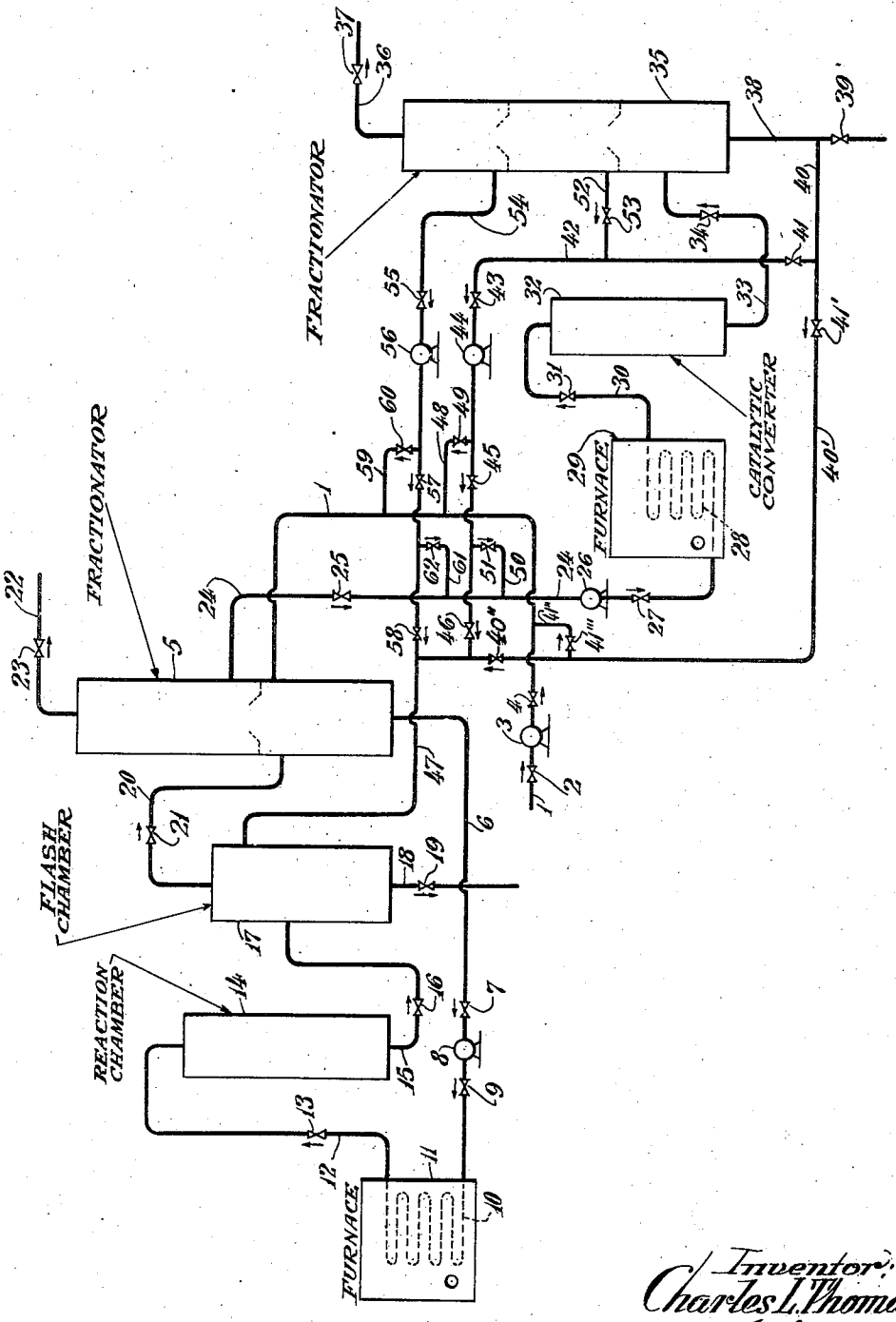
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CONVERSION OF HYDROCARBON OIL

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Inventor:
Charles L. Thomas
By Lee J. Gary
Attorney

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CONVERSION OF HYDROCARBON OILS

Charles L. Thomas, Chicago, Ill., assignor to Universal Oil Products Company, Chicago, Ill., a corporation of Delaware

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5 Claims. (Cl. 196—52)

This invention relates to the conversion of crude petroleum into substantial yields of motor fuel products and is a continuation-in-part of my co-pending application Serial No. 166,570, filed September 30, 1937. The process may also be applied to similar hydrocarbon distillates from other sources, such as shale oils, coal tars, etc.

