

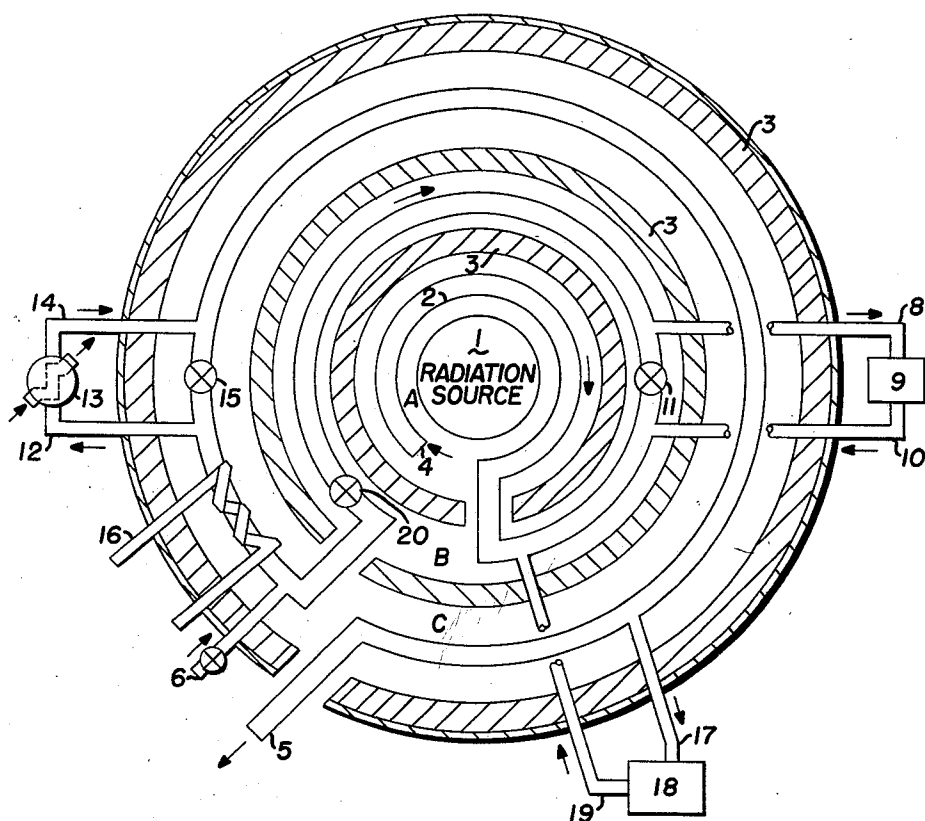
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P. J. LUCCHESI ET AL

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HYDROCARBON RADIOCHEMICAL CONVERSION PROCESS

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Peter J. Lucchesi
Chester L. Read
Robert B. Long

Inventors

By *L. A. Steinbeck* Attorney

1

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HYDROCARBON RADIOCHEMICAL CONVERSION PROCESS

Peter J. Lucchesi, Cranford, Chester L. Read, Westfield, and Robert B. Long, Wanamassa, N.J., assignors to Esso Research and Engineering Company, a corporation of Delaware

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This invention relates to an improved process for converting by high intensity ionizing radiation organic materials that tend to increase in molecular weight during conversion. It more particularly relates to an improved hydrocarbon radiochemical conversion process for polymerizing aliphatic hydrocarbons having from 2 to 20 carbon atoms per molecule, particularly saturated aliphatic hydrocarbons, by exposing the hydrocarbons to radiation, preferably neutrons and gamma rays.

In brief compass, this invention proposes an improved hydrocarbon radiochemical conversion process which comprises: exposing an aliphatic hydrocarbon to high intensity ionizing radiation comprising, preferably, neutrons, at an initial radiation intensity above 4×10^7 equivalent roentgens/hr. until the total energy absorbed by the hydrocarbon reactants is above 80 B.t.u.'s/lb.; then decreasing the flux to within the range of 4×10^6 to 4×10^7 equivalent roentgens/hr. until the total energy absorbed is above 100 B.t.u.'s/lb.; and, in a preferred embodiment, further decreasing the flux to below 4×10^6 , but at least 10^4 , equivalent roentgens/hr. and continuing the irradiation until a total of at least 120 B.t.u.'s/lb. of energy has been absorbed. The irradiated hydrocarbon reactant is then recovered as product.

