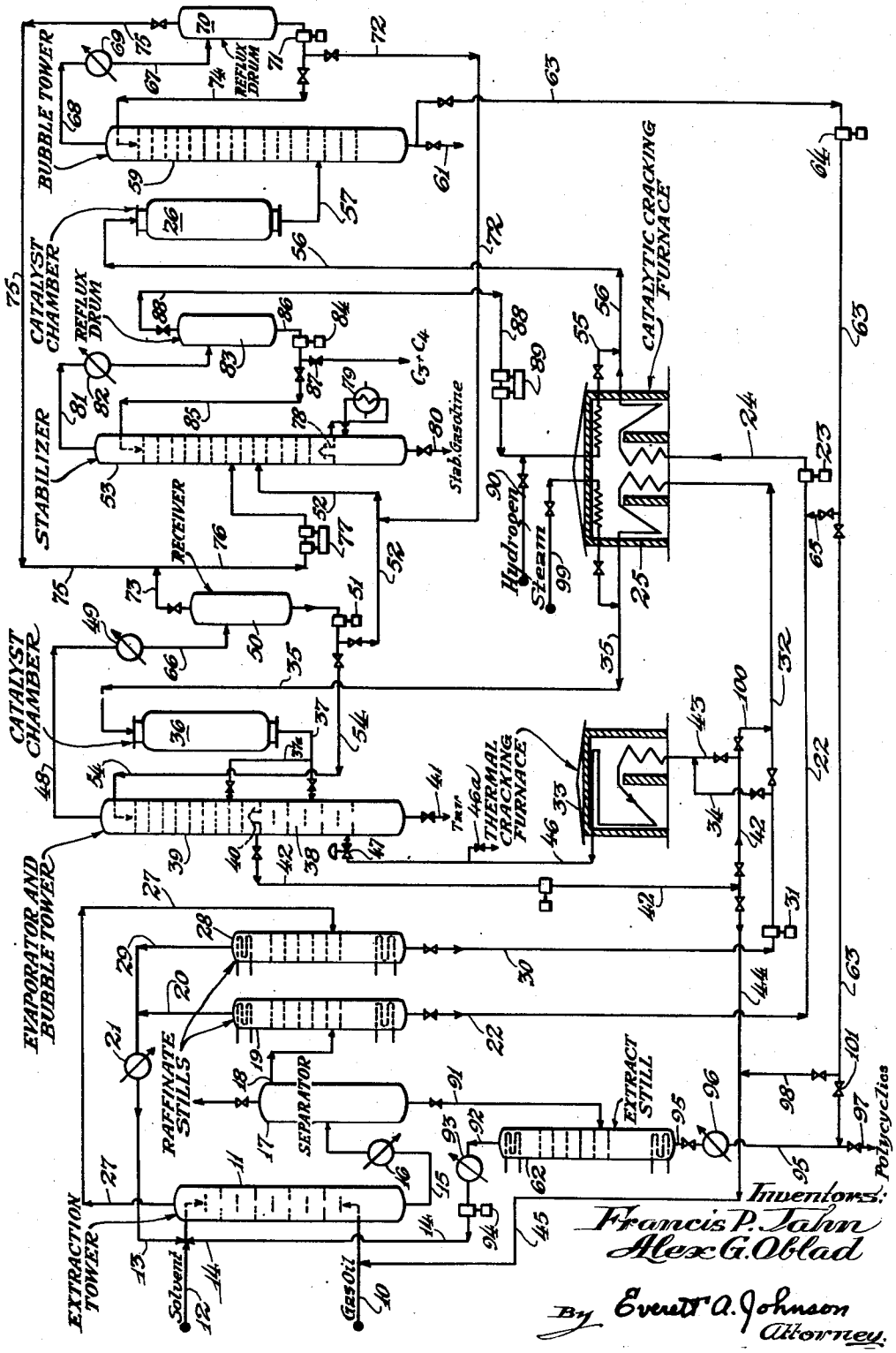
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CONVERSION OF HYDROCARBONS

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CONVERSION OF HYDROCARBONS

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This invention relates to the conversion of hydrocarbons by a combination of steps to produce gasoline and furnace oil.

It is an object of our invention to obtain larger yields of improved motor fuel and furnace oil. It is a further object of this invention to minimize operating difficulties and to obtain an improved product distribution. Other objects, uses and advantages of our invention will become apparent as the description thereof proceeds.

