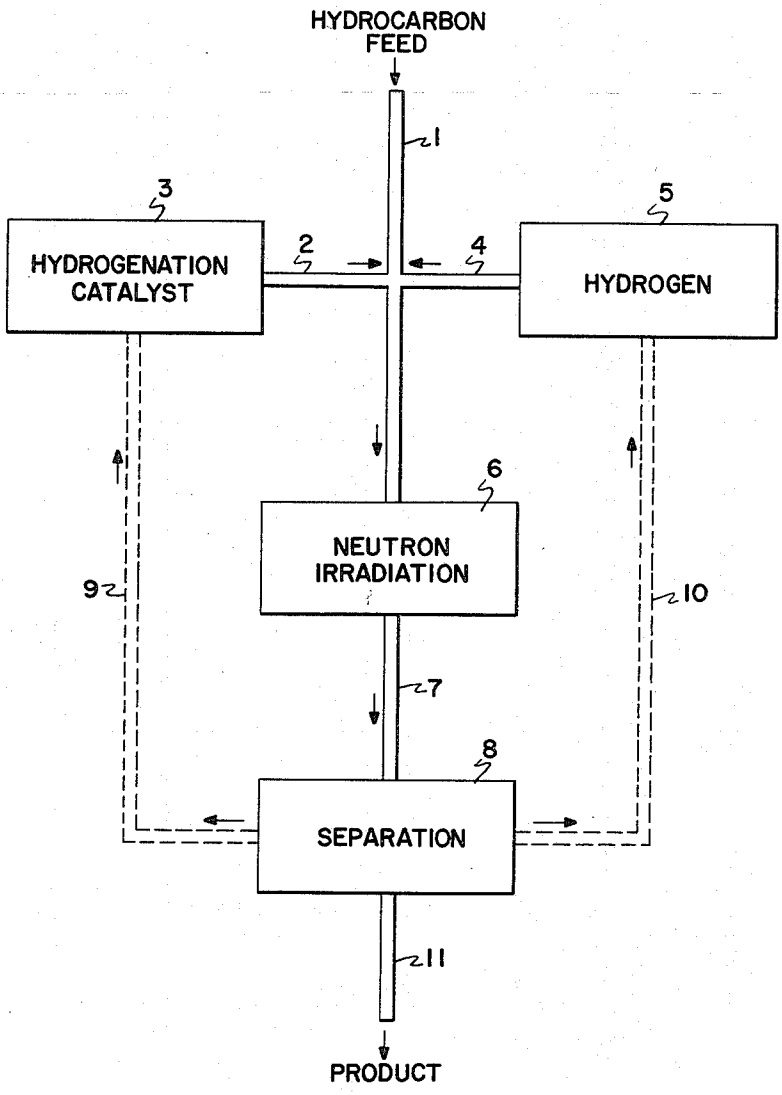
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CONVERSION OF HYDROCARBONS IN THE PRESENCE OF NEUTRON IRRADIATION AND A HYDROGENATION CATALYST

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CONVERSION OF HYDROCARBONS IN THE PRESENCE OF NEUTRON IRRADIATION AND A HYDROGENATION CATALYST

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6 Claims. (Cl. 204—154)

This invention relates to the radiolysis of hydrocarbons and is more particularly concerned with the conversion of petroleum hydrocarbons by neutron irradiation in the presence of a hydrogenation catalyst.

This application is a continuation-in-part of Serial No. 657,098, "Preparation of Lubricating Oils by Irradiation," filed February 23, 1956, by the present inventors, and now abandoned, and of Serial No. 547,860, "Hydrocarbon Conversion Process," filed November 18, 1955, also by the present inventors, and now abandoned.

In brief compass, this invention proposes a process wherein hydrocarbons are converted in a reaction zone by neutron irradiation in the presence of a significant amount of a hydrogenation catalyst at a temperature below 700° F., which is below the temperature range where the catalyst would have any appreciable effect on the reaction in the absence of radiation. A surprisingly saturated liquid product, as expressed by bromine number, is obtained in good yields.