It has now been found that the conversion of hydrocarbons by high intensity ionizing radiation is influenced not only by the amount of energy absorbed, but also by the rate of energy absorption. A corollary finding is that a more effective polymerization of hydrocarbons by irradiation is obtained by decreasing the flux or intensity of radiation during the course of the conversion.

It has also surprisingly been found that, at least with certain feed stocks, the rate of conversion increases with the amount of energy absorbed.

According to the present invention, better selectivities and better conversions are obtained and the tendency for reactor fouling is greatly minimized or eliminated during hydrocarbon radiochemical conversions, by decreasing, either stepwise or continuously, the flux or intensity of irradiation during the course of the conversion. The present invention proposes a method and apparatus for applying the above findings.

The aliphatic hydrocarbon feed stocks used in the present invention contain from 2 through 20 carbon atoms, including saturated or unsaturated and straight, branched or cyclic materials. The preferred hydrocarbons are normally liquid saturated hydrocarbons having from 5 to 20 carbon atoms. Mixtures of the hydrocarbons can, of course, be converted.

Suitable hydrocarbon reactants can be obtained by molecular sieve or urea adduct separation of conventional refinery streams to give concentrates of normal paraffins; solvent extraction or extractive distillation of refinery streams to get paraffin mixtures; low temperatures filtration similar to solvent dewaxing to get n- and isoparaffin mixtures; adsorption of non-paraffins on silica or alumina gel to prepare paraffin concentrates; or by combinations of these processes with other petroleum refining processes known in the art. In some cases paraffin concentrates can be obtained directly by distilling suitable fractions from selected crudes or from products from hydroforming or hydrogenation reactions.

2

The hydrocarbon reactant of this invention can contain or be diluted with other materials that do not appreciably affect the course of reaction, such as aromatics. In some cases solvents and/or emulsifiers such as ethers, ketones, aldehydes, carbon tetrachloride, chloroform, water and the like can be used to aid the conversion. In any event, it is preferred that the concentration of the C_2 - C_{20} aliphatic hydrocarbons in the reactant mixture be at least 50 wt. percent, and preferably, at least 90 wt. percent. The boiling range of the reactant mixture is preferably in the range of 100 to 700° F., although it can vary beyond these limits.

The irradiation used in the present invention can be obtained from particle accelerators, such as Van de Graaff accelerators; nuclear waste products, such as spent fuel elements; or products especially made radioactive, such as cobalt 60. The material can be exposed to the radiation source simply by flowing it in pipes past, through, or near the radioactive material. The use of shielding, the distance from the radiation source, and time of exposure are controlled to obtain the previously described intensities and energy absorptions.

It is much preferred, however, for reasons of economy and convenience, to use a nuclear reactor as a radiation source. When using a nuclear reactor, the aliphatic hydrocarbon feed stock can simply be flowed through pipes disposed in, around, or near the fissionable material. Conventional moderators such as carbon and water can be used. In some cases the hydrocarbon reactant can serve as a moderator.

The irradiation is preferably carried out in liquid phase and for that reason the pressure is sufficient to maintain substantially liquid phase conditions, although it can range from atmospheric pressure to 1000 p.s.i. or more. The temperature is preferably below thermal cracking temperatures, i.e., below 700° F., although it can range from 50 to 900° F. or more. The time of treatment is sufficient to obtain the above dosages and will usually lie within the range of about 10 to 150 minutes.

Inorganic solids such as adsorbents and/or catalysts can be used during irradiation. Thus materials such as kieselguhr, carbon or coke, and hydrocarbon conversion catalysts such as silica-alumina cracking catalyst or platinum on alumina hydrogenation catalysts can be used. The solid material can exist as fixed or fluidized beds in the reaction zone, or a suspensoid system can be used. The solids can be regenerated either continuously or periodically, either in or external of the reaction zone, by such means as chemical reworking, solvent treating, burning and classification. The hydrocarbon reactant can be contacted with the inorganic solid during all or only part of the conversion.