More specifically, the invention is concerned with a process involving both thermal and catalytic cracking with a definite interrelation of steps so that maximum benefits are obtained not only in respect to yields and antiknock value of the finished product, but also in respect to the life of the catalytic masses employed in the catalytic cracking step.

The limitations of ordinary non-catalytic cracking in the production of high yields of antiknock gasoline are fairly well recognized. The increasingly severe conditions of temperature, pressure and time result in increased antiknock value of the gasoline product up to a certain point after which there is a disproportionately large loss as gas and residue, so that the overall economics of such an operation reaches a more or less definite limit. In order to increase the antiknock value for a given yield of gasoline various catalytic masses have been used with some success.

Such catalytic masses have not been universally applicable to all types of hydrocarbon oils, particularly heavier fractions such as topped crude oil, reduced crude oil, etc. These masses have, however, been used successfully for processing distillate fractions of crude petroleum, and particularly such fractions as may be distilled under ordinary conditions of pressure without substantial decomposition, such as gas oils, kerosene, and the like.

During the catalytic cracking of petroleum fractions, carbonaceous materials deposit on the catalytic surfaces necessitating frequent regeneration by means of an oxygen-containing gas. When heavier fractions such as topped crude oils, and the like, are cracked the amount of such carbonaceous deposits becomes disproportionately large, and as a result reactivation becomes difficult because of the amount of carbon which must be consumed. For this reason the charging stocks used in catalytic cracking are limited more or less to distillate fractions. The present process, the character of which will be developed in succeeding paragraphs, is a novel contribution to practiced methods of cracking for increased yields and antiknock value by the combination of catalytic and non-catalytic cracking operations.

In one specific embodiment the present invention comprises a process for converting crude hydrocarbon oil into substantial yields of high octane number gasoline, which comprises charging said crude hydrocarbon oil to a primary fractionator, subjecting the heavy unvaporized portion of the oil to non-catalytic cracking in a tubular heating element followed by a reaction chamber operated at elevated temperatures and pressures to bring about substantial conversion to gasoline and gas, separating and recovering the heavier products from this step which are unsuitable for further conversion, fractionating the remaining products in the aforesaid primary fractionator to produced fixed gases, gasoline, and an intermediate distillate fraction, contacting said intermediate fraction in vaporous form with a cracking catalyst under conditions adequate to effect substantial cracking thereof, recovering the reaction products, separating the gas and gasoline in a secondary fractionation step, removing one or more intermediate boiling distillate fractions of insufficiently converted oil, returning a portion of said oil to the catalytic cracking step, and returning a second portion of said insufficiently converted oil to the non-catalytic cracking step.

The various cooperative features of the present invention may be further understood from a description of a process flow and for this purpose the accompanying drawing has been provided which shows, by the aid of conventional figures, a diagrammatic outline of interconnected units in which the process may be conducted. The apparatus has not been drawn to scale, nor has any attempt been made to proportionate the various units thereof. Furthermore, it has been simplified by leaving out various heat exchangers, condensers, stabilizers, and other parts of equipment which would be necessary in the operation of the process but are not special features of the invention. The invention should not be construed as being limited to the exact apparatus or conditions given therein.

The charging stocks used in this process may comprise distillate fractions of crude petroleum oils, crude oils themselves, or topped crude oils, or similar hydrocarbon oils from other sources. Referring to the drawing, the crude petroleum oil is charged through line 1, valve 2, pump 3, valve 4, into the lower section of fractionator 5 wherein the lower boiling fractions are vaporized. The unvaporized oil is removed through line 6, valve 7, pump 8 and valve 9 into heating coil 10 which is disposed in furnace 11. The tempera-

