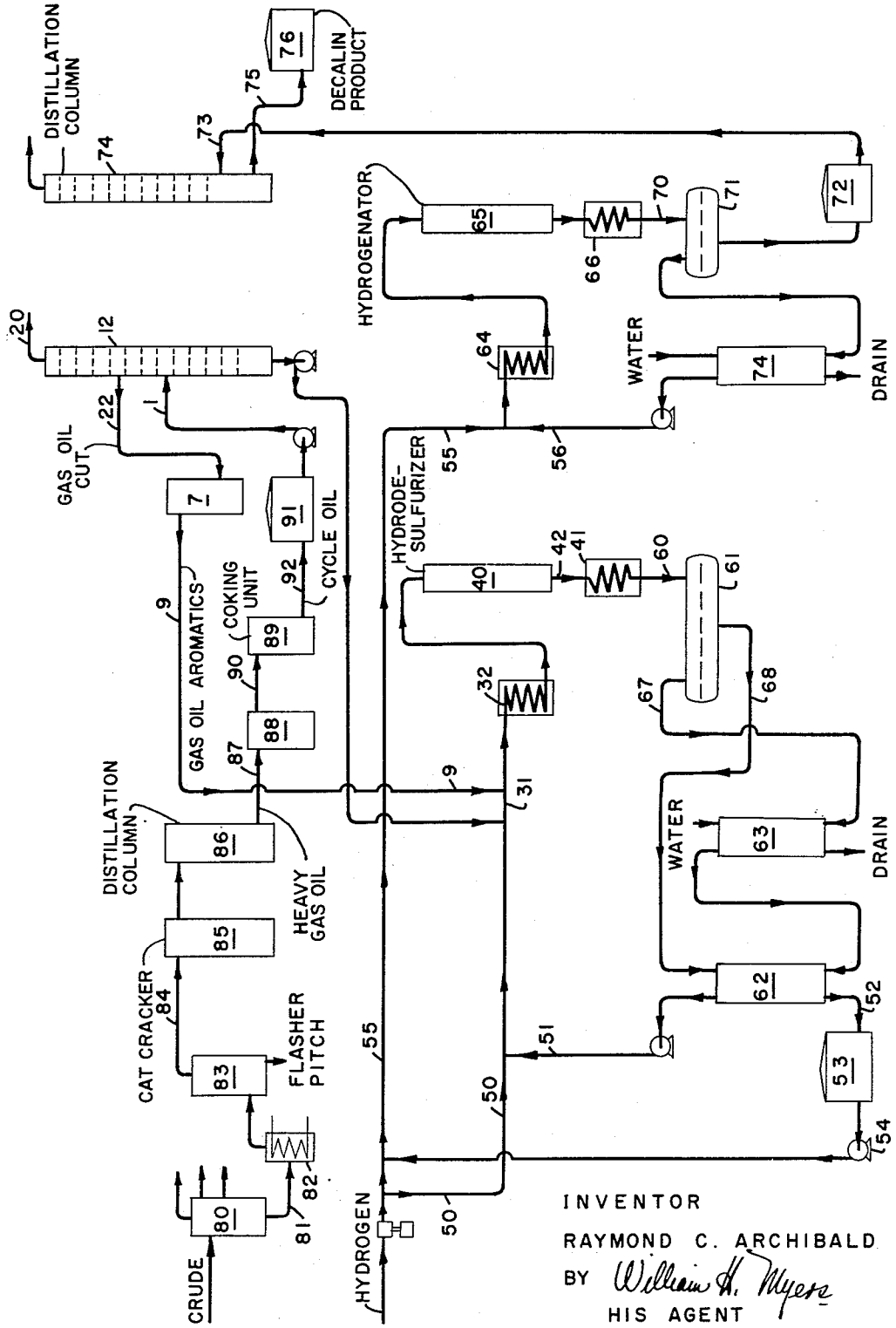
Oct. 31, 1961 R. C. ARCHIBALD 3,006,843

PREPARING HYDROCARBON FUELS BY SOLVENT EXTRACTION, HYDRODESULFURIZATION AND HYDROGENATION OF CRACKED GAS OILS

Filed Nov. 26, 1957



INVENTOR

RAYMOND C. ARCHIBALD

BY William H. Myers

HIS AGENT

United States Patent Office

3,006,843

Patented Oct. 31, 1961

3,006,843

PREPARING HYDROCARBON FUELS BY SOLVENT EXTRACTION, HYDRODESULFURIZATION AND HYDROGENATION OF CRACKED GAS OILS

Raymond C. Archibald, Berkeley, Calif., assignor to Shell Oil Company, a corporation of Delaware