Materials that give off secondary radiation upon neutron capture or photon incidence, such as boron 10, lithium 6, beryllium 9 and cadmium 113, can also be used. They can be used as pure isotopes or as the natural element containing these isotopes. They can be carried on solids such as those above identified, can exist as discrete solids in themselves, or can be used in solution, e.g., tri-n-dodecyl borate can be used.

After irradiation, the irradiated material can be further treated as desired, as by filtration, distillation, absorption, adsorption, extraction, crystallization, and ion exchange. Portions of the irradiated material can be recycled.

The drawing attached to and forming a part of this specification illustrates one preferred embodiment of this invention, wherein an aliphatic hydrocarbon reactant is continuously flowed through zones of decreasing radiation intensity.

A particularly preferred process of this invention is to convert normally liquid saturated aliphatic hydrocarbons containing from 5 to 20 carbon atoms by polymerization

to materials that make excellent lubricating oils or lubricating oil additives. The following description of the drawing is made in light of this preferred process. In this preferred lubricating oil production process, the rate of change in radiation intensity is related to the change in viscosity of the hydrocarbon undergoing polymerization for control purposes.

More specifically, the preferred process of this invention for the production of lubricating oil fractions comprises irradiating a mixture consisting essentially of C_5 to C_{20} saturated aliphatic hydrocarbons at an initial intensity above 4×10^7 equivalent roentgens/hr. until the total energy absorbed is above 80 B.t.u.'s/lb. and the viscosity of the mixture is increased to above 40 S.S.U. at $210^\circ F.$, and then decreasing the radiation intensity to below 4×10^7 , but at least 10^4 , equivalent roentgens/hr. and continuing the treatment until at least 120 B.t.u.'s/lb. of total energy has been absorbed and the viscosity of the mixture in the absence of solvents is at least 60 S.S.U. at $210^\circ F.$

The drawing illustrates one type of apparatus that can be used to carry out the teachings of this invention. As shown, the apparatus comprises a central radiation source 1, which can be radioactive material such as cobalt 60 but is preferably fissionable material such as uranium or plutonium. Disposed about this radiation source which preferably creates at least 1 megawatt of penetrating radiation is a conduit 2, or a plurality of conduits if necessary. The arrangement of the conduit is such that one portion is exposed to a considerably different amount of irradiation than another. If desired and preferably, the apparatus is divided into a plurality of zones A, B and C by suitable reflecting or shielding material 3, such as carbon, beryllium, concrete, cadmium, iron, cobalt, or other materials converting slow neutrons to penetrating radiation. Conduit 2 passes successively through these zones as shown, the spacing of the conduit and the amount of material 3, proscribing the amount of irradiation incident on the conduit 2 in each of the zones.

The material to be converted is, in accordance with this invention, introduced into the central zone A of the apparatus at point 4, then flows as indicated by the arrows through line 2, and is removed at point 5 for further processing as desired.

It will be understood that other types or arrangement of equipment can be used to carry out the process of this invention. The important consideration is that the design should meet the prescribed processing limitations in order to obtain improved results. For example, the apparatus has, of course, some depth and the pipes can be arranged in a spherical manner about the central core. Apparatus in the nature of a multi-tube multi-pass heat exchanger can be used with the hydrocarbon reactant being tube-side and the fissionable material, say as a homogeneous liquid, being shell side. Also, the conduits containing the reactants can be arranged in the form of banks of tubes as is done in conventional multi-tube steam generators in power plants.

The whole of the apparatus illustrated is, of course, provided with suitable shielding such as concrete. The apparatus can also be used simultaneously for other purposes such as for the production of power or the breeding of fissionable material. When using a nuclear reactor, it is preferred that the gamma rays associated with the neutrons account for at least 10% of the energy absorbed by the reactants.

The drawing illustrates several modifications of the invention. Other modifications will occur to those skilled in the art. As previously indicated, the reactants can or cannot initially contain such materials as solvents and/or catalyst. During the course of the reaction, such materials can be removed or added as desired. For example, after the reaction has proceeded for some time, a solvent such as diethyl ketone, ethers, aldehydes, carbon tetrachloride, or chloroform can be admitted to the reactants to control the viscosity, degree of conversion, etc., as by

line 6. Also, a portion or all of the circulating stream can be temporarily withdrawn as by line 3, solvents and/or catalysts or other solids removed or added in processing zone 9 and then returned by line 10, valve 11 being used to control the flow. Processing zone 9 can comprise, for example, suitable pumping facilities and slurring-in devices.

