with a combustion-supporting gas.

3. The process of claim 1 in which steam is added to said treating zone.

4. The process of claim 1 in which said mixture contains α -olefins.

5. The process of claim 1 in which said bauxite is activated by dehydrating at a temperature of about 1000°-1200° F. to a water content of less than 10%.

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