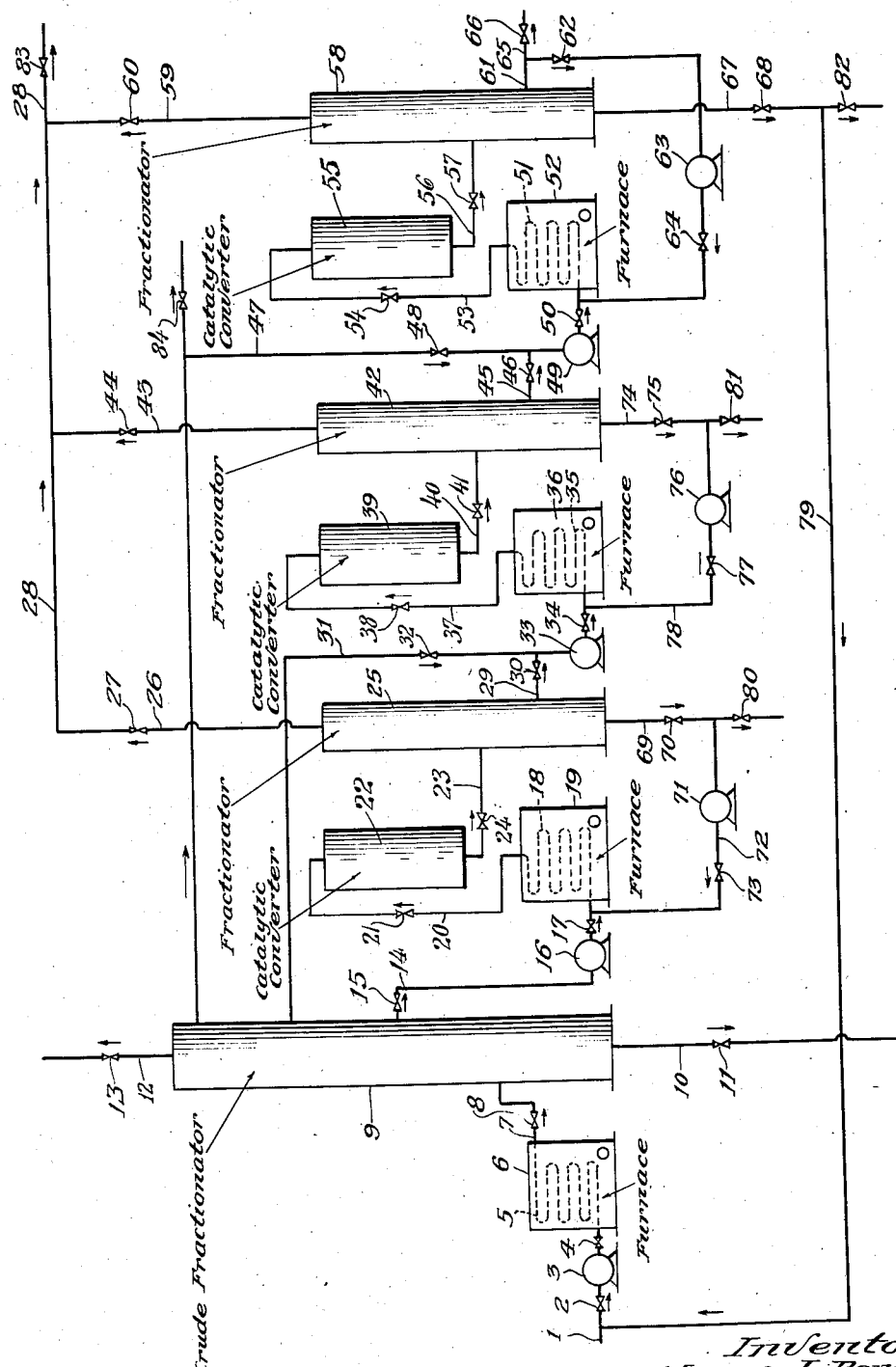
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MULTISTAGE CATALYTIC CONVERSION OF HYDROCARBONS

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MULTISTAGE CATALYTIC CONVERSION OF HYDROCARBONS

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This invention relates to the catalytic conversion of hydrocarbon distillates produced by the distillation of heavy hydrocarbonaceous materials, and more particularly distillates which are vaporizable without substantial decomposition. Although usually from petroleum sources, in certain instances distillates produced from coal tars, shale oils, and the like may be converted by this process.

