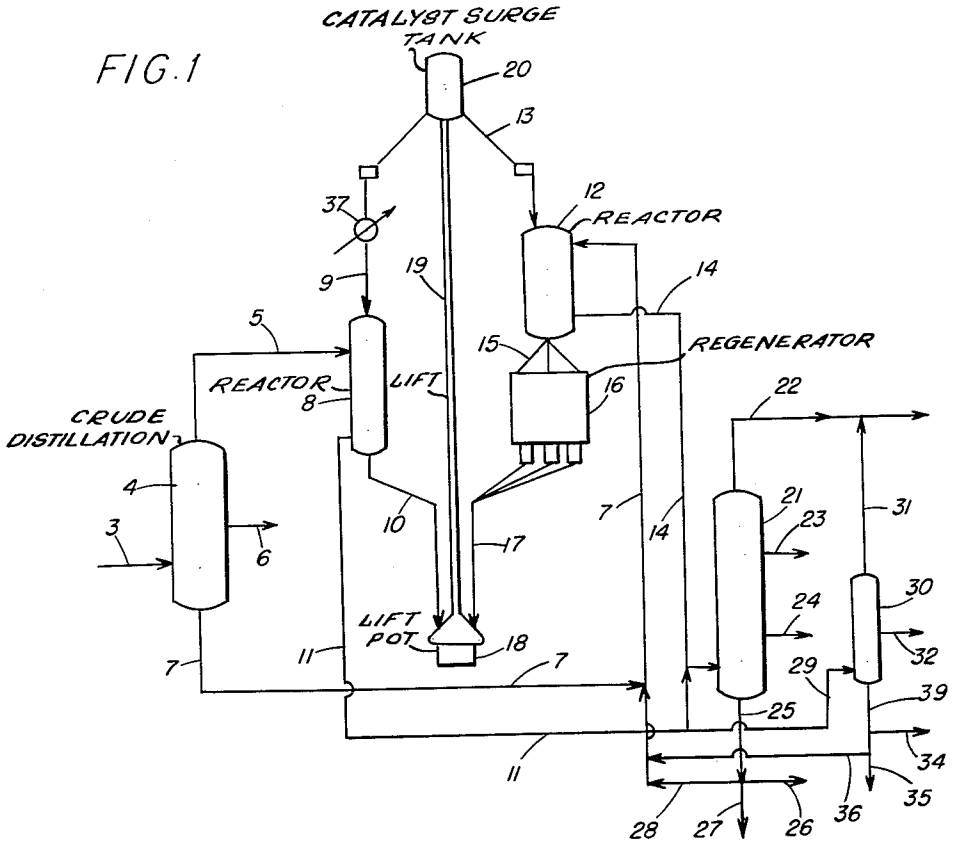
Aug. 4, 1964 E. V. BERGSTROM 3,143,491

CATALYTIC CONVERSION OF HYDROCARBONS WITH A SILICA-ALUMINA AND CRYSTALLINE ZEOLITE CATALYST COMPOSITE

Filed Feb. 20, 1962 2 Sheets-Sheet 1

FIG. 1



INVENTOR.

