

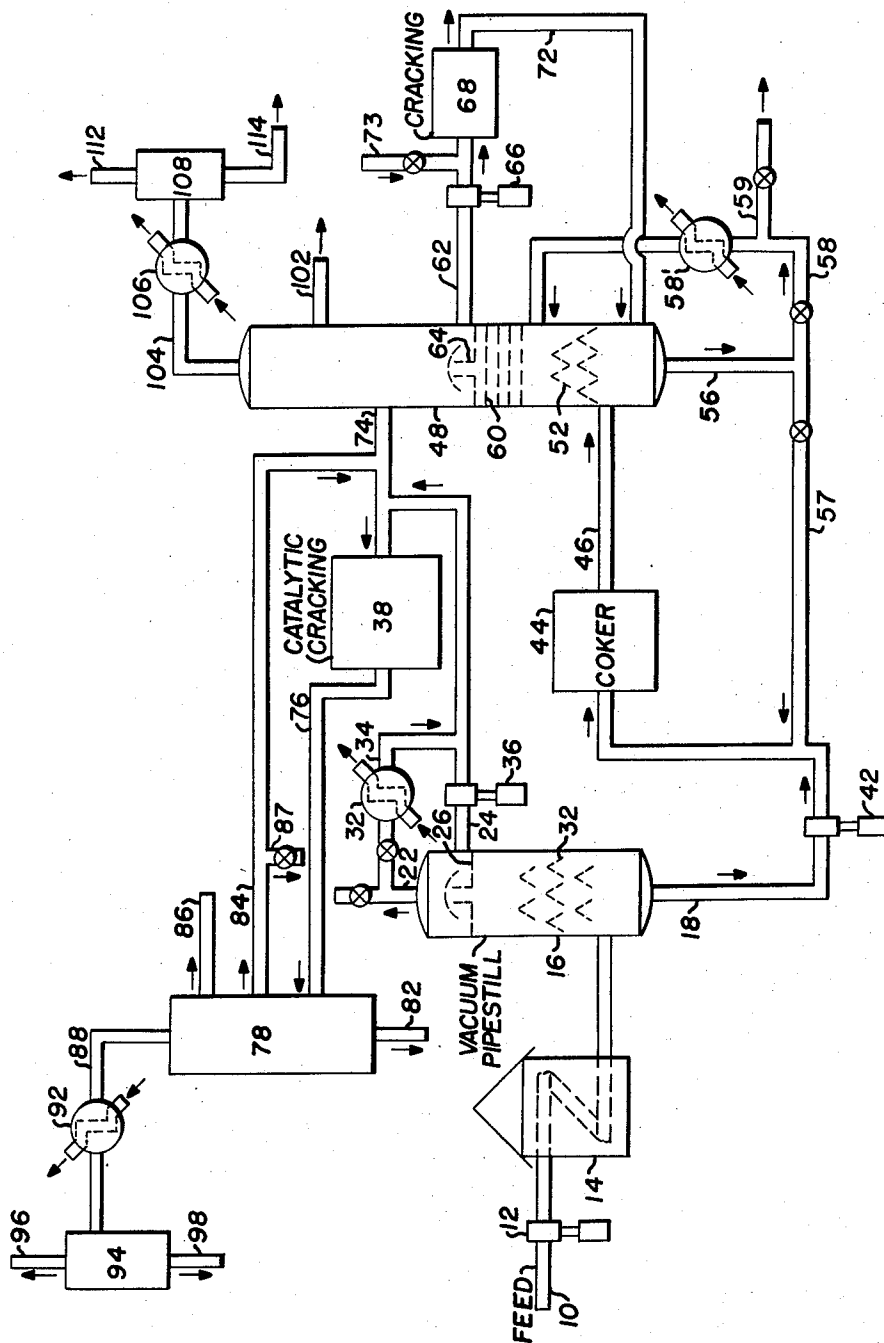
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CONVERSION OF HYDROCARBONS

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CONVERSION OF HYDROCARBONS

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This invention relates to cracking of hydrocarbons and more particularly relates to the preparation of hydrocarbon feed stock for catalytic cracking.

In the catalytic cracking of hydrocarbons there results contamination of the catalyst where the hydrocarbon feed contains certain contaminating materials. The contaminated cracking catalyst produces inferior product yields and also reduces throughput at constant carbon burning capacity by increasing carbon or coke make.

