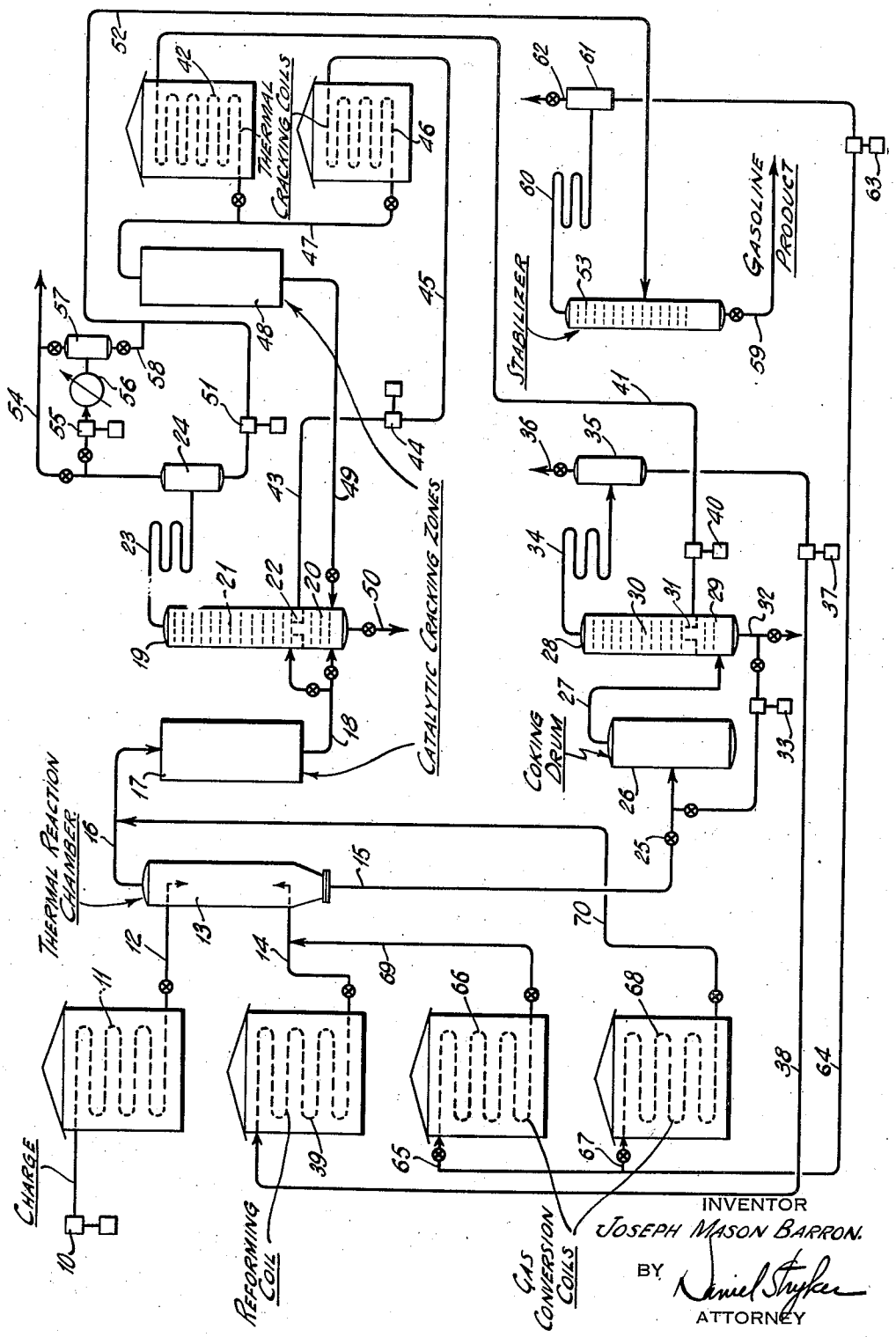
July 9, 1946. J. M. BARRON 2,403,486

COMBINATION CATALYTIC AND THERMAL CONVERSION

Filed Dec. 19, 1944



INVENTOR
JOSEPH MASON BARRON.
BY Daniel Stryker
ATTORNEY

Patented July 9, 1946 2,403,486

UNITED STATES PATENT OFFICE

2,403,486

COMBINATION CATALYTIC AND THERMAL CONVERSION

Joseph Mason Barron, Port Arthur, Tex., assignor to The Texas Company, New York, N. Y., a corporation of Delaware