Filed Nov. 26, 1957, Ser. No. 698,949
4 Claims. (Cl. 208—211)

This invention relates to an improved method for the production of improved hydrocarbon fuels. More particularly, it relates to a method of producing fuels having improved heats of combustion per unit volume.

In order to increase the range of volume limited jet aircraft and the like, a fuel with a high heat of combustion on a volume basis would be highly desirable. Furthermore, in order to have a reasonably universal aircraft fuel that can also be used in weight limited aircraft and in current engines, it would also be desirable to maintain, if possible, the heat of combustion per unit weight at least at the current level at the same time that the heat of combustion per unit volume is increased to a higher level. Aromatic hydrocarbons are undesirable in such fuels as major constituents due to their low heat of combustion per unit weight and also because of poor burning properties. Most paraffins are excluded because of their low density and hence their low heat of combustion per unit volume. Alkyl monocyclanes are somewhat better than paraffins but become much like paraffins with the addition of alkyl side chains to bring them into a suitable boiling range. Olefins are not considered to be desirable because of their instability, although some cyclic olefinic structures may deserve consideration when inhibited against oxidation. Consequently, it becomes necessary due to these exclusion factors to regard for primary consideration a group of polycyclic naphthenes which includes hydrocarbons containing two or more saturated carbocyclic rings. The rings may have no carbon atoms in common, or pairs of rings may share 1, 2, 3, or more carbon atoms. Rings may be connected directly together, or may be separated by one or more carbon atoms. Alkyl groups may be attached to the rings at various points so as to provide a suitable molecular weight and boiling point.

While it is possible to synthesize such materials directly, from the view point of large scale availability and cost, this approach ordinarily is impractical. Consequently, one object of the present invention comprises the establishment of a process for the economical and large scale production of the desired type of high density fuels from relatively low cost sources.

It is known that numerous petroleum refinery streams contain varying amounts of aromatics and among these are sources containing polycyclic aromatics. These, of course, could theoretically be hydrogenated and isolated along with polycyclic naphthenes originally present in order to obtain the desired type of fuel.

The difficulty with previous methods for obtaining such fuels from hydrocarbon and petroleum sources has comprised the lack of removal and, therefore, the presence of undesirable types of hydrocarbons having reduced heating value per unit volume or per unit weight. In many cases the starting materials have been such that maximum heating values could not be obtained. Thus, in the case where monoaromatics such as xylenes and toluene or benzene are pyrolyzed in order to obtain diphenyl structures, the resulting pyrolysis products then being hydrogenated, the product so obtained is in a relatively low yield and does not have the maximum heating value which can be obtained by the use of the present invention.

Some of the difficulties in preparing completely hydrogenated products from petroleum sources comprise,

first, the presence of sulfur compounds in such naturally occurring materials and, secondly the difficulty of completely hydrogenating certain hydrocarbons due to their refractory nature. Certain advances have been made in this type of operation by first subjecting petroleum refinery streams to hydrogenation in the presence of a sulfur resistant hydrogenation catalyst at relatively high temperatures and thereafter completing the hydrogenation of the essentially sulfur-free product by the use of a more active but sulfur-sensitive catalyst at a lower and more favorable hydrogenation temperature. However, in the use of this two-stage hydrogenation treatment the objective of the workers involved was to prepare an improved cracking feed. Consequently, the stream which they treated contained substantial amounts of olefins which upon hydrogenation would be converted to paraffins. These, as indicated above would be undesirable where the objective would be to obtain an aircraft fuel having maximum heating value per unit volume. Moreover, where the two-stage hydrogenation treatment has been used in the past, little attention was directed to the boiling range of the cuts treated since the object was to produce a catalytic cracker feed stock and not the production of an aircraft fuel.