Various methods have been suggested for removing contaminants from catalytic cracking feed stocks and for removing contaminants from the contaminated catalyst but none of these has proven of sufficient value to be adopted commercially. The contaminating material comprises compounds of nickel, iron, vanadium, sodium, copper, etc.

According to the present invention reduced crude oil or topped crude oil is heated and passed to a vacuum pipestill to recover a vacuum gas oil essentially free of contaminating metals together with a somewhat longer residuum than in normal operation. This longer residual oil is processed in a new coking-cracking combination to produce an additional amount of essentially contaminating metal-free gas oil as a feed stock for catalytic cracking. The bottoms or heaviest portion of the fractionated reduced crude oil containing most of the ash or contaminating metal material and Conradson carbon is cracked in a fluid coker or other coking unit. The cracked vaporous products from the fluid coker are passed to a combination fractionator which separates a substantially contaminating metal-free gas oil suitable for feed to a catalytic cracking unit. The cracked vaporous products of coking are further fractionated into a higher boiling gas oil fraction and bottoms.

The higher boiling gas oil fraction is further cracked either catalytically, thermally, in a suspensoid-type cracking operation or in fluid coking. The cracking of the higher boiling gas oil fraction is operated at low conversion and is primarily for reducing the boiling point of the heaviest gas oil below that of volatile metal contaminants. The cracking is substantially a visbreaking operation at a relatively low conversion to minimize the formation of naphtha or gasoline and gas.

In the drawing, the figure diagrammatically represents one form of apparatus adapted for carrying out the invention.

Referring now to the drawing, the reference character 10 designates a line through which the hydrocarbon feed oil is passed by pump 12 into furnace 14. The hydrocarbon feed oil is any heavy hydrocarbon oil but according to the preferred form of the invention is reduced crude or topped crude oil from an atmospheric still. The topped crude has a boiling point above about 800° F. In the furnace 14, the hydrocarbon oil feed is heated to a temperature between about 650° and 750° F. and the heated oil is introduced into vacuum pipe still 16 which is maintained under an absolute pressure of about 40 to 200 mm. of mercury. The heated oil and vapors are in-

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roduced into the bottom portion of the tower 16 below the shed section 32 and the vapors are fractionated in the tower 16 into a bottoms fraction which is withdrawn from the bottom of the tower 16 through line 18 and a relatively heavy gas oil which is withdrawn from an upper portion of the tower 16 through line 24 from the trapout tray 26. A relatively light gas oil passes overhead from the tower 16 through line 22 and may be withdrawn from the system or passed through cooler 32 in line 34 and mixed with the gas oil withdrawn through line 24.

The gas oil withdrawn through line 24 and the light gas oil from line 34 are substantially free of metal ash or contaminating metal compounds. The temperature during fractionation is maintained below about 600° F. to 700° F. The depth of distillation would be controlled by tower pressure at 40–100 mm. of mercury. The gas oil fraction withdrawn through line 24 has substantially no metal contaminating substance or material in it and the gas oil forms an excellent feed for catalytic cracking. The gas oil feed is passed through line 24 by pump 36 to the catalytic cracking step shown diagrammatically at 38.

Bottoms from the tower 16 are withdrawn through line 18 and passed by pump 42 to a fluid coking step diagrammatically shown at 44. The residual oil or bottoms from the tower 16 has a boiling point above about 1000° F. and is subjected to coking conditions in the coking unit 44. The temperature during coking is between about 900° and 1000° F. The fluid bed is made up of coke particles having a size between 20 and 1000 microns with the majority of the particles being below about 500 microns. During coking the residual oil or bottoms is coked and forms additional distillate stock such as gas oil and coke which is deposited on the coke particles. A small amount of gasoline or naphtha below about 20% by volume is produced during the coking operation. To supply heat to the coking step, coke is withdrawn from the fluid coker, mixed with air and passed to a burner where some of the coke is burned and the rest of the coke is heated to a temperature about 100° F. to 300° F. higher than the coking temperature in order to supply heat of cracking and the heat necessary to vaporize the residual oil or bottoms introduced as feed to the coking unit.