The above and other objects are attained by a combination of steps wherein we subject a feed stock, such as gas oil, to solvent extraction to produce fractions comprising paraffins and naphthenes, monocyclics, and polycyclics. The gas oil fraction substantially richer in mononuclear aromatics and substantially poorer in polynuclear aromatics than the virgin gas oil is subjected to catalytic cracking in the presence of hydrogen whereby the formation of polynuclear aromatic hydrocarbons heavier than gasoline is inhibited. The gas oil fraction substantially richer in paraffins and naphthenes and substantially poorer in aromatics than said gas oil is subjected to catalytic cracking. Any recycle gas oil is subjected to thermal cracking or to catalytic cracking. If desired the recycle gas oil fraction can be returned to thermal or catalytic cracking by way of the solvent extraction operation.

More particularly, according to our invention a fresh feed, for example virgin gas oil, is subjected to solvent extraction whereby at least one fraction substantially richer in mononuclear aromatics and substantially poorer in polynuclear aromatics, paraffins and naphthenes than the fresh feed is recovered. This preponderantly mononuclear fraction can be contacted with a solid cracking catalyst in the presence of hydrogen to effect substantial catalytic cracking whereby degradation of the mononuclear aromatic hydrocarbons to heavy polynuclear aromatic hydrocarbons is inhibited by the presence of hydrogen.

This fraction can be obtained by a number of well-known solvent extraction procedures. Thus all the gas oil can be solvent extracted with a single solvent or mixtures of solvents and the fractions removed by controlling the temperature or by adding anti-solvent materials. Likewise, a double solvent process employing two solvents which have relatively low mutual solubilities and one of which has preferential solubility characteristics towards the aromatics or paraffins, for example, is contemplated. One procedure which gives the desired result is the solvent extraction of virgin gas oil to recover a first raffinate consisting preponderantly of paraffins and naphthenes and an aromatic extract which is processed to produce a second raffinate fraction consisting preponderantly of mononuclear aromatics and an extract fraction consisting preponderantly of polycyclic aromatics. This final extract is a suitable furnace oil and can be blended with recycle gas oil produced by the cracking of the mononuclear fraction in the presence of hydrogen to produce a superior fuel oil.

Virgin or cracked gas oils usually contain varying amounts of mononuclear aromatics, substantial proportions of which form polynuclear aromatics boiling outside the gasoline boiling range when the gas oil is cracked in the absence of hydrogen. Cracking in the presence of hydrogen inhibits the degradation to polycyclics and the ultimate yield of gasoline is increased correspondingly. In addition to the yield advantage, the additional benzene derivatives in the gasoline boiling range enhance the octane number of the product.

Referring to the drawing, virgin charge, for example gas oil, enters the system by line 10 leading to extraction tower 11 where it is extracted by a suitable solvent introduced by line 12 together with any recycle solvent returning by lines 13 and 14. The gas oil introduced can suitably be Mid-Continent gas oil of 32° A. P. I. gravity and an initial boiling point of between about 375 and 525° F. and an end point of between about 650 and 800° F.

Suitable solvents are nitroparaffins such as nitroethane and nitromethane, SO_2, dimethyl ether, nitro-olefins, and other solvents of high selectivity for aromatics.

In separating the feed into three fractions, it is contacted in countercurrent operation with nitromethane, for example, in extraction tower 11 at temperatures within the range of between about 100° F. and 200° F., preferably within the range of from about 125° F. to about 160° F. Cooling means, not shown, at either or both ends of the tower can be provided, thus causing a separation of oil from nitromethane in the end zones which results in a refluxing and fractionating action. A solvent-to-oil volume ratio of between about 1:1 and 4:1, for example, 3:1, can be used. The solution of nitromethane and extracted material is withdrawn from the bottom of tower 11 by line 15, cooled by cooler 16 to a temperature below about 80° F., preferably about 60° F. and passed to separator 17. A phase separation takes place within separator 17, the preponderantly mononuclear aromatic fraction constituting the

new raffinate and the preponderantly polynuclear aromatic hydrocarbons being recovered in the extract layer.

The raffinate or preponderantly monocyclic fraction from separator 17 is conducted by line 18 to raffinate still 19 wherein solvent is distilled off by line 20, passed to cooler 21, and recycled by line 13 to extraction tower 11. The raffinate substantially free of solvent is conducted by valved line 22, pump 23 and line 24 to catalytic cracking furnace 25 and cracked in the presence of hydrogen or a hydrogen-rich plant stream. The conditions prevailing in catalyst chamber 26 ordinarily will be at a pressure between about 15 and about 400 pounds per square inch absolute and a temperature of between about 800° F. and 1000° F. Mol ratios of hydrogen-to-hydrocarbon can be from 0.5 to 10.0 a ratio of unity being preferred. Fixed bed granular, moving bed granular, or flowing powdered catalyst techniques can be used. In fixed or moving bed space velocities of between about 0.25 and 4.0 volumes of oil per gross volume of catalyst per hour are used.