It is an object of the present invention to produce an improved aircraft fuel. It is another object of the present invention to provide a fuel composition having improved, i.e. higher, heating value per unit volume. It is a further object of the present invention to provide a process for the preparation of such a fuel from petroleum refinery streams. Other objects will become apparent from the detailed description of the present invention.

Now, in accordance with the present invention a method for the preparation of such fuel oils comprises fractionally distilling an aromatic (usually sulfur containing) petroleum gas oil to isolate a fraction having a boiling range within the limits between about 400° F. and about 650° F.; isolating (or concentrating) aromatic hydrocarbons from the fraction; subjecting the segregated aromatics to desulfurizing hydrogenation at elevated temperatures so as to substantially desulfurize the fraction and reduce the aromatic content by hydrogenation of a substantial part of the aromatics present, using a sulf-active hydrogenation catalyst; completing the hydrogenation of the product (preferably at a lower temperature, by use of a relatively active sulfur-sensitive catalyst), at least until the aromatic content of the product is less than about 10% by weight; and fractionally distilling the hydrogenated product to isolate a fuel having a boiling range within the limits from about 325° F. to about 600° F.

The isolating treatment may, of course, be any one of a number of alternative procedures already well known in the art. These may include extraction, selective adsorption, or additional severe cracking to remove non-aromatics.

The gas oil selected for use in the present process for obtaining a high density fuel is preferably one which has been cracked so that long alkyl side chains will have been removed from the aromatic rings. The same cracking operation will also reduce the length and number of the chains on the polyaromatics as well as on the benzene nuclei so that there will be a higher concentration of potential naphthenes within the allowable boiling range. While any cracked gas oil stream should be satisfactory starting material the more severe the cracking has been the better because the higher will be the concentration of aromatic compounds and of aromatic ring carbon atoms. Still more preferably a gas oil which has been both thermally and catalytically cracked is a source having a still higher concentration of the desirable types of bicyclic aromatics which will provide the optimum hydrogenation feed. Such a material having the smallest

number of side chains and the lowest percentage of non-aromatic constituents comprises cycle gas oil from a coking operation wherein the feed is residue from prior catalytic and thermal cracking operations. Such materials are obtained, for example, by the distillation of a crude oil to remove overhead fractions and thereby isolate a straight run residue. The latter is then heated and sent to a vacuum flashing unit so as to obtain overhead fractions and a flasher pitch. The overhead fractions are sent to a catalytic cracking operation and the product therefrom is fractionally distilled to obtain a catalytically cracked heavy gas oil fraction. This in turn is subjected to thermal cracking to produce light products and a residue, and the residue then is sent to a coker. The preferred gas oils to be used in the present process have the following ranges of characterizing properties:

Average Molecular Weight	194	175-225
Gravity, API	7.6	6-30
Refractory Index N 20/D	1.6000	—
Saturates, percent	15	5-75
IBP, ° F. } To include fractions boiling 400-650° F.		
FBP, ° F. }		
Preferred Crude Sources:		
California crudes (high aromatic content).		
West Texas.		

Distillation may be carried out by any of the well known procedures such as passing the feed through a distillation column and isolating the fraction boiling between about 350 and 700° F., preferably 400–650° F.

The isolation step utilized after this fractional distillation may be any of the well known procedures for isolating or concentrating aromatics from refinery streams. The details of such operations are well known in the art. The preferred process comprises the use of solvent extraction which may be liquid-liquid extraction utilizing single contact, multiple contact or countercurrent contact procedures. Solvents suitable for this purpose include phenols, furfural, nitrobenzene, sulfur dioxide, aniline, mixtures of sulfur dioxide and benzene, mixtures of cresol with 5–15% water or the solvents employed in the Clorex, Duosol or Edeleanu methods.