It has now been found that when a hydrocarbon conversion reaction is carried out at moderate or low temperatures in the presence of a hydrogenation catalyst, unexpected results are obtained. While a reaction in the nature of hydrogen cleavage occurs, auto-hydrogenation takes place and the reaction products are largely saturated. As a result, the effects of conventional hydrogenating or hydrocracking of hydrocarbons can be obtained by the process of this invention while using no or minimal amounts, i.e., less than 100 standard cubic feet per barrel (s.c.f./bbl.), of extraneous hydrogen. More gasoline boiling range product, having a high octane number, is obtained and less polymer is formed when reforming reactions are carried out. The tendency of the hydrocarbons to polymerize or decompose into low molecular weight gases after being formed into radicals, is unexpectedly inhibited by the catalyst.

It has also surprisingly been found that during the irradiation of hydrocarbons in the presence of hydrogenation catalysts, the catalysts exert an appreciable influence on the selectivity of the reaction, even when the reaction temperature is relatively moderate, i.e., the temperature is substantially below incipient thermal cracking or conversion temperatures.

The lighter liquid products of this invention are especially useful in or as gasolines. In a preferred embodiment, the C_5—430° F. boiling range product has an octane number above 90 Research Leaded (3 cc.). By C_5 is meant hydrocarbons having 5 carbon atoms, the lowest boiling of which has a boiling point of 82° F. The heavier liquid products are useful in or as lubricants.

This invention is applicable to a wide range of gaseous and distillate hydrocarbon feed stocks boiling up to about 1150° F., including distillates derived from conventional

petroleum oils, shale oils, tar sand oils, asphalts, synthetic oils, natural and artificial hydrocarbon gases, etc. It has the greatest use in the conversion of petroleum derived oils such as whole crudes, distillate, extracts or concentrates therefrom, or mixtures thereof. A particularly preferred feed stock is a gas oil, especially a paraffinic one, boiling in the range of about 400° to 700° F.

By hydrogenation catalyst is meant one comprising a base material or carrier, which is preferably highly porous, and has as an active ingredient, a minor amount, i.e., less than 20 wt. percent on catalyst, of a hydrogenation component. Conventional hydrogenation catalyst bases known in the art can be used. These comprise, for example, dried hydrous oxides such as alumina, silica, zirconia, titania, and the like, and mixtures thereof. Other carriers such as activated carbon, kieselguhr, etc. can, of course, be used. The carrier material can be derived from natural sources such as from bauxite, or can be manufactured, e.g., by precipitating alumina from an alcoholate alumina or from an aluminum sulfate solution. It is preferred that the base material have a high surface area, i.e., an area above 50 square meters per gram ($m.^2/gr.$). This surface area and other desired properties can be incorporated into the carrier by heat treatment, e.g., calcination; chemical treatment, e.g., acid treatment or chlorine treatment; and similar methods known to the art. The active components in some instances can be incorporated into or onto the base during manufacture of the base.

The hydrogenation component used is preferably a metal, oxide, sulfide or salt of a group VI or VIII element. Specific preferred elements are nickel, cobalt, platinum, palladium, molybdenum, tungsten and mixtures thereof. Other known hydrogenation components can be such as copper, silver and zinc. The base material can be impregnated with a catalytic component or mixture thereof by known methods, such as by precipitation or mixing with a salt solution and drying. Preferred catalysts comprise an essentially pure alumina base and 0.01 to 2.0 wt. percent platinum, and an essentially pure alumina base and 1 to 15 wt. percent of molybdena.

The catalyst used preferably has a particle size under about 1000 microns, but can be much larger in size if desired, e.g., one inch or more. Pellets or compactions can be used. The surface area of the catalyst is above 50 $m.^2/gr.$ and usually does not exceed 600 $m.^2/gr.$, the true density is in the range of 2 to 4 gr./cc., and the pore size is in the range of 20 to 150 A. The catalyst can exist as discrete particles or can be in the form of compactions or pellets.

The catalytic and carrier materials used are normally those which, upon neutron bombardment, produce radioisotopes having short half lives, i.e., less than 10 weeks and preferably less than one week, or have small neutron capture cross-sections so that very little of the material becomes radioactive. Preferably, the fraction of any given element (wt. percent on catalyst) times its capture cross-section, for neutrons having an energy in the range of 0.03 to 100 electron volts (e.v.), is less than one barn.