Application December 19, 1944, Serial No. 568,886

6 Claims. (Cl. 196—49)

1

This invention relates to the combination catalytic and thermal conversion of hydrocarbons and contemplates particularly a method of processing high boiling or residual petroleum stocks to ultimate yields of coke and high antiknock gasoline or motor fuel.

In accordance with the invention, petroleum stocks such as crude oils and topped crudes are contacted with highly heated light stocks of the nature of gasoline or naphtha as well as normally gaseous hydrocarbons in a reaction zone maintained under superatmospheric pressure and at a cracking temperature. The contacting of these dissimilar stocks is conducted in such a way as to obtain thermal conversion of the intermingled constituents and also to obtain maximum vaporization so that the separated vapors will contain not only the gasoline components but also the bulk of the gas oil constituents. The thermal cracking to which the constituents are subjected in the reaction chamber functions particularly to crack paraffins and concentrate naphthenes and aromatics to produce good material for a succeeding catalytic cracking step. Products vaporized in this combination cracking and separating step constitute the charging material for a succeeding catalytic cracking step. The residual product from the thermal cracking and separating step is subjected to coking and vapors evolved in the coking operation are fractionated to separate lower boiling fractions from higher boiling fractions. The lower boiling fractions, after being subjected to thermal conversion or reforming, are directed to the thermal cracking and separating zone for promoting the vaporizing and cracking of the residual charging stock. Higher boiling fractions from the coking operation are passed through a heating zone and subjected to thermal cracking. Higher boiling fractions obtained in fractionating the catalytically cracked products are likewise passed through a heating zone and subjected to thermal cracking. The thermally cracked products from these two heating zones are combined and the mixture is subjected to catalytic cracking. Normally gaseous hydrocarbons recovered from the combination process are subjected to thermal conversion and then directed to the thermal cracking and separating zone or combined with the vaporized effluent therefrom, which passes to the catalytic cracking step mentioned.

For the purpose of completely disclosing the invention, reference is had to the accompanying drawing which is a flow diagram illustrating a particular embodiment of the invention.

Referring now to the drawing, charging stock

2

such as crude oil or topped crude containing a large content of gas oil is introduced by a pump 10 to heating coil 11 wherein it is heated to a cracking temperature. The heated effluent is directed through a transfer line 12 to the upper portion of a reaction chamber 13. Highly heated vapors and gases enter the lower portion of the reaction chamber through a line 14. The reaction chamber is maintained at a high cracking temperature of the order of 900° F. by reason of the heated entering fluids and maintained under a superatmospheric pressure such as 200–600 p. s. i. The downflowing liquid is subjected to countercurrent contacting with the upwardly rising vapors at the high temperature, in a zone free from baffles or other obstructions, to not only produce cracking but also to cause maximum vaporization. Liquid is prevented from accumulating by rapid withdrawal from the chamber through a line 15 and it is, in fact, best to operate the reaction chamber "dry," that is, without any liquid level therein.

The separated vapors pass from the separating and cracking chamber 13 through a vapor line 16 to a catalytic cracking zone 17 wherein the vapors are subjected to catalytic conversion in contact with a solid comminuted or pulverulent catalyst. The contacting of the vapors and gases with the catalyst may be accomplished in various ways, such as passing the vapors through a stationary bed of catalyst, passing the vapors over a continuously moving mass of granular catalyst, or by suspending finely divided or powdered catalyst in the stream of gases and vapors for conversion under fluid catalyst conditions. The preferred catalysts are the silica-alumina catalysts, such as in the form of activated clays or as synthetic precipitated composites of silica and alumina. When using the catalyst in the form of fixed beds a plurality of catalyst cases are employed which may alternate on processing and regenerating in a well-known manner, and when using catalyst suspended in the vapor stream or under fluid catalyst cracking conditions, the catalyst may be continuously withdrawn for regeneration. The vapors and gases are contacted with the catalyst at temperatures such as 800–1000° F. under moderate superatmospheric pressures, preferably not exceeding about 100 p. s. i. to affect the catalytic cracking of higher boiling hydrocarbons into lower boiling products of gasoline boiling range, while at the same time recombination reactions with the gaseous hydrocarbons and catalytic reforming of gasoline constituents takes place.