Having concentrated the polyaromatics from a fraction within the specified boiling range, the next stage in the process comprises desulfurizing hydrogenation which accomplishes the dual purpose of substantially completely removing sulfur compounds (in the form of H_2S) and also hydrogenating part of the aromatics, using sulfactive catalysts. The use and preparation of sulfactive (sulfur resistant) catalysts in processes of hydrogenation of hydrocarbons carried out at high temperatures and pressures is already known in the art. The term "sulfactive" as applied to these catalysts means that they retain their hydrogenating activity even in the presence of substantial quantities of sulfur or sulfur compounds. Particularly active catalysts of the sulfactive type comprise the oxides or the sulfides of metals of the sixth group of the periodic system, either alone or in admixture with oxides or sulfides of metals of the second and/or eighth group of the periodic system. Group eight sulfides are also active hydrogenation catalysts of the sulfur resistant type. Any of these catalytic materials or mixtures may be supported on suitable carriers known in the art. Examples of especially active catalysts of this type are (1) mixtures of molybdenum oxide, zinc oxide and magnesium oxide; (2) molybdenum sulfide; (3) tungsten sulfides supported on activated clay; (4) iron sulfides supported on activated bentonitic clay or the like. The temperatures employed during this first stage of the hydrogenation are preferably between 600 and 900° F., pressures within the approximate range of 500–4000 p.s.i., a feed rate of liquid oil to the reactor being between 0.5 and 4 volumes of oil per volume of catalyst per hour, and from 1000 to 20,000 cubic feet of hydrogen, measured at standard conditions, per barrel of oil.

The product resulting from this first stage of hydrogenation has substantially all of its sulfur content removed and the aromatic content reduced approximately 40–70% due to the hydrogenation of the aromatics to form the corresponding naphthenes. While this product is an improvement over the original aromatics for the purpose of fuel, it is not satisfactory insofar as maintaining maximum heating value per unit volume. Consequently, it is necessary to utilize a second stage of hydrogenation employing a more active (usually sulfur-sensitive) catalyst and lower temperatures so that hydrogenation of the material may be substantially complete or at least such that no more than 10% by weight of aromatics remain in the final product. This second stage of hydrogenation may be carried out with the same type of catalyst but it is preferred that a more active catalyst be employed. Such active catalysts include especially those of a sulfur sensitive type such as metallic nickel, platinum, palladium, cobalt, or iron deposited on aluminum silicate, silica, alumina clays of the bentonitic and montmorillinitic type. The quantity of metal in the catalyst may be between about 1 and 15% by weight and preferably between 4 and 10% by weight. Broadly speaking, the preferred catalyst employed in this second stage hydrogenation may be supported or unsupported metal and/or metal oxides of group eight elements of the periodic system. The conditions of the second stage hydrogenation include a lower temperature range, preferably between about 300 and 700° F. under a pressure of 250–5000 p.s.i. Gas rates may be in the order of 1,000–10,000 cubic feet of hydrogen per barrel of feed while the feed rate is in the range of between about 0.5 and 10 volumes of feed per volume of catalyst per hour.

The product resulting from these two stages of hydrogenation (each of which may involve one or more cycles through the particular hydrogenation and under the particular hydrogenation condition) comprises substantially polycyclic naphthenes as defined hereinbefore. In order to approach the optimum desirable heating value per volume of fuel, it is necessary to distill the product in order to remove lower boiling hydrocarbons which may have resulted from a minor amount of cracking during hydrogenation as well as to eliminate any high molecular weight materials. This fractional distillation may be conducted under known conditions and it is preferred that the final product having a boiling range within the lmits from about 325 to about 650° F., still more preferably between about 340 and 600° F.

The product obtained by the process of the invention is found to be optimum for the intended purpose in that it has the maximum heating value per unit volume which can be obtained directly by the described sequence of refinery process steps when utilizing a selected gas oil. Indicative of its suitability for the present purpose are its aromatics content which usually ranges between about 0.0 and 10%; its freeze point which normally is between about −20 and about −70° F.; its heat of combustion which is between about 127,000 and about 138,000 B.t.u. per gallon and between about 17,500 and about 19,000 B.t.u. per pound while its boiling range is between about 325° and 600° F., thus indicating that it is within the volatility range normally required for jet (including ram jet and turbo jet) engine operation as well as turbo prop engine operation.