BY

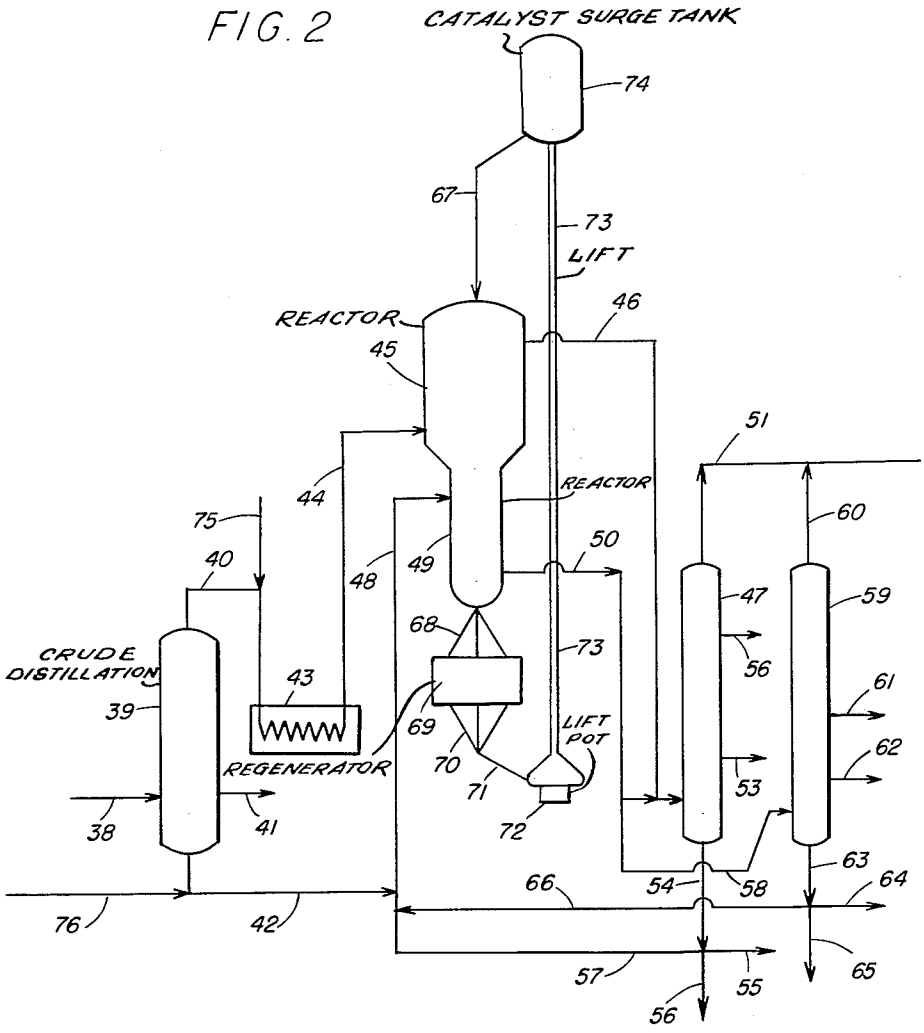
Attorney

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Filed Feb. 20, 1962 2 Sheets-Sheet 2

FIG. 2



INVENTOR.

BY

Attorney

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3,143,491

CATALYTIC CONVERSION OF HYDROCARBONS WITH A SILICA-ALUMINA AND CRYSTALLINE ZEOLITE CATALYST COMPOSITE

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1 Claim. (Cl. 208—74)

This invention is concerned with the direct working up of crude oil into a spectrum of products eminently suited for markets wherein the high quality automotive fuel product does not dominate the market, where lighter than gasoline fractions encounter a promising demand, and where demand for residual fuel oil is either light or met to a great degree by bottoms from the simple fractionation of cheap or refractory crude oils.

It is based in part upon the characteristics of newly available catalytic materials, and in part upon departures from conversion practices that have heretofore been conventional.

It has for its object the handling of crude oil and intermediate products to provide an amount of high quality gasoline relatively smaller than now considered conventional, an elimination of residual fuel oil, larger amounts of products lighter than gasoline, and distillate fuel oil products.

It has for an object the provision of a unitary and balanced process capable of producing such products with a maximum economy of heat, a minimum of apparatus, and with its various steps properly interrelated.

For a further object, it has the utilization in such a process of new and more active catalysts than those heretofore available.

These and other objects and the method of accomplishing them will be understood by consideration of the following description of the invention and from the drawings attached to and made a part of this specification.

As will be observed, the process is a moving bed catalytic conversion process, making use of the same catalyst for two conversions, one of gasoline and lighter products, the other for conversion of gas oil plus residual products, with a common regeneration zone.

In the drawings, which are diagrammatic flow sheets:

FIGURE 1 sets forth one version with one stream of catalyst through the light product operation and another through the gas oil-residuum operation.

FIGURE 2 sets forth another version, with all catalyst flowing serially through a light product operation and then through a gas oil-residuum cracking operation.