Suitable catalysts in the hydrogen cracking operation are silica-alumina, silica-magnesia, Super-Filtrol, and other of the catalysts disclosed in connection with the catalytic cracking in chamber 36. It is also contemplated that we may use group VI oxides on alumina as catalysts. Likewise, a mixture of group VI oxides on alumina and cracking catalysts of the silica-alumina type can be used. For example, 90 to 70 parts by weight of cracking catalyst of the solid metal oxide type and 10 to 30 parts by weight of a catalyst comprising group VI oxides on alumina can be used. More specifically, the 10 to 30 parts by weight of group VI oxides on alumina can comprise 5 to 25 parts by weight chromium oxide, molybdenum oxide, or vanadium oxide and 95 to 75 parts by weight alumina.

The raffinate from extraction tower 11 containing the paraffinic-naphthenic fraction is removed and conducted by line 27 to raffinate still 28 wherein solvent is distilled off by line 29 and the raffinate substantially free of solvent is conducted by line 30, pump 31 and valved line 32 to catalytic cracking furnace 25. If desired, all or a portion of the raffinate can be led to thermal cracking furnace 33 by valved line 34. Such operation makes possible high cracks per pass without severe coking.

When the paraffinic-naphthenic fraction is catalytically cracked, the heated materials from furnace 25 are passed by line 35 to cracking catalyst chamber 36. The cracked material from this chamber passes through line 37 into evaporator 38 which is shown integral with bubble tower 39 and separated therefrom by trap-out plate 40. From the base of epavorator 38 a tar fraction can be removed through valved line 41. If desired, all or a part of the cracked material is passed into bubble tower 39 by valved line 37a.

The diagrammatic representation of the catalytic reaction chamber 36 (as well as chamber 26) is intended to include stationary bed, moving bed or powdered catalyst operations. For example, the reaction chamber can be a low velocity upflow reactor wherein powdered catalyst and hydrocarbon vapors are introduced at a point near the bottom of the reaction chamber, the hydrocarbons are cracked in the low velocity upflow chamber, the cracked products and suspended catalyst are removed overhead and the catalyst subsequently is removed from the treated hydrocarbon vapors for regeneration or recycling to the low velocity upflow reactor.

Various catalysts can be used. It is preferred, however, to employ solid refractory cracking catalysts of the metal oxide type such as silica-alumina, silica-magnesia, alumina-zirconia, silica-zirconia-alumina, silica gel promoted with metal oxides adsorbed thereon, for example magnesia and alumina, Super-Filtrol, acid treated bentonite and other acid treated clays, and other natural and synthetic refractory catalysts of the solid metal oxide type.

In fixed or moving bed operations a space velocity within the range of 0.5 and 6 volumes of oil per volume of gross catalyst space per hour, for example, a space velocity of 1.0, and a catalyst residence or holding time of between about 10 minutes and 4 hours, for example, one hour, can be used. In powdered catalyst technique a space velocity of between about 1 and 20, for example 5 volumes of oil per volume of catalyst per hour, and a holding time of between about 0.2 and 60 minutes, for example about 5 minutes, can be used. In powdered catalyst technique the volume of catalyst is the volume occupied by the catalyst present in the reactor at any one instant measured at rest or in the compacted condition. In each of the above techniques, a pressure of between about 0 and 50 pounds per square inch gauge and a reaction temperature within the range of about 800° F. to 1000° F. are preferred. It is contemplated that low space velocities will be coupled with high holding times or that high space velocities will be used with low holding times, or intermediate velocities and intermediate holding times can be combined to give a desired degree of cracking. Steam can be injected by valved line 99 into this catalytic cracking step to the extent of between about 5 and 20 weight percent of the oil.