In order to illustrate a suitable process for the use of the present invention, the FIGURE shows a petroleum crude oil being subjected to fractionation in a distillation unit **80**, the straight run residue from which passes by means of line **81** through heater **82** to a flasher **83** for the removal of volatile products. The flasher pitch from this unit is sent to further processing elsewhere while the volatile products are sent by means of line **84** to a catalytic cracking unit **85**, the product from said cracker being fractionated in a distallation column **86**. The heavy catalytically cracked gas oil fraction from this column

is conducted by means of line 87 to a thermal cracking unit 88 and the thermally cracked residue is then sent to a coking unit 89 by means of line 90.

The cycle gas oil from this coking unit constitutes the preferred starting material for use in the present process and is sent from the coking unit (or fractionating column in association therewith) to feed tank 91 by means of line 92. From this feed tank the heavily thermally and catalytically cracked coker gas oil is introduced into the present system through line 1 to a distillation column 12 where the oil is subjected to a distillation process in order to isolate the preferred boiling range as stated hereinbefore. This isolated fraction is then conducted through line 22 to a solvent extraction unit 7 wherein the non-aromatic constituents are eliminated or at least substantially removed. The aromatic concentrate thus obtained is then conducted by means of line 9 to line 31 (for admixture with hydrogen) and thence to a heating coil 32 and thence to the hydrogenation zone 40.

In this first stage of hydrogenation, the oil feed, which contains sulfur compounds but substantially no olefinic or paraffinic materials, is hydrogenated to an extent that the sulfur compounds are substantially eliminated and portions of the aromatics are converted to the corresponding naphthenes. The product is removed from the reactor 40 by way of line 42 and passed through cooler 41 and line 60 to a liquid gas separator 61 where the liquid aromatic and naphthenic constituents are separated from the gaseous sulfur and nitrogen-containing impurities and gases produced by slight cracking in 40. It is desirable to pass the material through a scrubber 62 by way of line 68 for the purpose of removing additional quantities of sulfur and nitrogen compounds.

The separator gas, which has previously been washed in scrubber 63, is used to remove these volatile compounds from the product in scrubber 62 after which it is returned to the hydrogenation unit through line 51. Alternatively, scrubber 62 may be replaced by a conventional liquid phase washing system employing acid and caustic solutions for the removal of any non-volatile nitrogen and sulfur compounds formed during the hydrogenation in reactor 40 and not completely removable by gas blowing.

The scrubbed product then passes through line 52 to storage tank 53 from which it is drawn by pump 54 and thereafter mixed with hydrogen or hydrogen-containing gas from lines 55 and 56 and passed to the fired coil 64 where it is reheated. The vaporized mixture is then passed into a second hydrogenation reactor 65, containing a body of the more active catalysts such as nickel supported on silica. The mixture of hydrogen and hydrocarbons passes through the reactor and a body of the catalyst; during this passage through the catalyst the aromatics are fully hydrogenated. Thereafter the product issuing through cooler 66 and line 70 to the liquid gas separator 71 is released to storage tank 72 from which it passes by means of line 73 to a distillation column 74 so as to recover a fraction having a boiling range within the limits as set out hereinbefore. The product is then removed by means of line 75 to a storage tank 76 and constitutes the product which is the primary objective of the use of the present invention.

The following examples illustrate the use of the present method:

Example I

A Mid Continent coking cycle stock was distilled to give a sulfur-containing fraction boiling between 400° F. and 650° F. An aromatic concentrate was obtained by extraction of this fraction with furfural. This concentrate was subjected to hydrogenation using a $W/Ni/Mo/Al_2O_3$ catalyst, pressure of 3,000 p.s.i.g., temperature of 600–750° F., LHSV of 0.6 and hydrogen consumption of 3,650 s.c.f./bbl. In the second stage of hydrogenation a Ni/SiO_2 catalyst was employed, other conditions including 1500 p.s.i.g. pressure, 390–420° F., LHSV of 2.2 and hydrogen consumption of 200 s.c.f./bbl. The product was distilled to isolate the fraction distilling between 325 and 600° F. This product contained 0.4% aromatics, substantially no paraffins or olefins and was comprised essentially of naphthenes. The product had a heat of combustion of 18,400 B.t.u. per pound and 133,000 B.t.u. per gallon; a freezing point of −62 and a viscosity of 24 cs. at −30° F.