The hot vaporous cracked products from the coker 44 are passed through line 46 into the bottom portion of a combination fractionator 48 below the shed section 52. The cracked products are fractionated in the tower 48 to separate a bottoms residual fraction which is withdrawn from the bottom of the tower through line 56 and which may be all or in part recycled through line 57 to the coking unit 44. Or a part of this bottoms fraction may be cooled in cooler 58' and passed through line 58 and recycled to the tower 48 above the shed section 52 so as to remove heat and to wash down the shed baffles. If desired, a portion of the bottoms fraction may be withdrawn from the process through line 59. A refluxing section 60 is provided above the shed section 52 and includes a plurality of perforated plates or the like. The improvement in fractionation resulting from refluxing allows the maximum amount of gas oil to be taken overhead with a specified content of metals contamination.

The vapors as they pass upwardly through the combination fractionating tower 48 are fractionated and a heavy gas oil fraction is withdrawn from an intermediate portion of the tower 48 through line 62 from trapout tray 64. This gas oil has a boiling range between about 900° and 1100° F. and contains metal contaminating material such as nickel and/or vanadium and/or iron compounds. The temperature of the tower in the region of the trapout tray 64 is maintained at a temperature be-

tween about 500 and 700° F. which is below the volatilizing temperature of metal contaminating materials so that these contaminating materials remain in the gas oil fraction withdrawn through line 62.

The relatively heavy gas oil fraction containing the metal contaminating materials and withdrawn through line 62 are passed by pump 66 to the cracking unit 68 and the cracked vaporous products are passed through line 72 and returned to the bottom of the fractionating tower 48 below the shed section 52. Steam is introduced into line 62 via line 73. The cracking step carried out in the cracking unit 68 is operated at low conversion preferably between about 10% and 40% 430° F. conversion, that is, the conversion equals 100% minus the volume percentage of products boiling above 430° F. The cracking step is intended primarily to reduce the boiling point of the heaviest gas oil fraction below that of the volatile metal contaminants and is in effect a visbreaking operation to form lower boiling gas oil constituents without the formation of any appreciable amount of naphtha or gasoline.

This cracking step in the cracking unit 68 may be a catalytic cracking step utilizing contaminated catalyst and operating at low conversion with steam diluent rates between about 5 and 20 weight percent on feed, high w./hr./w. (weight of oil per hour per weight of catalyst) and relatively high reactor temperature between about 950° to 1000° F. Under these conditions the catalyst contamination is not injurious to catalytic cracking yields. The catalytic cracking step cracks the metal contaminating material and deposits metal compounds on the catalyst so that the contaminating material is removed from the gas oil. If the catalyst in the cracking unit 68 becomes contaminated to too great an extent, portions of the catalyst may be removed and replaced by spent catalyst from the primary catalytic cracking unit 38 described above.

Where a catalytic cracking unit is used as the cracking unit 68 the fluid catalyst comprises silica-alumina, silica-magnesia, acid treated bentonite clays and so forth and the catalyst particles are of a size between about 20 and 100 microns with the major portion of the particles being between about 40 and 80 microns. During the cracking step, coke or carbonaceous material is deposited on the catalyst particles and they are withdrawn from the cracking unit and passed to a regeneration unit where they are mixed with air and the carbonaceous material is burned off the catalyst particles. The temperature during regeneration is between about 950° and 1200° F. and the catalyst particles at a temperature above the cracking temperature are returned to the cracking unit to supply heat of vaporization and cracking for the contaminated gas oil being passed through the cracking unit.

Instead of a catalytic cracking unit at cracking step 68 a thermal cracking step may be used including a high pressure coil in which the heavy gas oil containing contaminating material is maintained under a pressure of about 100 and 600 p.s.i.g. and the temperature during cracking is between about 850° and 1050° F. Where a thermal cracking step is used and the gas oil is visbroken, it is desirable to produce as little naphtha and gasoline and gas as possible and normally the amount of gasoline should be maintained below about 10% by volume of the feed.

Instead of thermal cracking, especially if used catalyst is available, the catalyst may be added to the liquid oil in the cracking coil in a suspensoid type operation where about 2 lbs. to 20 lbs. of finely divided catalyst per barrel of feed oil is used. In the suspensoid type cracking, the temperature is maintained between about 850° and 1050° F. and the pressure is maintained between about 100 and 500 p.s.i.g.

Or a fluid coking zone can be used for the cracking step at 68 but in this event a low conversion fluid coking step is used and the naphtha or gasoline yield is kept be-

low about 10% by volume of the feed by minimizing vapor cracking time and maintaining the time of cracking below about 10 seconds.