In FIGURE 1, crude oil (whole crude) heated (in a heater not shown) to a temperature of the order of 700–750° F., enters through pipe **3** into crude fractionator **4**, there to be divided into an overhead product comprising straight-run gasoline and hydrocarbons lighter than gasoline which pass out through pipe **5**, a kerosine cut or product of similar boiling range taken as a side stream through pipe **6** and a residual product, comprising all portions of the crude heavier than kerosine, leaving as a distillation residue through pipe **7**. In case the material of kerosine-like boiling range found in the original crude is unsatisfactory for kerosine manufacture or for use as a distillate fuel, it may be combined with the residuum, withdrawn through pipe **7**.

The straight-run gasoline and gas component of the crude passes through pipe **5** into a reactor **8** where it is contacted with a catalyst, which enters through conduit **9** and leaves through conduit **10**. The operation conducted in reactor **8** is essentially one of catalytic reforming in the absence of added hydrogen and is later referred to herein, as is the catalyst. Effluent from reactor **8** departs through pipe **11**.

Reduced crude, i.e., crude devoid of lighter constituents, also referred to herein as crude residue, passes through pipe **7** to a cracking reactor **12**, where it contacts catalyst supplied through conduit **13**, and effluent from this cracking operation passes out through pipe **14**.

Catalyst departing from reactor **12** through conduits **15** enters multi-compartment regenerator kiln **16** and departs therefrom through conduit **17** to enter air-lift feed pot **18**, whence it, together with catalyst coming from reactor **8** through conduit **10**, is lifted through lift-pipe **19** to the catalyst surge and supply vessel **20**.

Under conditions discussed below the effluent from reactor **8**, flowing in pipe **11**, together with effluent from reactor **12**, flowing in pipe **14**, enter a fractionation system diagrammatically designated by vessel **21**. From the top of this vessel, products lighter than gasoline depart through pipe **22**, gasoline through pipe **23**, cuts of the nature of light gas oil, distillate fuel oil, etc. (if desired), through pipe **24**, and heavy gas oil fractions through pipe **25**. This heavy gas oil may be diverted to fuel oil sales, as through pipe **26**, to plant fuel, as through pipe **27**, or even recycled to cracking, as through pipe **28**.

Under other conditions discussed below, the effluent from reactor **12** may be handled alone in fractionation system **21**, while the effluent from reactor **8** will be taken through pipe **29** to a second fractionation system designated by vessel **30**, from which overhead products lighter than gasoline depart through pipe **31**, gasoline product through pipe **32**, and heavier than gasoline through pipe **33** to be disposed of as a product, as through pipe **34**, or for internal plant disposition as through pipe **35**, or even recycled to reactor **12** as through pipe **36**.

This inventive concept is based upon the capabilities of newly developed catalytic materials. These materials are composite, one ingredient being the amorphous acidic silica-alumina cracking catalyst conventionally known, which may be produced, as is known by co-gelation procedures, by co-precipitation procedures, both involving the combination of selected proportions of silica and alumina in a material which is finished by base exchange and calcination. Similar materials may be prepared from selected clays. The characterizing material of the composite which gives rise to the desirable features of the newly developed catalyst is an alumino-silicate material of ordered structure, of generally zeolitic nature, capable of base exchange, preferably treated to arrive at an acidic or "H" form by removal of part or all of the alkali metal content of the "salt" form of the zeolitic material, and frequently used in a form in which a partial base exchange has been effected with rare-earth salts.

As an example of such alumino-silicate material, there may be cited a compound prepared by base-exchanging an alumino-silicate described in United States Patent 2,882,244 with a solution of rare-earth chlorides, in known manner, to produce a product having about 1.0 to 1.5% (wt.) of sodium and about 25% (wt.) of rare-earth elements calculated as Re_2O_3.

When this is incorporated in the composite with acidic amorphous silica-alumina to the extent of from about 1% (wt.) upwards, preferably about 5 to 15% (wt.), followed by appropriate forming and finishing techniques, catalytic composites as herein used are formed.

In some cases, finely divided alumina, or finely divided solid material of the same composition as the composite may be added for control of physical properties.

These catalytic materials are herein spoken of as a catalytic composite of a microporous amorphous acidic silica-alumina cracking catalyst and an alumino-silicate material of ordered structure and capable of base exchange. Such catalytic materials, themselves, form no part of this invention except as it is directed to methods for their economic use.