Example II

A light catalytically cracked gas oil was distilled to isolate a cut boiling between 400 and 650° F., then phenol extracted (1:1 oil:solvent) to obtain a 50% of the cut as an aromatics concentrate (90% aromatics). This was hydrogenated in a first stage using the following conditions:

Pressure, p.s.i.g	3,000
Temperature, ° F	750
LHSV	0.6
Hydrogen consumed, s.c.f./bbl	3,650
Catalyst	$W/Ni/Mo/Al_2O_3$

The product was subjected to a second stage hydrogenation under the following conditions:

Pressure, p.s.i.g	1500
Temperature, ° F	400
LHSV 2.2	2.0
Hydrogen consumed, s.c.f./bbl	200
Catalyst	Ni/SiO_2

The product was distilled to yield a fuel having the following properties:

Percent aromatics	0.5
IBP/FBP, ° F	325/600
Heat of combustion:	
B.t.u./lb.	18,400
B.t.u./gal.	133,000
Freeze point, ° F	−40.5

I claim as my invention:

1. The method of preparing liquid hydrocarbon fuels which comprises fractionally distilling a sulfur-containing cracked gas oil, whereby a fraction boiling over a substantial portion of the range from about 400 to 650° F. is isolated, solvent extracting said fraction whereby an aromatic concentrate substantially free from aliphatic hydrocarbons is obtained, partially hydrogenating said aromatic concentrate at a temperature within the range from about 600 to about 900° F. in the presence of hydrogen and a sulfur resistant hydrogenation catalyst whereby the aromatic content of the product is reduced 40–70%, substantially completely hydrogenating the partially hydrogenated product at a temperature within the range from about 300 to about 700° F. and fractionally distilling the hydrogenated product, whereby a substantially alicyclic fuel substantially free of acyclic aliphatic and aromatic hydrocarbons and having a boiling range within the limits from about 325° F. and about 650° F. is obtained.

2. A process according to claim 1 wherein the cracked gas oil is a gas oil which has been both thermally and catalytically cracked.

3. A process according to claim 1 wherein the gas oil is a gas oil fraction obtained in the coking of thermal residue of catalytically cracked gas oil.

4. The process for the preparation of liquid hydrocarbon fuels which comprises fractionally distilling a gas oil fraction produced in the coking of thermal residue of catalytically cracked gas oil to isolate a fraction boiling over a substantial portion of the range from about 400° F. to about 650° F., isolating polyaromatics therefrom by solvent extraction, subjecting said isolated polyaromatics to partial hydrogenation and desulfurization in the presence of a sulfur-resistant molybdenum containing hydrogenation catalyst at a temperature witihn the range between about 600 and about 900° F., whereby the aro-

matic content of the product is reduced 40–70% substantially completely hydrogenating the product so obtained by subjecting it to hydrogenation in the presence of a nickel hydrogenation catalyst at a temperature within the range between about 300° F. and 700° F., and fractionally distilling the hydrogenated product, whereby a substantially saturated polycyclic hydrocarbon fuel substantially free of acyclic aliphatic and aromatic hydrocarbons and boiling between about 325° F. and about 600° F. is obtained.

References Cited in the file of this patent

UNITED STATES PATENTS

1,908,286	Dorrer	May 9, 1933
2,481,921	Gwynn	Sept. 13, 1949
2,534,025	Howes et al.	Dec. 12, 1950
2,671,754	DeRosset et al.	Mar. 9, 1954
2,769,753	Hutchings et al.	Nov. 6, 1956
2,911,352	Goretta et al.	Nov. 3, 1959
2,911,354	Holder et al.	Nov. 3, 1959