The products of the catalytic conversion pass

through a transfer line 18 to a fractionator 19. The fractionator is preferably formed with a primary section 20 and a secondary section 21 separated by a condensate tray 22 and the transfer line 16 is branched so that the catalytically cracked products may be delivered to either the primary or secondary fractionating zones. The fractionator is provided with suitable cooling and refluxing means so as to take off as vapors a product of desired end point, as for example, 400° F. end point for ordinary motor fuel or 375° F. end point for aviation motor fuel. The overhead vapors are condensed in a cooler 23 and the distillate is collected in a distillate drum or gas separator 24.

Referring now to the disposition of the residue withdrawn from the reaction chamber 13 through line 15, this residue is directed through a pressure reducing valve 25 to a coking drum 26. By reason of the manner of contacting the heavy stock with the light stream of gases and vapors in the reaction chamber it is possible to maintain the liquid residue being withdrawn at a sufficient temperature and sufficiently free from gas oil constituents that this residue may be flashed to coke in the coking drum solely by its contained heat. While any deficiency in heat may be overcome by including a portion of the vapors with the residue withdrawn from the reaction chamber, it is preferable to maintain the quantity of vapor thus withdrawn at a minimum and to rely on the temperature of the liquid residue to accomplish autogenous coking. By withdrawing the residue at temperatures around 920–930° F. conversion to a marketable coke may be accomplished by flashing solely by the contained heat of the residue. In practice, a plurality of coking drums are employed so as not to interrupt the continuity of the complete process. The coking drum is maintained at low pressure such as 50 p. s. i. down to approximately atmospheric pressure.

The vapors evolved in the coking drum pass through a vapor line 27 to a fractionator 28 which is preferably formed with a primary section 29 and a secondary section 30, separated by a condensate tray 31, with the vapor line entering the primary fractionating zone 29. In the latter fractionating zone the vapors are subjected to a primary dephlegmation at relatively high temperatures approximating 800° F. throughout the zone to separate out the synthetic tar. This tarry product may be withdrawn as a fuel oil product through line 32 or directed by a pump 33 to the coke drum 26 for conversion to coke. The gas oil condensate is collected on the tray 31; the naphtha vapors pass to a cooling coil 34 for condensation and the naphtha distillate is collected in a receiving drum or gas separator 35, having a gas line 36 which may extend to a low pressure gas recovery system (not shown).

The coke still naphtha is withdrawn from the receiver 35 and directed by pump 37 through line 38 to a heating coil 39 wherein it is subjected to thermal reforming at temperatures such as 900–1050° F. under pressure such as 400–600 p. s. i. The vaporous products of conversion are directed through the transfer line 14 to the lower portion of the reaction chamber 13.

Condensate from tray 31 is directed by a pump 40 through line 41 to a heating coil 42 wherein the condensate is subjected to conditions of thermal cracking. The catalytic gas oil collected on the tray 22 of fractionator 19 is withdrawn through a line 43 and directed by pump 44 through