Further up the fractionating tower 48 a lighter gas oil stream is withdrawn through line 74 and passed to the first-mentioned catalytic cracking unit 38. This lighter gas oil is substantially free of metal contaminating material and forms an excellent feed for catalytic cracking. This lighter gas oil has a boiling range between about 600° and 1000° F. As above pointed out as additional feed to the catalytic cracking unit 38 the gas oil fraction from the first tower 16 is withdrawn through line 24 and passed to the catalytic cracking unit 38. The catalyst in the cracking unit 38 may be any conventional cracking catalyst such as silica-alumina, silica-magnesia, silica-alumina-magnesia, acid treated bentonite clays and so forth. While any of a number of catalytic cracking units may be used, such as the fixed bed cracking unit, the moving bed cracking unit using relatively large catalyst particles or piled catalyst, the fluid catalytic cracking unit is preferred and in this unit the catalyst particles having average size between about 20 and 100 microns with the major portion of the particles being between about 40 microns and 80 microns. The temperature during cracking is between about 850° and 1000° F. The catalyst to oil ratio may be between about 1 and 20. The w./hr./w. may be between 1 and 10. The 430° F. conversion is higher than in the other catalytic cracking unit 68 and is maintained between about 40 and 80%.

During cracking, carbonaceous material is deposited on the catalyst particles and the catalyst particles are withdrawn from the cracking unit and pass to a regeneration unit where the carbonaceous material is burned off by using air. The temperature during regeneration is maintained between about 900° and 1200° F. In using the fluid technique, the superficial velocity of the hydrocarbon vapors passing up through the reactor and the superficial velocity of the air passing up through the regenerator is between about 0.5 and 5 feet per second.

The vaporous cracked products leave the catalytic cracking unit 38 through line 76 to a third fractionating tower 78 where the products are fractionated into motor fuel and higher boiling fractions. The bottoms fraction is withdrawn through line 82 and this bottoms fraction may be discarded or in part recycled to the catalytic cracking unit 38 or to the coking unit 44. A relatively light gas oil or cycle oil is withdrawn from an intermediate portion from the tower 78 through line 84 and preferably recycled to the inlet of the catalytic cracking unit 38 to be combined with the gas oil fraction in line 74. If desired, a portion of this cycle oil from line 84 may be withdrawn from the system through line 87. A heating oil comprising a lower boiling fraction than the light gas oil or recycle oil may be withdrawn from the upper portion of the tower 78 through line 86.

The fractionated vapors leave the top of the fractionating tower 78 through line 88, are passed through condenser 92 and passed to a liquid-gas separator 94 in which the gas is taken overhead through line 96 and the liquid which comprises gasoline or motor fuel is withdrawn through line 98. If desired, a portion of the liquid from line 98 may be returned to the top of tower 78 as reflux liquid.

Returning now to the combination fractionation tower 48 a heating oil fraction may be withdrawn from the upper portion of the tower 48 through line 102. The remaining fractionated vapors pass overhead from the tower 48 through line 104, are condensed by passing through condenser 106 and the cooled stream is passed to a liquid-gas separator 108 where the gas is taken overhead through line 112 and the liquid is withdrawn from the bottom of the separator 108 through line 114. The liquid withdrawn through line 114 comprises motor fuel such as gasoline but this gasoline is of a lower quality than that withdrawn from the other liquid gas separator

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94 through line 98. It is also possible to eliminate tower 78 by introducing the vapors of line 76 into tower 48 above tray 64.

With the present process there are certain advantages over present refinery practice. In the first place the process provides for a higher feed rate of residual oil to the vacuum pipe still 16. Also there are better yields and higher feed rates of excellent gas oil to existing catalytic cracking units. There is a minimum amount of cracking on contaminated catalyst intended primarily to make lower boiling catalytic cracking feed. In addition, re-fractionation of the heavy gas oil from the vacuum pipe still in the combination fractionator makes it possible to produce a maximum yield of ash-free catalytic cracking feed.