ture of the oil is raised to a suitable cracking temperature within the range of 850°–1000° F. and pressures within the range of 100–500 pounds per square inch or more. The heated oil leaves the furnace through line 12, valve 13 and enters reaction chamber 14 wherein the major portion of the conversion to gasoline and gas occurs. The reaction products are withdrawn through line 15 and valve 16 into flash chamber 17 wherein the pressure is reduced to a point sufficient to bring about substantial vaporization of the valuable liquid products. Residual oil unsuitable for further conversion in the process is withdrawn through line 18 and valve 19 to storage. The overhead products pass through line 20 and valve 21 to fractionator 5 wherein the lower boiling materials are vaporized. The gasoline and gas are withdrawn through line 22 and valve 23 to suitable stabilizers, heat exchangers, coolers, etc., not shown. An intermediate distillate fraction is withdrawn through line 24, valve 25, pump 26 and valve 27 and passed to coil 28 which is disposed in furnace 29. The fraction is heated to a desired conversion temperature and passed through line 30 and valve 31 in vaporous form into catalytic converter 32, wherein a suitable cracking catalyst is disposed. The catalytic converter may comprise any suitable form such as bundles of tubes containing the catalyst, reaction chambers, etc. The converters are usually used in pairs, the two converters being alternated between conversion and reactivation steps. The reaction products leave the catalytic converter through line 33 and valve 34 and enter fractionator 35. Gas and gasoline are withdrawn through line 36 and valve 37 through heat exchangers, stabilizers, condensers, receivers, etc., not shown. A portion of the insufficiently converted oil may be withdrawn through line 38 and valve 39. A portion of the insufficiently converted oil may be passed through line 40, valve 41', line 40' and valve 40'' to line 58 and thence to flash chamber 17. Alternatively, the oil may be passed through line 41'' and valve 42''' to line 1 and thence to the fractionator. One or more intermediate fractions may be withdrawn from fractionator 35 in a manner about to be described. A portion or all of the insufficiently converted fraction may be withdrawn through line 38, line 40, valve 41, line 42, valve 43, pump 44, valve 45, line 50, valve 51 and line 24 to be returned to the catalytic cracking step.

Alternatively a portion of the oil may be passed through line 48, valve 49 and line 1 to fractionator 5. An intermediate fraction may be withdrawn through line 52 and valve 53 which joins with line 42 and passed to either the thermal or the catalytic cracking step as just described. A portion of the heavy oil from lines 38 and 40 may be mixed with the fraction from line 52.

In a further alternative a side cut may be withdrawn through line 54, valve 55, pump 56, valve 57 and valve 58 to flash chamber 17, or a portion or all of the oil may be passed through line 59, valve 60 and line 1 to the fractionator. A portion of the fraction may be passed through line 61 and valve 62 which joins with line 24, and thus returned to the catalytic cracking step.

According to a further alternative a heavy fraction may be withdrawn from fractionator 35 as outlined in the foregoing description, and returned to the catalytic cracking step by means of line 42, valve 43, pump 44, valve 45, line 50, valve 51, line 24, pump 26, valve 27, coil 28, line 30 and valve 31. Simultaneously a lighter fraction of insufficiently converted oil may be withdrawn through line 54, valve 55, pump 56, valve 57, valve 58 and line 47 to flash chamber 17.

In another alternative all or a portion of the lighter fraction of insufficiently converted oil may be passed through line 54, valve 55, pump 56, valve 57, line 61, valve 62 and line 24 through previously described routes to the catalytic cracking step. At the same time a heavy fraction of the insufficiently converted oil may be withdrawn through line 38, line 40, valve 41, line 42, valve 43, pump 44, valve 45, valve 46, and line 47 to flash chamber 17.

Moreover, a portion of both light and heavy recycle stock consisting of insufficiently converted oil may be mingled with the charge to the catalytic cracking step in line 24 by withdrawing regulated portions of each of the lighter and heavier oils through valves 51 and 62 and lines 50 and 61, thereby regulating the composition of the charge to the catalytic cracking step as may be desired, and at the same time returning the remainder of insufficiently converted oil to the non-catalytic cracking step. The use of the intermediate fractions of insufficiently converted oil as recycle stock in the manners described above is an important feature of the process since the life of the catalyst mass and the extent of conversion can be regulated in any desired manner depending upon the products desired and the charging stocks used.

The optimum temperature range for catalytically cracking the hydrocarbon vapors is within the range of approximately 800°–1200° F., and pressures are suitably atmospheric or only slightly superatmospheric up to approximately 100 pounds per square inch.