line 45 to a heating coil 46 wherein the oil is subjected to conditions of thermal cracking. In the cracking coils 42 and 46 the oil is subjected to temperatures such as 900–1000° F. with coil outlet pressures of from 400–700 p. s. i. to produce extensive thermal conversion. The particular conditions obtained in the cracking coils 42 and 46 may be varied in accordance with the character of the stocks directed to these coils, but in general the catalytic gas oil being cracked in coil 46 will stand a soaking volume factor of from 5–7 (basis 750 p. s. i.) at about 950° F. heater outlet temperature, and the gas oil from the coking operation being cracked in coil 42 will stand a soaking volume factor of 8–10 with a coil outlet temperature of about 1000° F. In the cracking coils 42 and 46 extensive thermal conversion takes place which involves particularly the cracking of olefins and paraffins, with the result that the effluent from these cracking coils is of reduced paraffinicity and contains high concentrations of olefins, naphthenes and aromatics. The thermal cracking not only produces gasoline but also yields higher boiling components of increased susceptibility to catalytic cracking.

The effluent from the thermal cracking coils 42 and 46 is combined in a transfer line 47 which leads to a catalytic cracking zone 48 wherein the mixture is subjected to catalytic cracking in contact with cracking catalysts, such as any of those previously mentioned, in accordance with any of the several methods which have been outlined for the catalytic cracking zone 17. The mixed stocks subjected to catalytic cracking undergo various reactions including conversion into lower boiling hydrocarbons accompanied with exchange reactions and cyclization functioning to form constituents in the gasoline boiling range of high antiknock quality. And the olefin content of the gasoline constituents, formed by the preceding thermal cracking, is reduced.

The catalytically cracked products are directed through a line 49 to the fractionator 19 or more particularly to the fractionating section 20 thereof. The effluent from the catalytic cracking zone 48 will generally contain some higher boiling constituents of a somewhat more refractory nature than those contained in the effluent from the catalytic cracking zone 17 and consequently it is ordinarily desirable to direct the products from the cracking zone 48 to the primary separating section 20 while delivering the products from cracking zone 17 to the secondary fractionating section 21. A quantity of residue may thus be separated in the dephlegmator 20 which may be withdrawn through a line 50. This residue may be removed from the system as a product of the process or it may be sent to the fractionating zone 29 for refractionation therein.

The ultimate gasoline product resulting from the combination of the several thermal and catalytic conversion processes described herein is collected in the receiving drum 24. This distillate may be withdrawn from the receiving drum and directed by pump 51 through line 52 to a stabilizer 53. Uncondensed constituents are removed from the receiver 24 through a line 54. On account of the relatively low pressure existing in the receiver 24 the gases will contain considerable quantities of hydrocarbons adapted for inclusion in the gasoline product. To recover these constituents the gases flowing in line 54 may be diverted to a pump or compressor 55 by which the gas may be placed under several hundred pounds pressure and directed through a

cooler 56 to a drip drum 57 from which condensate may be withdrawn through a line 58 and sent to the stabilizer 53. The latter is provided with suitable cooling, refluxing and reboiling means (not shown) for rectifying the gasoline distillate, the final stabilized product being withdrawn through a line 59. Uncondensed constituents pass through cooler 60 to a distillate drum 61 from which uncondensed gases are removed through a line 62.

The distillate collecting in drum 61 under pressures of 200–400 p. s. i. consists largely or essentially of C_3 and C_4 hydrocarbons. These normally gaseous constituents are directed by a pump 63 through a line 64, thence through a branch line 65 to heating coil 66 or through a branch line 67 to heating coil 68, or a portion of the gases may be directed to each of these heating coils. The gases are subjected in these heating coils to high conversion temperatures of the order of 1000° F.–1100° F. under 400–800 p. s. i. to effect the cracking of paraffins as well as the polymerization of olefinic constituents. The effluent from gas conversion coil 66 is delivered through a transfer line 69 to the lower portion of the reaction chamber 13, together with the effluent from the naphtha reforming coil 39. The effluent from the gas conversion coil 68 is delivered through a transfer line 70 to the vapor line 16. The stream from the coil 68 may thus serve to increase the temperature of the vapors flowing from the reaction chamber to the catalytic cracking zone 17 and also to vary the space velocity or time of contact of the hydrocarbons with the catalyst.

Although a preferred embodiment of the invention has been described herein, it will be understood that various changes and modifications may be made therein, while securing to a greater or less extent some or all of the benefits of the invention, without departing from the spirit and scope thereof.