More specifically, the invention is concerned with the conversion of hydrocarbons by means of specially prepared catalysts which are selective in promoting the formation of high octane number gasoline, and gases of a particularly desirable composition.

The art of producing gasoline and gas by thermal cracking of petroleum oils is extensive and has been developed to the point where the principles involved are well understood. The catalytic conversion of hydrocarbons, and more specifically catalytic cracking of high boiling hydrocarbon distillates to produce gasoline and gas is not so well comprehended. Such deductions as have been made are largely of an empirical nature and a discussion of these reactions is, therefore, best confined to facts.

Many catalysts have been proposed to assist the thermal conversion of hydrocarbon distillates into gasoline and gas, among which are certain types which promote as the predominating reaction, the formation of gas rather than gasoline. Such catalysts include the reduced metal catalysts, such as nickel and iron and their ores. These catalysts are, furthermore, subject to poisoning by sulfur compounds and tend to produce coke-like materials which deposit as a film around the catalyst particles and render them inactive. Other types of catalysts promote dehydrogenation reactions, that is, splitting at the carbon-hydrogen bond rather than at the carbon-carbon linkage, and as a consequence the character of the gases and the antiknock properties of the gasoline produced are considerably different from those which are produced according to the present invention.

In one specific embodiment my invention comprises the separation of crude petroleum into a plurality of fractions, contacting each fraction with a cracking catalyst in a separate conversion stage at a temperature suitably adjusted for maximum catalytic conversion of said fraction, said temperature being generally progressively higher for progressively lower boiling fractions, separating gasoline and gas between each conversion stage, combining a major portion of the unconverted oil from a lower temperature stage with the raw charge to a succeeding higher temperature stage, and recycling a major portion of the unconverted oil from the final conversion stage to said stage.

It has been found that certain stocks require somewhat different conditions of cracking for the production of maximum yields depending upon the character of the crude oils from which they are derived. Also that charging stocks of varying boiling range from a given crude oil source require different temperature conditions and space velocities to produce extensive catalytic conversion. For example, for a given catalyst, higher temperatures are required for the reforming of naphthas than are needed for the cracking of kerosene distillates, and these in turn require higher temperatures than do gas oils which have a higher boiling range. Moreover, considerable benefit may be obtained by catalytically cracking an oil in two or more relatively narrow boiling fractions under optimum conditions for each fraction over cracking the total distillate in one step. In the latter case the high boiling material would necessarily be overcracked if the low boiling material were treated at sufficiently high temperature to obtain suitable conversion. Likewise if the high boiling material is cracked under the best conditions, the conversion of the low boiling material is greatly reduced. When hydrocarbon oil is catalytically cracked in the form of fractions, there is a tendency for the yield per pass to be increased and the deposition of coke and the formation of gas to be reduced.

In addition it has been found that the unconverted portion of the original charging stock (i. e., bottoms remaining after conversion and separation of gasoline and gas) is of a somewhat more refractory nature than the virgin stock which cannot be readily attributed to its physical and chemical characteristics. It has been found that cracking the unconverted bottoms under the same conditions as the virgin oil results in decreased conversion per pass. It has been further found that the yield can be materially increased by removing the gasoline and gas and charging the unconverted oil to a succeeding body of catalyst and adjusting the temperature and space velocity so as to produce a maximum conversion. The conditions for optimum conversion of any type of oil cannot be specified exactly, but must be established as a result of examination of the oil and trial under the operating conditions.

In view of the increasingly refractory character of the unconverted oil after one stage of catalytic cracking and also that lighter gravity, lower boiling distillates from a given crude source require increased temperatures for the best operation, it has been determined to be advantageous as well as economical, to separate the crude oil into relatively narrow boiling fractions and crack each fraction in a catalytic conversion stage under temperature conditions most suitable for optimum conversion and combine it with a major portion of the unconverted bottoms from a preceding stage operating at a lower temperature whereby both virgin distillate and recycle oil are jointly cracked under conditions designed to produce the best yield. A portion of the unconverted bottoms may be withdrawn continuously from any or all of these conversion stages but preferably only from the final stage, and a major portion of the unconverted oil is recirculated to said final stage. This method of operation has the advantage that each portion of the distillate as well as the recycle stock, is treated under the optimum conditions for maximum conversion to motor fuel and a minimum of gas and carbon formation.

As an alternative operation a portion of the heavier, unconverted oil from each conversion stage may be recycled to said conversion stage for further treatment.