Coming now to a specific example, about 10,000 barrels per day of topped crude is passed through line 10 and heated to a temperature of about 725° F. in furnace 14. The topped crude has an initial boiling point of about 800° F., an API gravity of 17.7°, a viscosity of 735 SSF at 122 and a Conradson carbon number of 4.8, 0.45% sulfur, 0.2% nitrogen, 27 p.p.m. Fe, 10 p.p.m. Ni, 0.8 p.p.m. V. The heated topped crude is introduced into the vacuum pipe still 16 and fractionated into a bottoms fraction having a boiling point above about 1000° F. and withdrawn through line 18. The bottom of the tower 16 is at a temperature of about 700° F. At the trapout tray 26 the liquid temperature of the tower 16 is about 500° F. so that the gas oil withdrawn through line 24 is substantially free of metal contaminating materials. These metal contaminating materials have a higher boiling point and are contained in the heaviest portion of the residual oil or bottoms withdrawn through line 18. About 5500 barrels per day of gas oil are withdrawn through lines 24 and 34 and about 4500 barrels per day of bottoms are withdrawn through line 18.

About 2350 barrels of gas oil substantially free from metal contaminating materials are withdrawn through line 74 from the combination fractionator 48 and this gas oil plus the gas oil from line 24 form the feed to the catalytic cracking unit 38. The gas oil withdrawn through line 74 has a boiling range between about 650° F. and 950° F. The gas oil feed stock to the catalytic cracking unit 38 has below about 0.1 part by weight of nickel per million parts by weight of oil and below about 0.1 part by weight of vanadium per million parts by weight of oil and this is sufficiently low so that there is substantially no contamination of the cracking catalyst in the cracking unit 38.

The bottoms from line 18 are coked in the fluid coking unit 44 where the cracking temperature is maintained at about 950° F. and the feed is maintained under low conversion conditions so that there is a minimum cracking of heavy gas oil to gasoline. The conversion to gasoline is maintained low, about 15%. About 44 volume percent of gas oil on feed from line 18 having a boiling point between about 650° and 950° F. is produced in coking unit 44. The coked products are introduced into the bottom portion of the combination fractionator 48 which is maintained at a temperature of about 750° F.

About 2600 barrels per day of heavy gas oil containing metal contaminating materials are withdrawn from trapout tray 64 of combination fractionator 48 through line 62. The temperature in the region of the trapout tray 64 is maintained at about 600° F. so that the gas oil withdrawn through line 62 contains the metal contaminants or the compounds containing contaminating metals such as nickel and vanadium. The heavy contaminated gas oil in line 62 has a boiling range between about 950° and 1100° F. and is cracked in the catalytic cracking unit 68 using silica-alumina catalyst, with a catalyst to oil ratio of about 10. The catalytic cracking unit is maintained at a relatively high temperature of about 950° to 1000° F. with a relatively high steam diluent rate of about 20 weight percent on feed. The w./hr./w. is about

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8. Under these conditions the catalyst contamination is not injurious to the catalytic cracking yields and under these conditions about 12% by volume of feed of gasoline is produced. The higher boiling gas oil constituents are cracked to a lower boiling range. The contaminating metal material is deposited on the catalyst in the cracking unit 68.

The cracked vaporous products at a temperature of 1000° F. are passed through line 72 into the bottom portion of the combination fractionation zone 48 below the point of entry of the cracked vaporous products from the coker 44. In this way heat is supplied to the bottom of the fractionator 48 and also the light hydrocarbon material acts as a stripping agent as it passes upwardly through the fractionator column 48.

About 940 barrels per day of heating oil is withdrawn through line 102 as a side stream from fractionator 48. About 600 barrels per day of 400° F. endpoint gasoline are withdrawn through line 114 from the gas-liquid separator 108. The octane number is about 85 clear research compared to about 77 octane from the coker 44 alone.

The catalytic cracking unit 38 is maintained at a temperature of about 900° F., a catalyst to oil ratio of 8, a w./hr./w. of 3. The superficial velocity of the gases passing upwardly through the cracking unit is about 2 feet per second. The catalyst of silica-alumina catalyst of about 20-100 microns average size. About 3 weight percent on feed of steam is introduced into the cracking unit.

The cracked vaporous products leave the cracking unit 38 through line 76 and are introduced into the bottom portion of the fractionating tower 78 where they are fractionated into a bottoms fraction 82 comprising 100 barrels per day and a heating oil fraction withdrawn through line 86 and comprising 2200 barrels per day. About 4300 barrels per day of high quality 400° F. endpoint gasoline is withdrawn through line 98 from the gas-liquid separator 94. This gasoline has a clear research octane number of 94.