I claim:

1. In the combination thermal and catalytic cracking of hydrocarbon oils for the unitary processing of a charging stock obtained from crude petroleum and containing both residual and gas oil components thereof, the process that comprises introducing said charging stock to a reaction chamber, passing lower boiling hydrocarbons through a heating zone wherein they are heated to a cracking temperature, directing the resultant heated products to said reaction chamber to subject the residual stock to cracking and vaporization therein, passing separated vapors from the reaction chamber to a catalytic cracking zone wherein such fractions are subjected to catalytic cracking, withdrawing residual products from the reaction chamber and subjecting them to coking, fractionating vapors evolved from the coking operation to separate lighter fractions from higher boiling fractions, directing said lighter fractions to the aforesaid heating zone for conversion, subjecting said higher boiling fractions to cracking temperature with sufficient time of reaction to effect extensive thermal conversion including the cracking of olefins and paraffins, subjecting the resultant thermally cracked products of reduced paraffinicity to catalytic cracking and fractionating the products produced in the catalytic cracking operations to recover the catalytically cracked gasoline.

2. In the combination thermal and catalytic cracking of hydrocarbon oils for the unitary processing of a charging stock obtained from crude petroleum and containing both residual and gas oil components thereof, the process that comprises introducing said charging stock to a reaction chamber, passing naphtha through a heating zone wherein it is heated to a cracking temperature and subjected to reforming, introducing the heated naphtha into said reaction chamber to subject the residual stock to cracking and vaporization, passing separated vapors from the reaction chamber to a catalytic cracking zone wherein the vapors are subjected to catalytic cracking, fractionating the resultant catalytically cracked products in a fractionating zone to separate higher boiling from lower boiling products, passing the higher boiling products to a heating zone wherein they are subjected to cracking temperature with sufficient time of reaction to effect extensive thermal cracking including the cracking of olefins and paraffins, withdrawing residual products from the reaction chamber and subjecting them to coking, fractionating the vapors from the coking operation to obtain a lower boiling fraction comprising gasoline constituents and a higher boiling fraction, directing said lower boiling fraction to the aforesaid heating zone for reforming therein, directing said higher boiling fraction to a heating zone wherein it is heated to a cracking temperature and subjected to extensive thermal cracking including the cracking of olefins and paraffins, combining the resultant heated products of reduced paraffinicity from said thermal cracking operations and subjecting the mixture to catalytic cracking and passing the resultant catalytically cracked product to said fractionating zone.

3. In the combination thermal and catalytic cracking of hydrocarbon oils for the unitary processing of a charging stock obtained from crude petroleum and containing both residual and gas oil components thereof, the process that comprises passing lower boiling fractions through a heating zone wherein they are heated to a cracking temperature, directing the resultant heated products to the lower portion of a vertically disposed reaction chamber maintained under superatmospheric pressure and wherein separation of vapors from liquid residue takes place, introducing said charging stock to the upper portion of the vertically disposed reaction chamber, subjecting the down-flowing liquid and upwardly rising vapors to countercurrent contacting within the reaction chamber at cracking temperature, passing separated vapors from the reaction chamber to a catalytic cracking zone wherein such fractions are subjected to catalytic cracking, withdrawing residual products from the reaction chamber and subjecting them to coking, fractionating vapors evolved from the coking operation to separate light fractions from higher boiling fractions, directing said light fractions to the aforesaid heating zone for conversion, subjecting said higher boiling fractions to cracking temperature with sufficient time of reaction to effect extensive thermal conversion including the cracking of olefins and paraffins, subjecting the resultant thermally cracked products of reduced paraffinicity to catalytic cracking and fractionating the products produced in the catalytic cracking operations to recover the catalytically cracked gasoline.