Numerous types of cracking catalysts may be used, among which are fuller's earth or other clays which have been treated with acids or other chemicals, which have been promoted by the addition of metals or metal oxides. Another type of catalyst which may be used to advantage comprises refractory oxides such as those of aluminum or magnesium which have been promoted by the addition of small percentages of metal oxides including those of chromium, molybdenum, vanadium, tungsten, iron, etc. One type of catalyst which has been particularly useful comprises a composite of a major portion of precipitated silica having added thereto alumina and/or zirconia. These catalysts are prepared by mixing the precipitated and washed hydrogels or coprecipitating the masses under conditions whereby alkali-metal compounds are substantially eliminated. The masses are then formed into shapes by compression or extrusion methods, dried, and calcined at temperatures in excess of 800° F. prior to their use in the process. The ratio of the added compound to silica may vary over a considerable range and is normally within the limits of approximately 5–30% by weight.

The following example is given for purposes of illustration but should not be interpreted as limiting the process to the exact conditions given therein.

A 26° A. P. I. Midcontinent topped crude oil was charged to the fractionating column 5 and the unvaporized portion was passed through coil 18 and reaction chamber 14 where it was cracked at a temperature of 950° F. and a pressure of 400 pounds per square inch. The reaction prod-

ucts were passed to flash chamber 17 from which a residual fuel oil having a Furol viscosity of 500 seconds at 122° F. was withdrawn. The vaporized products were passed to reaction chamber 5 and the gasoline and gaseous products were taken overhead. An intermediate boiling fraction of approximately 35 gravity was withdrawn from fractionator 5 and passed through coil 28 wherein it was vaporized and heated to the cracking temperature. The vapors were passed through catalytic converter 32 where they contacted a precipitated silica-12% alumina-4% zirconia catalyst mass at a temperature of 975° F. The reaction products were passed to fractionator 35 from which the gasoline and gas were removed. The heavy recycle oil was withdrawn through line 38 and line 40 and, as described in the foregoing specifications, returned to flash chamber 17. An intermediate boiling fraction of insufficiently converted oil was withdrawn through line 54, and returned by previously described routes to the catalytic conversion step 32 for further conversion to gasoline and gas. A total yield of approximately 59% of gasoline was obtained in this manner. The catalytically cracked fraction had an octane number of 81 and the thermally cracked portion had an octane number of 72, the total octane number of the blend of material being 76. The yield of 76 octane number-gasoline obtainable from this stock by non-catalytic cracking alone was approximately 51%.

I claim as my invention:

1. A process for converting a hydrocarbon oil into substantial yields of relatively high antiknock gasoline which comprises charging said oil to a primary fractionation step and therein vaporizing a substantial portion of the oil, separating a relatively heavy unvaporized fraction of the oil, subjecting said fraction to non-catalytic cracking in a heating coil and communicating reaction chamber at a temperature and pressure adequate to effect substantial cracking thereof, passing the reaction products into a vaporizing zone at a reduced pressure, separating a residual fraction unsuitable for further conversion, passing the vaporized portion of the reaction products from said vaporizing zone to said primary fractionation step, separating the gas, gasoline, and an intermediate-boiling fraction, contacting said intermediate fraction and distillate fractions of the charging oil in vaporous form with a cracking catalyst in a catalytic cracking step under conditions adequate to effect substantial cracking thereof, passing the reaction products to a secondary fractionation step, recovering the gas and gasoline, separating the insufficiently converted oil from said catalytic cracking step into a low-boiling, an intermediate-boiling and a high-boiling fraction, mixing the high-boiling fraction with the low-boiling fraction, supplying the mixture to the aforesaid vaporizing zone of the non-catalytic cracking step, and returning the intermediate-boiling fraction from said secondary fractionation step to said catalytic cracking step.