These catalytic materials have considerably greater activity than the conventional silica-alumina catalysts and may be hereinafter spoken of as high activity catalysts. These catalysts have considerably greater capability of handling residual oil cracking, are heat stable to regenerating temperatures of the order of 1200–1350° F., and have good capability for a reforming type of reaction with straight-run gasoline constituents at relatively low temperatures and in the absence of added hydrogen, in which relatively small amounts of "coke" are deposited.

Referring to FIGURE 1, a typical operation on Kuwait-Sahara crude oil mixture of about 37° API gravity with this arrangement, with the stream from reactor **8** combined with that from reactor **12** and fractionated at **21**, there would be produced as overhead at **22** about 10% by volume of the crude charged as products lighter than gasoline, to be separated into about 3% (on crude), as "city" gas, the remainder to be sold as liquefied petroleum gas or, if desired, a cut of C_4 hydrocarbons may be removed for alkylation. About 30–35% by volume of the crude charged would be gasoline of good quality, and the streams of intermediate distillate nature withdrawn at pipes **6** and **24** would amount together to about 30% by volume of the crude charged. The major change would be that no residual fuel oil is produced, but instead there is produced at **25** a heavy gas oil, and in an amount about two-thirds of the residual fuel oil produced by conventional operation.

If it is desired to produce a premium gasoline, the stream from reactor **8** (the temperature of which may be controlled by catalyst cooler **37**) is diverted to a second fractionation system as at **30**. This operation will result in about the same total amount of gasoline, divided between a high quality premium gasoline and a regular gasoline of quality below that of the composite stream, but still quite acceptable in quality.

An interesting method of utilizing the capability of this high activity catalyst is shown in FIGURE 2.

In this operation, crude oil, heated in a heater not shown, to a temperature of 700° F. to 750° F. enters at pipe **38** to fractionator **39**, with an overhead composed of straight-run gasoline and lighter products departing through pipe **40**, a side stream of kerosene or diesel fuel nature, as before leaving through pipe **41** and a distillation residue, combining all fractions heavier than taken through side stream **41**, departs at **42**.

The overhead product in pipe **40** passes through a "trim" or temperature adjusting heater **43** and then through pipe **44** into reactor **45**. Effluent from reactor **45** is led through pipe **46** into a fractionation system indicated by vessel **47**.

The residual material in pipe **42** passes through pipe **48** into reactor **49**, and effluent from this reactor passes through pipe **50**, normally to be combined with that in pipe **46** and so into fractionation at **47**.

In fractionation at **47**, there is produced an overhead fraction of products lighter than gasoline departing through **51**, gasoline, as at **52**, light gas oil or distillate fuel as at **53**, and heavy gas oil as at **54**. This heavy gas oil may be diverted to fuel oil sales, as through pipe **55**, to plant fuel as through pipe **56**, or even recycled to cracking, as through pipe **57**.

If it is desired to produce premium gasoline, a dual fractionation system is provided, with effluent from reactor **49** passing through pipes **50** and **58** to a fractionation system indicated by vessel **59**, with lighter than gasoline overhead departing through pipe **60**, gasoline through pipe **61**, light gas oil, etc., through pipe **62**, and heavy gas oil through pipe **63**, to disposal, as before to fuel oil sales indicated by pipe **64**, to plant fuel, as indicated at **65**, or to recycle as indicated by **66**. The effect of this is to isolate, as a high quality product, the gasoline produced in reactor **45**.

Catalyst, in this case, flows serially through reactors **45** and **49**, being supplied thereto by conduit **67**. Fouled catalyst passes through conduits **68** to a multi-section regeneration kiln **69**. Regenerated hot catalyst passes through conduits **70** and **71** into lift pot **72**, and through air-lift conduit **73** to catalyst surge and supply vessel **74**.

In operating according to the scheme shown in FIGURE 2, with production of high quality premium gasoline, charging Kuwait-Sahara mixed crude oil (about 37° API), the temperatures of operation will be about as follows:

Crude oil to fractionater **39**, 700° F.–750° F.; light overhead from fractionator **39** through "trim" furnace to reactor **45**, 750° F.–800° F.; catalyst from regenerator in catalyst surge tank **74**, 1250° F.; top of reactor **45**, 1200° F.–1250° F.; catalyst at point between reactors **45** and **49**, 1050° F.