4. In the combination thermal and catalytic cracking of hydrocarbon oils for the unitary processing of a charging stock obtained from crude petroleum and containing both residual and gas oil components thereof, the process that

comprises passing naphtha through a heating zone wherein it is heated to a cracking temperature and subjected to conversion, introducing the heated naphtha into the lower portion of a vertically disposed reaction chamber maintained under superatmospheric pressure and wherein separation of vapors from liquid residue takes place, heating said charging stock to cracking temperature and directing the heated oil to the upper portion of the vertically disposed reaction chamber, subjecting the downflow liquid and upwardly rising vapors to countercurrent contacting within the reaction chamber at cracking temperature, passing the separated vapors to a catalytic cracking zone wherein the vapors are subjected to catalytic cracking, fractionating the resultant catalytically cracked products in a fractionating zone to separate higher boiling from lower boiling products, subjecting the higher boiling products to cracking temperature with sufficient time of reaction to effect extensive thermal cracking including the cracking of olefins and paraffins, withdrawing residual products from the reaction chamber and subjecting them to coking, fractionating the vapors from the coking operation to obtain a lower boiling fraction containing gasoline constituents and a higher boiling fraction, directing said lower boiling fraction to the aforesaid heating zone for reforming therein, directing said higher boiling fraction to a heating zone wherein it is heated to a cracking temperature and subjected to cracking temperature with sufficient time of reaction to effect extensive thermal conversion including the cracking of olefins and paraffins, combining the resultant heated products of reduced paraffinicity from said thermal cracking operations and subjecting the mixture to catalytic cracking and passing the resultant catalytically cracked products to said fractionating zone.

5. In the combination thermal and catalytic cracking of hydrocarbon oils the process that comprises passing naphtha through a heating zone wherein it is heated to a cracking temperature and subjected to conversion, introducing the heated naphtha into the lower portion of a vertically disposed reaction chamber maintained under superatmospheric pressure and wherein separation of vapors from liquid residue takes place, heating a residual stock to cracking temperature and directing the heated oil to the upper portion of the vertically disposed reaction chamber, subjecting the downflow liquid and upwardly rising vapors to countercurrent contacting within the reaction chamber at cracking temperature,

passing the separated vapors to a catalytic cracking zone wherein the vapors are subjected to catalytic cracking, fractionating the resultant catalytically cracked products in a fractionating zone to obtain fractions comprising a normally gaseous fraction, a gasoline fraction and a higher boiling fraction, heating the normally gaseous fraction to subject it to thermal conversion and directing the resultant conversion products into the lower portion of said vertically disposed reaction chamber, heating the higher boiling fraction to a cracking temperature to subject it to thermal cracking, withdrawing residual products from the reaction chamber and subjecting them to coking, fractionating the vapors from the coking operation to obtain a lower boiling fraction containing gasoline constituents and a higher boiling fraction, directing said lower boiling fraction to the aforesaid heating zone for reforming therein, directing said higher boiling fraction to a heating zone wherein it is heated to a cracking temperature and subjected to thermal cracking, combining the resultant heated products from said thermal cracking operations and subjecting the mixture to catalytic cracking and passing the resultant catalytically cracked products to said fractionating zone.

6. In the combination thermal and catalytic cracking of hydrocarbon oils the process that comprises introducing a heated residual stock to a reaction chamber, passing lower boiling hydrocarbons through a heating zone wherein they are heated to a cracking temperature, directing the resultant heated products to said reaction chamber to subject the residual stock to cracking and vaporization therein, passing lighter fractions evolved from the reaction chamber to a catalytic cracking zone wherein such fractions are subjected to catalytic cracking, withdrawing residual products from the reaction chamber and subjecting them to coking, fractionating vapors evolved from the coking operation to separate lighter fractions from higher boiling fractions, directing said light fractions to the aforesaid heating zone for conversion, subjecting said higher boiling fractions to thermal cracking, subjecting the resultant thermally cracked products to catalytic cracking and fractionating the products produced in the catalytic cracking operations to recover the catalytically cracked gasoline and a normally gaseous fraction, heating the normally gaseous fraction to subject it to thermal conversion and directing the resultant conversion products to said reaction chamber.

JOSEPH MASON BARRON.