The catalyst can be used as a suspension in the hydrocarbon reactant, or as fixed, fluid, or gravitating beds, all of which methods are known in the art. The catalyst, if contaminated, as by carbon deposition, can be regenerated by known methods such as burning, acid treating, chemical reworking and the like. The solids can be regenerated in place or external of the reactor, and either continuously or periodically, as the need arises.

This invention is based in part upon the important finding that hydrogenation catalysts surprisingly display an

appreciable effect on selectivity at moderate temperatures, i.e., at temperatures below 700° F. This means that it is now possible to operate at lower temperatures, heretofore unattractive because of the slowness of the reaction rate, and this permits the obtainance of reactions and selectivities not previously possible. Of prime interest is that undesirable secondary reactions can be avoided.

This invention is applicable to conversion reactions wherein the reactants are wholly or partly in the gas, liquid, or solid phase. It is most advantageously used with liquid phase reactions and the pressure used is, therefore, preferably sufficient to maintain substantially liquid phase conditions.

It has been found that even during the cracking of what have customarily been thought of as hydrogen-deficient materials, the lighter cracked products obtained are relatively highly saturated. The present invention can, therefore, secure operation equivalent to hydrogenation operations without the use of, or with very limited amounts of extraneous hydrogen. While it is preferred to utilize the advantages of this invention by operating at pressures below 15 atmospheres (atm.), higher pressures, e.g., up to 1000 atm. or greater, with or without the use of small amounts, i.e., less than 100 s.c.f./bbl. of extraneous hydrogen, will favor saturation of the product fractions. The total liquid product obtained has a bromine number below 20, which indicates that it is highly saturated. Expressed somewhat differently, the olefin/paraffin ratio of the C_5 product is less than 0.3.

The process of this invention can most conveniently be carried out, particularly on a commercial scale, by employing a nuclear reactor and can be carried out either on a batch or a continuous basis. The present process is preferably carried out with some type of agitation or continuous flow, so that there is sufficient contact between the oil, the radiation, and the subdivided catalytic solids. To carry out a continuous process, the material to be irradiated can be simply pumped through the pile itself, or through pipes disposed in the pile. In some instances, the hydrocarbon reactant can also serve as a moderator for the nuclear reactor.

The drawing attached to and forming a part of this specification schematically illustrates this invention.

In the drawing, a hydrocarbon material, e.g., a distillate virgin naphtha, is introduced into the process by line **1**. A hydroforming catalyst, e.g., alumina impregnated with platinum, supplied by line **2** from source **3**, is mixed with the feed material. The preferred catalyst to oil ratio is in the range of 0.1 to 2.0. As shown here, hydrogen supplied by line **4** from reservoir **5** is admixed with the hydrocarbon feed, although its use in many cases is not necessary. The resulting mixture is then passed through irradiation source **6**. The preferred feed rate is in the range of 36 to 3600 liquid volumes of feed per hour per volume of catalyst-free space (v./v./hr.), to obtain an average linear flow rate in the range of 0.01 to 1.0 feet per second (ft./sec.).

The radiation from the atomic pile consists primarily of neutrons and gamma rays. The results of this invention are dependent on neutron irradiation, probably because of the propensity of neutrons to favor C—H bond cleavages over C—C bond cleavages. Other types of radiation do not give equivalent results. The neutron flux used is preferably above about 10^{11} neutrons per square centimeter per second (n/cm.^{2}/sec.), and the associated gamma ray dosage is above about 10^6 roentgens per hour (R./hr.). Usually the neutron flux need not be above 10^{15}n/cm.^{2}/sec., and the associated gamma dosage need not be above 10^8 R./hr. The present process is most effectively carried out employing fast neutrons, i.e. neutrons having an energy above 30 e.v. Preferably the majority of the neutrons are fast neutrons. It is also preferred that of the energy absorbed by the hydrocarbon, at least 75% is derived from the neutrons. The total dose, for all types of radiation received by the feed, will vary somewhat with the feed, conditions, desired product, etc., but is preferably in the range of 0.3 to 3000 B.t.u.'s/lb. of fresh feed. The irradiation temperature is below 700° F., and is usually above 50° F.