Although the present process may have more or less applicability when using various types of recognized cracking catalysts such as those which may be produced by the acid or other chemical treatment of naturally occurring clays, the preferred catalysts comprise specially prepared synthetic masses, for example, silica-alumina, silica-zirconia, silicia-alumina-zirconia, and silica-alumina-thoria having a very high degree of catalytic activity. These masses are prepared by combining the constituents in various ways such as mixing, coprecipitation and the like under conditions whereby alkali metal ions are excluded. In these catalysts the ratio of the components may vary within wide limits and the masses may be considered to comprise intimate or possible molecular admixtures, all of the components indicating more or less low activity individually but in the aggregate displaying high activity. The activity also is not an additive function of the individual component, it being relatively constant for a wide range of proportions whether in molecular, or fractions of molecular proportions. It appears that no one component can be determined as the one component for which the remaining components may be considered as the promoter according to conventional terminology. In the present invention these catalysts are used in the form of sized particles or other formed shapes such as pellets produced by compression or extrusion methods. The pressed composites after drying and forming into definite shapes are calcined at temperatures above 800° F. prior to contacting with the hydrocarbons.

The character of the catalysts described may vary depending upon the exact method of preparation and their composition. All of them have been found to have good catalytic activity although they are not necessarily exactly equivalent in this respect. Some catalysts may be more useful for the conversion of naphthas or reforming of gasolines, others more efficient for the cracking of kerosene, and still others for the conversion of higher boiling distillates. The catalysts have been found to accelerate the cracking of petroleum and other hydrocarbon distillates to increase the yields of high octane number gasoline, as well as the yields of polymerizable olefins which are readily converted to high octane number motor fuel. These particular catalysts have been found to be selective in bringing about the reactions resulting in the production of premium quality gasoline, and at the same time are of such a character that they stand up under severe conditions of handling, as well as the changing conditions of successive operation and regeneration. They are further characterized by the ease and accuracy with which they may be reproduced.

The removal from the synthetic catalytic masses of the alkali metal ions and particularly sodium during preparation is of particular importance, which may possibly cause a decrease at elevated temperatures in the internal surface and porosity of the catalysts resulting in reduction of activity to an extent such that the predominant reaction is no longer of a catalytic nature. It may also be possible that the alkali metal compounds tend to catalyze reactions of an undesirable character. Whatever the explanation, the removal of alkali metal compounds is important and the preferred catalysts are of this type. Under certain circumstances it may be desirable to use catalysts of different composition in the different conversion steps of our process, although from a practical standpoint this is seldom the case.

One embodiment of the present invention is illustrated in the attached drawing. However, it should be borne in mind that the exact conditions, flow or apparatus employed therein are not to be construed as limiting the invention in exact correspondence therewith. The drawing is given as an example and illustration of one method of conducting our process. The crude oil is pumped through line 1, valve 2, pump 3, and valve 4 into coil 5 in furnace 6 from which it passes through line 7 and valve 8 into the crude fractionating column 9 where it is divided into whatever fractions are to be treated in the succeeding stages. A heavy fuel oil or reduced crude oil is withdrawn through line 10 and valve 11 to storage or to non-catalytic cracking units as may be desired. Intermediate boiling cuts are taken through the draw-off lines as indicated. Gas and a light gasoline fraction may be removed through line 12, and valve 13 to suitable stabilizers and coolers and finally to storage. A heavy gas oil may be withdrawn through line 14 and valve 15, pump 16 and valve 17 into coil 18 which is disposed in furnace 19 wherein it is heated to a desired cracking temperature and passed through line 20 and valve 21 to catalytic converter 22 which is operated at a suitable temperature to produce substantial yields of cracked gasoline and of gas high in polymerizable olefins. The reaction products pass through line 23 and valve 24 into a fractionator and separator 25 where the gasoline and gas are separated and passed through line 26 and valve 27 to the common gasoline rundown line 28. The gasoline may properly pass through an intermediate stabilizer for separation of gases and production of proper vapor pressure and thence through heat exchangers and condensers not shown to storage. The unconverted oil may pass through line 29 and valve 30 to join with line 31 in which light gas oil or kerosene removed from the crude fractionator 9 passes to mingle with the unconverted bottoms from fractionator 25 and be pumped by