Because of the excellent quality gas oil feed passing to the catalytic cracking unit 38 there is no metal contamination of the cracking catalyst and the activity and selectivity of the catalyst is maintained relatively high. After the activity and selectivity of the catalyst have dropped off due to continued usage, some of the catalyst may be withdrawn from the cracking unit 38 and used as makeup catalyst for the contaminated catalytic cracking unit 68. The catalyst withdrawn from the first cracking unit 38 is replaced by fresh cracking catalyst.

What is claimed is:

1. A process for converting hydrocarbons which comprises fractionating a reduced crude in a vacuum tower to separate a gas oil fraction substantially free of metal contaminants and a bottom fraction containing metal contaminants, passing said bottoms fraction to a coking zone maintained under relatively mild coking conditions to form lower boiling gas oil hydrocarbons and coke but only a small amount of gasoline, passing cracked vaporous products from said coking zone directly to the bottom portion of a combination fractionation zone, separating from said last-mentioned cracked products a higher boiling gas oil fraction containing metal catalyst contaminants and a lower boiling gas oil fraction substantially free of metal contaminants, subjecting said last mentioned higher boiling gas oil fraction to a cracking step in a first low conversion catalytic cracking zone containing contaminated catalyst to produce vaporous lower boiling gas oil hydrocarbons, returning the cracked vaporous products from said first catalyst cracking zone to the lower portion of said combination fractionation zone and fractionating said cracked products therein to separate gasoline and a lower boiling gas oil fraction substantially free of metal contaminants and combining the lower boiling gas oil fraction from said vacuum

tower with said lower boiling gas oil from said combination fractionation zone and passing the combined lower boiling gas oil fractions to a second catalytic cracking zone containing active cracking catalyst to produce motor fuel and separating a high quality gasoline from the catalytically cracked gas oils.

2. A process for converting hydrocarbons which comprises separating a reduced crude hydrocarbon oil into a bottoms fraction containing metal catalyst-contaminating material and a gas oil fraction substantially free of metal catalyst-contaminating materials, subjecting said bottoms fraction to a low conversion coking operation, passing all of the vaporous cracked products from said coking operation directly into the bottom portion of a combination fractionation zone to separate a higher boiling gas oil fraction containing metal catalyst-contaminating materials from a lower boiling gas oil fraction substantially free of metal catalyst-contaminating materials, cracking said higher boiling gas oil fraction in a separate catalytic cracking step to remove metal catalyst-contaminating material from said higher boiling gas oil fraction without producing an appreciable amount of gasoline, passing vaporous cracked products from said catalytic cracking step into the bottom of said combination fractionation zone, recovering additional lower boiling gas oil substantially free of metal catalyst-contaminating material from the last mentioned cracked products from the last mentioned catalytic cracking step, combining said last mentioned additional lower boiling gas oil and said first mentioned gas oil fraction substantially free of metal catalyst-contaminating materials, passing said combined gas oils to a second separate catalytic cracking zone containing active catalyst to subject them to cracking and to produce vaporous cracked products and passing said last mentioned vaporous catalytically cracked products to a separate fractionation zone to separate high octane gasoline.

3. An apparatus of the character described including in combination, a vacuum pipestill, means for introducing residual hydrocarbon oil thereto, said pipestill having a bottom withdrawal line and only one upper liquid with-

drawal line, a coking vessel communicating with said bottom withdrawal line, a combination fractionator, a pipe leading directly from said coking vessel to the bottom portion of said combination fractionator to pass all of the coker products from said coking vessel to said fractionator, a top withdrawal line leading from said combination fractionator to remove cracked gasoline, a side withdrawal line communicating with an intermediate portion of said combination fractionator for withdrawing a relatively heavy gas oil fraction, a cracking vessel communicating with said side withdrawal line, a second pipe leading from said cracking vessel to the bottom portion of said combination fractionator for leading the cracked products to said combination fractionator, an upper liquid withdrawal line leading from the upper portion of said combination fractionator, a catalytic cracking vessel communicating with said last mentioned upper liquid withdrawal line and with said first mentioned upper liquid withdrawal line from said pipestill for receiving lower boiling gas oil feed stock to be cracked, an outlet line for catalytically cracked products from said catalytic cracking vessel, and a second separate fractionation zone communicating with said catalytic cracking vessel to receive said catalytically cracked products and fractionate them to separate high octane gasoline.

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