Although a suspensoid system is shown in the drawing, i.e., the solids are carried by the hydrocarbon reactant through the reaction zone, the catalyst can exist as fixed, fluid, or gravitating beds within the radiation zone **6**. With fluid beds, the pipes carrying the reactant through the atomic pile are preferably vertical with upflow of the fluid reactant.

The irradiated material is transferred by line **7** to separation zone **8**. The separation zone comprises means for recovering the catalyst such as by distillation, filtration, and absorption. The recovered catalyst can be directly recycled, if desired, by line **9** or can be first treated as by burning, steaming, and the like, to remove contaminates and/or improve its properties before being recycled.

The hydrocarbon products and unused hydrogen, if any, are also separated in zone **8**. Thus distillation, extraction, or absorption, as with molecular sieves, can be used. If desired, the hydrogen and/or some of the hydrocarbon product can be recycled by line **10**.

Separation zone **6** can also include means for removing and/or neutralizing radioactive waste products. Such means can include storage tanks to permit decay of radioactivity, ion exchange apparatus, distillation columns, and solvent extraction units. The finished product is removed from the process by line **11**.

The conversion of feed, expressed as material converted out of the feed boiling range, is above 10%. The selectivity to normally liquid product obtained is high, being above 80 wt. percent, based on feed boiling in the range of 400° to 1150° F. As previously indicated, the liquid product is surprisingly saturated.

The following examples serve to further illustrate this invention.

The air cooled, natural uranium, graphite moderated research reactor of the Brookhaven National Laboratories was used for these tests. This pile was operating at a total power of about 24 megawatts at the time, which gave the following flux distribution at the point where the oils were irradiated:

Slow neutron flux (.03 e.v.)$=2.5\times10^{12}$n/cm.^{2}/sec.
Fast neutron flux (>30 e.v.)$=0.7\times10^{12}$n/cm.^{2}/sec.
Fast neutron flux (>1 m.e.v.)$=0.5\times10^{12}$n/cm.^{2}/sec.
Gamma dosage $=1.7\times10^6$ R./hr.

The core of the reactor was approximately a 20 ft. x 20 ft. x 20 ft. lattice of graphite with horizontal one-inch diameter aluminum-clad uranium rods spaced evenly throughout the reactor extending from the north to south faces of the core. This core was completely surrounded by 5 ft. of concrete shielding. The sample holes used for irradiation were horizontal 4-inch x 4-inch square holes extending through the 5 ft. concrete shield and into the carbon core for a distance of 10 ft. from the core face. Normal operating temperatures in the experimental hole were from 250° to 400° F.

Three one-quart samples were irradiated at one time by placing them in three 3-inch diameter aluminum containers which were mounted on a horizontal aluminum sled. Vents of aluminum tubing extended from the vapor space of the containers out of the core and through the shielding to a sample receiver system where gases and condensable liquids were metered and collected. The samples were prepared by adding the solids to the container to fill it, evacuating the void space in the container, and sucking the oil into the container with a vacuum. The samples were then purged with purified nitrogen and inserted in the pile during scheduled shutdowns. After irradiation for ten days, they were withdrawn from the pile during shutdown.

Three oils were treated:

Oil A.—Oil A was a narrow boiling virgin gas oil distilled from "paraffinic" South Louisiana crude. It had a 30.7° API gravity, bromine numper of 1.25 centigrams per gram; 34.4 SSU viscosity at 210° F., viscosity index of 67, and a 0.14 wt. percent sulfur content.

Oil A had the following distillation characteristics:

Cuts [1]:	Vol. percent
430°/600° F.	4.7
600°/700° F.	85.4
Above 700° F.	9.9

[1] At atmospheric pressure.

Oil A contained about 55% naphthenes, about 20% paraffin and about 25% of aromatics by volume.

Oil B.—Oil B was a narrow boiling "naphthenic" virgin gas oil distilled from West Texas crude. It had a

31.1° API gravity, a bromine number of 2.47 centigrams per gram, 33.0 SSU viscosity at 210° F., viscosity index of 67, and a 0.14 wt. percent sulfur content.