means of pump 33 through valve 34 into coil 35 in furnace 36. The combined distillate then passes through line 37, valve 38 to catalytic converter 39 which is operated at a substantially higher temperature than converter 22 although it may have similar structure. The conversion products pass through line 40 and valve 41 to fractionator and separator 42 in which the gasoline and gas are removed through line 43, valve 44 to the rundown line 28. The unconverted or partially converted oil may then pass through line 45, containing valve 46 into line 47 where it mingles with a primary light fraction which may suitably be of the nature of a heavy naphtha and include some of kerosene boiling range distillate which passes from the fractionator 9 through line 47 and valve 48, th ecombined feed then being pumped by pump 49 through valve 50 into coil 51 in furnace 52. The oil passes through line 53 and valve 54 into catalytic converter 55 which is maintained at a temperature substantially higher than catalytic converters 22 or 39 so as to produce a maximum yield of gasoline and polymerizable gas from the combined feed being supplied. The conversion products pass through line 56 and valve 57 to fractionator and separator 58. The gasoline and gas pass through line 59 and valve 60 to the run-down line 28. The unconverted and insufficiently converted oil from separator 58 passes through line 61 and valve 62 by means of pump 63 and valve 64 where it joins with the incoming charge from line 47 and is recirculated to catalytic converter 55 by previously described routes. A minor portion of the oil may be suitably withdrawn through line 65 and valve 66 although it is preferable to withdraw the heavier bottoms through line 67 and valves 68 and 82. Alternative methods of operation are to return a portion of the heavy recycle oil from fractionator 25 through line 69 and valve 70 by means of pump 71 through line 72 and valve 73 to line 14 where it passes through coil 18 and thence by previously described routes to catalytic converter 22. In a like manner a minor portion of the unconverted oil from separator 42 may pass through line 74, valve 75 by means of pump 76, valve 77 and line 78 to join with the combined feed in line 31 and thence through coil 35 to catalytic converter 39 by routes previously described.

Another suitable method of operation which is of benefit in some instances is to pass the unconverted bottoms which are withdrawn from fractionator 58 through line 67 and valve 68 through line 79 and thence to the crude fractionator 9 by means of line 1 and previously described routes. In this way the lighter gravity material may be returned to the catalytic conversion system while the heavy oil will combine with the reduced crude oil and be passed to whatever means of disposal has been provided for it, such as to use as fuel oil or as charging stock for thermal cracking. Valves 80, 81, and 82 are drain lines from the various fractionators. Valves 83 is a control valve in the gasoline-gas collection system. Valve 84 permits the withdrawal from the crude fractionating system of a portion or all of the high boiling naphtha cut, should this be desired.

The process is highly flexible and the number of stages used will be entirely dependent upon the crude input which, of course, governs the amount of any given distillate which can be produced. The number of fractions and their respective boiling ranges and gravity will be entirely dependent upon the specific needs of the refiner, for example, the cut taken for conversion in the first catalytic converter 22 may be a heavy gas oil having gravity, for example, of approximately 20° A. P. I. and may be cracked at temperatures of 800–930° F. The next higher cut which is processed in converter 39 may suitably be of a light gas oil with an initial, for example, in the kerosene boiling range and an end point approximately that of the initial of the heavy distillate processed in the first stage, and may be processed at 930°–1100° F. The distillate removed for the third and final catalytic stage may suitably consist of a heavy naphtha which may include some material in the lower limits of the kerosene boiling range and may be cracked at 1050°–1200° F. Normally the material boiling below 250°–300° F. has good antiknock properties and is not processed. It may be removed and later blended back with the finished gasoline. In certain instances it may be practical to include still another conversion stage and it is understood that such additional conversion zones as may be practical are intended to be covered by the present invention. Normally three conversion stages are sufficient and in some instances this may even be reduced to two.

An alternative method of operation which has not been described and which illustrates the flexibility of the present invention may consist of the removal of two distillates from the crude fractionating column and processing them as previously described in the first two catalytic conversion stages. An end point gasoline which requires no reforming is removed from the crude fractionator, and the unconverted bottoms from fractionator 42 are processed alone in the third conversion stage at a suitably high temperature to produce substantial conversion to gasoline. As in the previously described operation a major portion of the recycle oil is returned to the final conversion stage and a minor portion is withdrawn and used as a domestic fuel oil, or if desired returned to the crude fractionator as described above. In this case with the present hook-up it would only be necessary to increase the top temperature of the crude fractionating column to remove end point gasoline and to close valve 48 so that no naphtha side cut is removed.