Pressures in the reactors **45** and **49** will be of the order of 15–25 p.s.i.g.

Yields from this operation would be approximately as follows: Permanently gaseous materials lighter than propane, i.e., "city gas," about 12% by volume on crude (as equivalent barrels); about 14% of a C_3–C_4 cut to be sold as liquefied petroleum gas (from which, if desired, a butane-butene cut could be recovered for alkylation); about 14% by volume of premium gasoline; about 12% (by volume) of regular grade gasoline; about 15% (volume) of automobile diesel fuel; about 11% (volume) of light distillate fuel oil; and about 15% (volume) of heavier distillate fuel oil. The remainder, about 7% by volume of the original crude, is practically all coke, burned off in regenerator **69**, providing, in hot catalyst, a major portion of the heat consumed in the operation.

Another interesting operation which may be conducted in the set-up of FIGURE 2 is the charging of a straight run gasoline fraction direct through "trim" heater **43** by pipe **75** and thence to reactor **45**, and a crude residue from a preheater (not shown) at about 700–750° F. through pipe **76** and pipes **42** and **48** to reactor **49**. The straight run gasoline will be converted into light products and high quality gasoline in reactor **45** as before, while the crude residuum will undergo conversion in reactor **49** similar to that previously described.

Assuming, in such an operation, the charging of 5000 barrels per day of straight run gasoline and 5000 barrels per day of residue of 6.6° API from Kuwait crude, yields, as barrels or equivalent barrels, would be about as follows: City gas 2500 b./d., L.P.G. 2300/d.; premium gasoline 3200 b./d., light distillate fuel oil 1100 b./d., heavy distillate fuel oil 500 b./d. The remainder, as before, would be substantially all "coke," burned in the regenerator, and supplying reactor heat.

It will be noted that the low coke-forming capability of this catalyst composite where used for the conversion of low boiling materials is taken advantage of in significant process simplifications.

In the operation of FIGURE 1, where the object of gasoline conversion is basically reforming, the effluent catalyst composite is sufficiently low in coke content to permit re-use when combined with the regenerated catalyst composite coming from regenerator **16**. In the operation of FIGURE 2, where the object of gasoline conversion is basically a combination of light hydrocarbon gas production and reforming in reactor **44**, the entire cycling catalyst composite is used and flows from **44** into reactor **49**.

This feature permits significant economy of investment and operation in that only a single catalyst lift operation is necessary. A further feature of this combination of operations is that regenerator heat, as sensible heat of catalyst composite, is available for the heat demands of reactor **8** in FIGURE 1 operation and of reactors **44** and **49** in FIGURE 2 operation.

It will be obvious from the above that this novel method for the conversion of petroleum and petroleum fractions has advantages of major importance for those areas and situations where the production of gaseous fractions and fractions lighter than gasoline, as well as

the non-production of residual fuels are of importance. It is also noted that the capabilities of the process, in its various embodiments, is directed to areas heretofore carefully avoided in the conventional conversion of petroleum.

I claim:

That method for the catalytic treatment of petroleum to convert it substantially to products of gas oil and lower boiling nature, including gasoline of good anti-knock quality which comprises:

vaporizing and separating from the crude oil a straight-run gasoline fraction which includes any material boiling below gasoline,

subjecting this straight-run gasoline fraction to contact with a catalyst comprising a composite of a microporous amorphous silica-alumina cracking catalyst and crystalline aluminosilicate at temperatures of the order of 1000° F. to 1200° F. to convert a substantial portion thereof to materials boiling below the gasoline boiling range,

passing the residual remainder of the crude oil into contact with a similar catalyst at temperatures of

the order of 800° F. to 1000° F. to convert it to products lighter than gasoline, gasoline, gas oil fractions and coke,

and fractionating the products of said conversions,

the said conversion catalyst being circulated cyclically through the several conversion zones, and regenerated by burning after withdrawal from the crude residue conversion zone,

the entire regenerated catalyst being introduced to the straight-run gasoline conversion zone at a temperature of the order of 1250° F., and after exit from such zone the entire catalyst stream is then introduced directly into the crude residue conversion zone.

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