Oil B had the following distillation characteristics:

Cuts [1]:	Vol. percent
430/600° F.	12.6
600/676° F.	85.1
Above 676° F.	2.3

[1] At atmospheric pressure.

Oil B contained about 36% naphthenes, about 12% paraffins and about 52% aromatics by volume.

Oil C.—Pure cetane (n-hexadecane).

The results of these experiments are given in Table I. For comparison, runs made in the absence of a catalyst are included.

Table I

Run	1	2	3	4	5	6
Catalyst	Yes	No	Yes	No	Yes	No
Feed	A	A	B	B	C	C
Catalyst/oil ratio	1/1		1/1		1/1	
Days irradiated	10	10	10	10	10	10
Temperature, °F	330	150	295	150	330	260
Conversion to:						
Gas, wt. percent on feed	19.0	3.8	2.6	4.3	8.2	(A)
C_5 Olefin to paraffin, ratio in gas	0.1	1.0	0.3	1.1	0.02	
C_5 Iso- to n-paraffin, ratio in gas	0.9	1.0	1.0	0.7	0.05	
Naphtha:						
Boiling range, °F	0/430	0/430	0/430	0/430	0/430	0/430
Percent on feed	2.4	0.9	0	1.8	19.8	0
Lamp sulfur, wt. percent	0.03	0.04		0.44		
Vol. percent aromatics	5.3	7.8		10.4	3.0	
Vol. percent olefins	15.5	39.1		42.7	3.0	
Vol. percent saturates	79.2	53.1		46.9	94.0	
Refractive Index @ 20° C	1.4070	1.4322		1.4338	1.4073	
Gravity, °API	52.5			51.1	61.5	
Bromine No., cgs./cc	15.8			46.3	1.1	
Calculated octane No., research leaded (3 cc.)	93		92			
Heating Oil:						
Boiling range, °F	430/600	430/600	430/600	430/600	430/540	430/540
Percent on feed	6.6	5.1	5.1	10.4	5.1	1.3
Lamp sulfur, wt. percent	0.02	0.04	0.66	0.95	0.001	
Vol. percent aromatics	7.8	8.1	16.9	19.5	1.8	0.9
Vol. percent olefins	31.1	52.3	37.3	37.7	3.6	30.7
Vol. percent saturates	61.1	39.6	45.8	42.8	94.6	68.4
Refractive Index @ 20° C	1.4413	1.4651	1.4728	1.4688	1.4271	1.4340
Gravity, °API	38.0	35.2	36.0	35.7	52.7	
Bromine No., cgs./cc	15.1	11.0	25.5	29.9	1.1	17.7
Aniline pt., °F	164	158	146	150		
Diesel Index	62	56	52	54		
Feed:						
Boiling range, °F	600/700	600/700	600/700	600/700	540/560	540/560
Percent on feed	29.3	32.1	48.0	39.2	22.2	11.7
Lamp sulfur, wt. percent	0.04	0.09	0.98	1.58		0.0004
Vol. percent aromatics					1.4	1.0
Vol percent olefins					2.7	16.7
Vol percent saturates					95.9	82.3
Refractive Index @ 20° C	1.4601	1.4808		1.4886	1.4321	1.4401
Gravity, °API	50.9	30.1		29.9	50.3	49.8
Bromine No., cgs./cc	13.9	5.0		21.7	0.4	9.6
Aniline pt., °F						198
Diesel Index						99
High Boiling Fractions:						
(1) Boiling range, °F					560/700	560/610
Percent on feed					3.3	1.9
Vol. percent aromatics						0.0
Vol. percent olefins						13.5
Vol. percent saturates						86.5
Refractive Index @ 20° C						1.4390
Gravity, °API						48.5
Bromine No., cgs./cc						10.8
(2) Boiling range, °F						610/700
Percent on feed						2.7
Refractive Index @ 20° C						1.4493
Gravity, °API						44.0
Bromine No., cgs./cc						24.9
(3) Boiling range, °F	808/900	735/900	700/900	700/900	700/900	700/900
Percent on feed	6.0	5.8	8.6	1.5	16.3	5.4
Refractive Index @ 20° C					1.4545	1.4632
Gravity, °API					44.9	41.2
Bromine No., cgs./cc					0.9	
Viscosity—						
SSU @ 210° F	54.79	47.49	53.89	46.79	37.84	41.65
SSU @ 100° F	426.8	250.0	389.3	235.4	76.6	110.7
Index	65	71	71	72	144	139
Pour point, °F	30	40	5		60	55
(4) Boiling range, °F	900/990	900/975	900/1000	900/955	900/920	900/970
Percent on feed	9.7	9.7	16.3	9.8	1.8	2.8
Refractive Index @ 20° C						1.4700
Gravity, °API						38.5
Bromine No., cgs./cc						18.9
Viscosity—						
SSU @ 210° F	106.7		79.32	60.88		50.78
SSU @ 100° F	2,081.4		1,305.1	571.4		218.5
Index	56		35	65		127
Pour point, °F	−10		−5	−15		