Since the catalyst employed in these reactions is of a type that decreases in activity because of the accumulation of carbon, it is necessary to regenerate at intervals. This may be carried out in any suitable manner. For example, the catalytic converter which may comprise tubes filled with catalyst, or chambers or cases of various types may be arranged in pairs whereby the distillate is treated in one reactor while the other reactor is being regenerated. The regeneration is accomplished by treating the catalyst with regulated quantities of oxygen-containing gases whereby the carbon deposited on the catalytic surface is burned off. The temperature during this treatment is controlled to prevent excessive shrinkage and decreased activity of the catalyst. The means of regeneration and the type of reactor employed are not a feature of the present invention. Any suitable method of carrying out the reactivation may be employed. Coolers, stabilizers, heat exchangers and such equipment which are obviously necessary for carrying out the operation are not

shown in the attached drawing in the interests of simplifying said drawing.

The following example is given to illustrate my invention and is not intended in any way to limit the invention to the exact conditions given therein. A Pennsylvania crude oil was distilled to produce the following fractions, a cut boiling up to 250° F. and having an octane number of 65 was removed for use as a blending stock in other refinery operations. A heavy naphtha having an end point of 520° F., a light gas oil cut and a heavy gas oil cut were removed as charging stocks for catalytic cracking. The heavy gas oil distillate was cracked in the first conversion stage at 920° F., the light gas oil fraction was cracked at 975° F., in the second conversion stage and the naphtha fraction was cracked in the final conversion stage at a temperature of 1050° F. Small portions of the unconverted oil from the first two conversion stages were recycled to said conversion stages, the major portion of the unconverted oil passing to the succeeding conversion stage where it was processed at the higher temperature. The major portion of the recycle oil from the final conversion stage was returned to said conversion stage for further cracking and a portion thereof was withdrawn continuously from the system for use as a domestic fuel oil. The gasoline and gas from the various fractionators were separated in a stabilizer and the gases were then passed through a catalytic polymerization plant where the gaseous olefins were converted to motor fuel and blended with the cracked gasoline produced in the catalytic cracking plant. The overall yield of 81 octane number gasoline including the polymer amounted to 86% of the total oil charged to the various catalytic conversion stages.

I claim as my invention:

1. A process which comprises separating hydrocarbon oil into a plurality of fractions, maintaining a series of separate conversion steps of progressively increasing temperature, contacting each of said fractions with a cracking catalyst in a conversion stage maintained at the temperature suitable for optimum conversion of each fraction, combining unconverted oil from a lower temperature stage with the fraction charged to a succeeding higher temperature stage, separating gasoline and gas between conversion stages from the unconverted oil and returning at least a portion of the unconverted oil from the final conversion stage to the zone in which the charging oil is separated into fractions.

2. A process which comprises separating hydrocarbon oil into a plurality of fractions, contacting each fraction with a cracking catalyst in a separate conversion stage at a temperature suitable for optimum conversion of said fraction, maintaining the conversion stages as successively higher temperatures, ranging between 800° F. and 1200° F. combining unconverted oil from a lower temperature stage with the fraction charged to a succeeding higher temperature stage, separating gasoline and gas between conversion stages, and recycling heavy unconverted oil from the final stage to the first-mentioned separating step.

3. A process which comprises separating crude hydrocarbon oil into a plurality of fractions, maintaining a series of separate conversion steps of progressively increasing temperature ranging between 800–1200° F., contacting each of said fractions with a cracking catalyst in a conversion stage maintained at the temperature suitable for maximum conversion of each fraction, returning a minor portion of unconverted oil from each stage to the same stage, combining a major portion of unconverted oil from a lower temperature stage with the fraction charged to a succeeding higher temperature stage, and separating gascline and gas between stages from the unconverted oil.

4. The process claimed in claim 3, wherein at least a portion of heavy unconverted oil from the final stage is returned to the zone wherein the crude oil is separated into fractions.

5. A hydrocarbon oil conversion process which comprises fractionating the charging oil and separating therefrom relatively light and heavy fractions, subjecting the heavier fraction to catalytic cracking in a first conversion stage, subjecting the lighter fraction to catalytic cracking at higher temperature in a second conversion stage, supplying a major portion of the unconverted oil from the first stage to the second stage for further cracking treatment therein at the higher temperature in admixture with the lighter fraction, and returning a minor portion of said unconverted oil to the first stage for retreatment therein together with said heavier fraction.

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