2. A process for converting a hydrocarbon oil into substantial yields of relatively high antiknock gasoline which comprises charging said oil to a primary fractionation step, separating a relatively heavy unvaporized fraction of the oil, subjecting said heavy fraction to a non-catalytic cracking step in a heating coil and communicating reacting chamber at a temperature and pressure adequate to effect substantial cracking thereof, passing the reaction products into a vaporizing zone, separating a residual fraction unsuitable for further conversion, passing the vaporized portion of the reaction products to the primary fractionation step, separating the gas, gasoline and an intermediate-boiling fraction, contacting the last-named fraction in vaporous form with a cracking catalyst in a catalytic cracking step under conditions adequate to effect substantial cracking thereof, passing the reaction products to a secondary fractionation step, recovering the gas and gasoline, separating the insufficiently converted oil in said secondary fractionation step into a lower-boiling fraction, an intermediate-boiling fraction, and a residual fraction, supplying said lower-boiling fraction and a portion of said residual fraction to said non-catalytic cracking step, mixing said intermediate-boiling fraction of insufficiently converted oil with a portion of the residual fraction, and returning said mixture to said catalytic cracking step.

3. A process for converting a hydrocarbon oil into substantial yields of relatively high antiknock gasoline which comprises charging said oil to a primary fractionation step and therein vaporizing a substantial portion of the oil, separating a heavy unvaporized fraction of the oil, subjecting said fraction to non-catalytic cracking in a heating coil and communicating reaction chamber at a temperature and pressure adequate to effect substantial cracking thereof, passing the reaction products into a vaporizing zone at a reduced pressure, separating a residual fraction unsuitable for further conversion, passing the remaining portion of the reaction products to said primary fractionation step, separating gas, gasoline and an intermediate-boiling fraction, contacting said intermediate fraction and distillate fractions of the charging oil in vaporous form with a cracking catalyst in a catalytic cracking step under conditions adequate to effect substantial cracking thereof, passing the reaction products to a secondary fractionation step, and separating the gas and gasoline from insufficiently converted oil, returning a relatively light fraction of the insufficiently converted oil to said catalytic cracking step, and supplying a heavier fraction of said insufficiently converted oil to said primary fractionator.

4. A process for converting a hydrocarbon oil into substantial yields of relatively high antiknock gasoline which comprises charging said oil to a primary fractionation step, separating a relatively heavy unvaporized fraction of the oil, subjecting said fraction to non-catalytic cracking in a heating coil and communicating reaction chamber at a temperature and pressure adequate to effect substantial cracking thereof, passing the reaction products into a vaporizing zone at a reduced pressure, separating a residual fraction unsuitable for further conversion, passing the vaporized portion of the reaction products to said primary fractionation step, separating gas, gasoline and an intermediate-boiling fraction, contacting said intermediate boiling fraction in vaporous form with a cracking catalyst in a catalytic cracking step under conditions adequate to effect substantial cracking thereof, passing the reaction products to a secondary fractionation step, recovering the gas and gasoline, separating the insufficiently converted oil in said secondary fractionation step into a low-boiling fraction, an intermediate-boiling fraction, and a high-boiling fraction, mixing a portion of said intermediate-boiling fraction and a portion of the low-boiling

fraction of insufficiently converted oil and returning the mixture to said catalytic cracking step, mixing a second portion of the low-boiling fraction and a second portion of the intermediate-boiling fraction with the high-boiling fraction and returning the mixture to the aforesaid vaporizing zone.

5. A process for converting a hydrocarbon oil into substantial yields of relatively high anti-knock gasoline which comprises charging said oil to a primary fractionation step, separating a relatively heavy unvaporized fraction of the oil, subjecting said fraction to non-catalytic cracking in a heating coil and communicating reaction chamber at a temperature and pressure adequate to effect substantial cracking thereof, passing the reaction products into a vaporizing zone at a reduced pressure, separating a heavy residual fraction unsuitable for further conversion, passing the vaporized portion of the reaction products from said vaporizing zone to the primary fractionation step, separating therefrom the gas, gasoline, and an intermediate-boiling fraction, contacting said intermediate fraction in vaporous form with a cracking catalyst in a catalytic cracking step under conditions adequate to effect substantial cracking thereof, passing the reaction products to a secondary fractionation step, separating the gas and gasoline, separating the insufficiently converted oil into a low-boiling fraction, an intermediate-boiling fraction and a residue, returning the low-boiling fraction to said vaporizing zone, returning the intermediate-boiling fraction of insufficiently converted oil to said catalytic cracking step, and mixing said residue of insufficiently converted oil with the aforesaid hydrocarbon oil being supplied to the primary fractionation step.

CHARLES L. THOMAS.