All material lighter than tar passes overhead from evaporator 38 through trap-out plate 40 into bubble tower 39. A gas oil cycle stock is withdrawn by means of valved line 42. This gas oil is recycled to completion, entering the feed stream to furnace 25 and/or 33 and/or to the feed stream entering the extraction tower 11 for processing as described herein. Thus all or a portion of the cycle gas oil can be passed by valved line 43 to thermal cracking furnace 33. Likewise all or a portion of the recycle stock can be sent by valved lines 44 and 45 to extraction tower 11 wherein it is extracted along with the fresh feed. From thermal cracking furnace 33 the cracked materials pass through transfer line 46 and pressure reduction valve 47 into evaporator 38. All or a portion of the cycle stock can be conducted by valved line 100 to line 32 and thence to catalytic cracking furnace 25. It is contemplated, however, that the quantity of cycle stock necessary to pass to the extraction step will be minor in comparison to the amount to be passed to the furnace, except in those cases where the raffinate contains a high percent of naphthenes and other components which upon cracking form either polycyclic aromatics or high boiling monocyclic aromatics.

Gasoline and lighter hydrocarbons are removed from bubble tower 39 by vapor line 48 leading to condenser 49 and receiver 50. The condensate then is withdrawn from receiver 50 by pump 51 and valved line 52 to stabilizer 53 where the desired gasoline is separated as hereinafter described. Part of the condensate can be led back into bubble tower 39 by valved line 54 as reflux.

Reverting to the catalytic treatment of the monocyclics, hydrogen is injected into the heated monocyclics by line 55 and the mixture passed by line 56 to catalyst chamber 26 where the hydrocarbons are cracked under the conditions hereinbefore described. The cracked material from this chamber passes through line 57 into bubble tower 59 where a gas oil fraction is separated. All or a portion of the cycle stock can be recycled to catalytic cracking furnace 25 by valved line 63, pump 64 and line 65, or by valved line 98 to the feed stream to extraction tower 11. Likewise, a furnace oil can be removed as gas oil cycle stock by draw-off 61 or by valved line 101 and blended with the polycyclics from extract still 62.

From bubble towers 39 and 59 materials lighter than gas oil, which consist generally of gasoline range hydrocarbons and lighter materials including hydrogen pass overhead through lines 48 and 68 and thence through condensers 49 and 69 respectively, and lines 66 and 67 to reflux drums 50 and 70. The gases from these reflux drums are taken overhead through valved lines 73 and 75 and line 76 to compressors 77 from which they pass to stabilizer 53.

Condensate from reflux drums 50 and 70 is removed through pumps 51 and 71 respectively, and a portion is returned to the appropriate bubble tower by means of valved lines 54 or 74. The remainder of this condensate passes through valved lines 52 and 72 respectively and thence into stabilizer 53.

Stabilizer 53 is operated at an elevated pressure in the conventional manner. If desired, separate stabilizers for the products of the separate cracking operations can be used. The stabilizer 53 is equipped with a reboiler which includes conventional trap-out plate 78 and heater 79. The stabilizer is provided also with reflux and the pressure, reboiling, and reflux are controlled to take stabilized gasoline off the base of tower 53 through valved line 80 for storage, further treatment or use.

Gases eliminated in producing stabilized gasoline pass overhead from stabilizer 53 through line 81 and condenser 82 and thence to reflux drum 83. Condenser 82 is operated to condense such portion of the C_4 hydrocarbons as cannot be utilized in the finished gasoline, together with a considerable amount of C_3 hydrocarbons. This condensate is removed from the base of reflux drum 83 by means of valved line 86 and pump 84 and a portion of it is returned to stabilizer 53 through valved line 85 as reflux. The remainder of the condensate is removed from the system through valved line 87 for storage or use. These liquid C_3 and C_4 hydrocarbons can be recycled to either of the cracking operations. For example, these hydrocarbons can be subjected to gas reversion by introducing them into line 30 and treated in thermal cracking furnace 33. Thus these hydrocarbons are treated to produce higher yields of gasoline and reduce the tendency to coke formation.

The hydrogen-rich gas from reflux drum 83 can be passed by line 88 and compressors 89 to catalytic cracking furnace 25. The stream of hydrogen-rich gases can be supplemented by introducing extraneous hydrogen by valved line 90. In some instances it will be desirable to scrub the gases recovered by line 88 to increase the hydrogen concentration. The presence of hydrogen in the cracking of the monocyclic fraction results in the formation of benzene derivatives boiling in the gasoline range and diminishes the reactions tending to form polynuclear aromatics outside the gasoline boiling range.