Footnote at end of table.

Table I—Continued

Run	1	2	3	4	5	6
Bottoms:						
Boiling range, °F	990+	975+	1,012+	955+	920+	970+
Percent on feed	19.0	38.4	19.6	24.9	19.8	18.0
Viscosity—						
SSU @ 210° F	231.8					
SSU @ 100° F	2,605.4					
Index	−138					
Pour point, °F	80					0

(A) No gas samples taken.

These data show a high degree of utilization of available hydrogen, even at atmospheric pressure, for the paraffinic feed stocks. This process is similar to hydrocracking in products except that hydrocracking does not take place at this temperature without catalyst or without radiation. It is to be noted that the hydrogenation catalyst increases the selectivity of conversion toward lighter products at the expense of polymers and helps to control product distribution. The relatively slight effect on the naphthenic feed is largely due to sulfur poisoning of the platinum catalyst with this high sulfur feed. The effectiveness of the catalyst in saturating products and increasing conversion to low boiling products lines up according to the sulfur contents of the feeds. Thus, sulfur resistant catalysts, e.g., catalyst containing molybdenum, would be needed with high sulfur feeds. It is apparent from these data that the products of this invention are useful as gasolines, diesel fuels, and lubricants.

Having described this invention, what is sought to be protected by Letters Patent is succinctly set forth in the following claims.

What is claimed is:

1. A process comprising exposing a hydrocarbon boiling up to 1150° F. in the presence of a significant amount of a hydrogenation catalyst comprising a porous carrier impregnated with a minor but catalyzing amount of a hydrogenation component, said catalyst having a surface area above 50 m.²/gr., and in the presence of under 100 s.c.f. of added hydrogen/bbl. of feed, to radiation comprising neutrons, at a neutron flux in the range of 10^{11} to 10^{15} n/cm.²/sec., and at a temperature in the range of 50° to 700° F. until 0.3 to 3000 B.t.u.'s of radiant energy per pound of fresh feed have been received and the conversion of said hydrocarbon is at least 10%, and recovering a liquid product in yields above 80 wt. percent, based on converted feed, said liquid product having a bromine number below 20.

2. The process of claim 1 wherein said hydrogenation catalyst consists of the dry hydrous oxides of a material selected from the group consisting of alumina, silica, zirconia, titania and mixtures thereof, impregnated with under 20 wt. percent of a hydrogenation component selected from the metals, oxides, sulfides, and salts of elements selected from the group consisting of nickel, cobalt, platinum, palladium, molybdenum, tungsten, and mixtures thereof.

3. The process of claim 1 wherein said hydrogenation catalyst comprises an essentially pure alumina base with 0.01 to 2.0 wt. percent of platinum distended thereon.

4. The process of claim 1 wherein said liquid product is separated to recover a fraction boiling in the range of 82°–430° F., said fraction having a Research Leaded octane number above 90.

5. The process of claim 1 wherein said irradiation also comprises gamma rays and is obtained from a nuclear reactor, and wherein at least 75% of the energy absorbed by said hydrocarbon is derived from neutrons.

6. The process of claim 1 wherein said hydrocarbon consists of a paraffinic gas oil boiling in the range of about 400° to 700° F.

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