Reverting to the extract removed from separator 17, the solution of solvent and extracted material is withdrawn by valved line 91 leading to extract stripper 62 where the solvent is distilled off and recycled by line 92 to condenser 93 whence it flows by pump 94 and line 14 back to the extraction tower 11. The extract oil substantially free of solvents and comprising polycyclics is withdrawn from stripper 62 by valved line 95, passed to cooler 96 and blended with the furnace oil cut from bubble tower 59 to form a balanced fuel oil that is withdrawn by valved line 97.

The control of the degree of extraction is familiar to those skilled in the art and depends on a number of factors including the character of the feed stream to extraction tower 11, the temperature in tower 11 and separator 17, the solvent chosen, the solvent-oil ratio, etc. Conditions are chosen such that the amount of extract falls within the range of 5% and 50% and usually between about 10% and 35% of the feed stream to extraction tower 11.

Thus it will be seen that our new combination cracking operation includes solvent extraction of a feed stock to produce a preponderantly paraffinic-naphthenic fraction, a fraction substantially richer in mononuclear hydrocarbons and substantially poorer in paraffins, naphthenes and polynuclear aromatics than said feed stock and a preponderantly polcycyclic fraction; catalytically cracking the monocyclic fraction in the presence of hydrogen to produce gasoline and a fuel oil cut which is blended with the polycyclic fraction; and catalytic and/or thermal cracking of the paraffinic-naphthenic fraction with recycle to thermal or catalytic cracking.

In a modification of our process we can catalytically treat the gasoline fraction from the thermally cracked product in line 46 over a clay-type catalyst such as Super-Filtrol or synthetic zeolite catalyst to isoform the product to high octane number blending gasoline in which case separate fractionation and stabilization equipment, not shown in the drawing, will be required. Valved line 46a is provided for this purpose.

The flow diagram of our process as well as the description thereof is highly simplified and various details such as heaters, coolers, pumps, valves, catalyst regenerators, etc. have been omitted which add little to the knowledge of those skilled in the art and which would merely encumber this specification unnecessarily.

While our invention has been described with reference to certain embodiments thereof, it is to be understood that they can be modified in various ways without departing from the invention and that we do not mean to be limited thereby but only by the appended claims.

We claim:

1. A combination cracking process comprising the steps of solvent extracting a fresh feed to produce at least one fraction substantially richer in mononuclear and poorer in polynuclear aromatics than said fresh feed, and at least one fraction substantially richer in paraffins and naphthenes than said fresh feed, subjecting the mononuclear fraction to catalytic cracking in the presence of added hydrogen, subjecting the paraffin-naphthene fraction to a thermal cracking operation, separately fractionating the thermally and catalytically cracked products to recover a desired gasoline product fraction and a gas oil fraction from each of said product streams, com-

bining at least a portion of said gas oil fractions, subjecting at least a portion of the combined gas oils to a solvent extraction operation to recover at least one fraction substantially richer in polynuclear aromatics than said combined gas oil and at least one fraction substantially poorer in polynuclear aromatics than said combined gas oil, discarding the fraction which is substantially richer in polynuclear aromatics, and recycling at least a portion of the fraction which is poorer in polynuclear aromatics to a cracking operation.

2. A combination cracking process comprising the steps of solvent extracting a gas oil to produce at least one fraction both substantially richer in mononuclear and substantially poorer in polynuclear aromatic hydrocarbons than said gas oil, and a second fraction substantially richer in paraffins and naphthenes than said gas oil, subjecting the mononuclear fraction to catalytic cracking in the presence of added hydrogen, subjecting the said second fraction to thermal cracking, recovering a cracked gas oil from each of said cracking operations, subjecting at least a portion of said thermal gas oil to catalytic cracking in the presence of steam, and subjecting at least a portion of said gas oils to solvent extraction.

3. A combination cracking process comprising the steps of solvent extracting a gas oil to produce at least one fraction substantially richer in mononuclear and poorer in polynuclear aromatic hydrocarbons than said gas oil, and a second fraction substantially richer in paraffins and naphthenes than said gas oil, subjecting the mononuclear fraction to catalytic cracking in the presence of added hydrogen, subjecting the said second fraction to a separate cracking operation, recovering a cracked gas oil from each of said cracking operations, subjecting at least a portion of said gas oil to catalytic cracking in the presence of steam, fractionating products from said cracking in the presence of steam to recover desired gasoline components and a gas oil fraction, subjecting at least a portion of said last mentioned gas oil fraction to thermal cracking, fractionating the thermal cracking products with the products from said cracking in the presence of steam, recovering a combined gas oil fraction from said fractionation and subjecting at least a portion of the combined gas oil to solvent extraction.

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