It is advantageous also to control the temperature of the reactants, either by heating or cooling. This can be done, for example, by withdrawing a portion or all of the reactants from conduit 2 by line 12, circulating it through a heating or cooling means 13 such as a furnace or heat exchanger, and returning it by line 14 with valve 15 being used to control the flow. Alternatively the heating or cooling can be done while the material is within conduit 2, as by heating or cooling element 16 disposed about conduit 2 such as a refrigerated water coil or electrical heating element.

While a portion of the product removed at 5 can be recycled, it is advantageous, to aid in the control of the conversion and selectivity, to recycle a portion of the product as by withdrawing it via line 17, passing it through pump 18 and returning it to a zone of higher intensity radiation by line 19. The pressure in each one of these zones can be altered if desired. For example, a valve 20 can be used to decrease the pressure of the flowing reactants. The flow rate can be altered, besides using recycle operations, by changing the size and/or length of conduit 2 or by using substantially inert diluents.

EXAMPLE

Cetane is converted by continuously passing it through a conduit disposed about a nuclear reactor in a 4-zone system similar to the one illustrated in the drawing. The core of the reactor comprises a homogeneous water solution of uranyl sulfate.

The following Table I gives the average conditions maintained in the 4-zone system.

Table I

	Time, min.	$^\circ F.$ Temp.	Pres- sure, p.s.i.g.	Gamma ray in- tensity, r/hr.	Neutron intensity, n/cm. ² / sec.	Total energy absorbed, B.t.u.'s/ lb.
1st Step-----	10	350	400	2×10^7	4×10^{14}	85
2d Step-----	10	375	300	1×10^7	1×10^{14}	105
3d Step-----	23	400	200	4×10^6	1×10^{13}	115
Final-----	60	450	100	2×10^6	4×10^{12}	120

Over 50 wt. percent based on feed of a viscous liquid polymer-like material is obtained that serves as an excellent lubricating oil additive.

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 for the production of a lubricating material which comprises irradiating a mixture consisting essentially of C_5 to C_{20} saturated aliphatic hydrocarbons with high energy ionizing radiation at an initial intensity above 4×10^7 equivalent roentgens/hr. until the total energy absorbed is above 80 B.t.u.'s/lb. and the viscosity of the mixture is increased to above 40 S.S.U. at $210^\circ F.$, then decreasing the radiation intensity to within the range of 4×10^6 to 4×10^7 equivalent roentgens/hr., and then further decreasing the radiation intensity to below 4×10^6 , but at least 10^4 , equivalent roentgens/hr. and continuing the treatment until at least 120 B.t.u.'s/lb. of total energy has been absorbed and the viscosity of the mixture in the absence of solvents is at least 60 S.S.U. at $210^\circ F.$

2. A process for the production of a lubricating material which comprises irradiating cetane with high energy ionizing radiation at an initial intensity above 4×10^7 equivalent roentgens per hour until the total energy absorbed is above 80 B.t.u.'s per pound, then decreasing the

5

radiation intensity to within 4×10^6 to 4×10^7 equivalent roentgens/hr., and then further decreasing the radiation intensity to below 4×10^6 but at least 10^4 equivalent roentgens per hour and continuing the treatment until at least 120 B.t.u.'s per pound of total energy have been absorbed. 5

3. An improved radiochemical hydrocarbon conversion process which comprises exposing a normally liquid saturated aliphatic hydrocarbon containing in the range of 5 to 20 carbon atoms to high energy ionizing radiation at an initial intensity above 4×10^7 equivalent roentgens per hour until the total energy absorbed is above 80 B.t.u.'s per pound, then decreasing the flux to within the range of 4×10^6 to 4×10^7 equivalent roentgens per hour until the total energy absorbed exceeds at least 100 B.t.u.'s per lb., further decreasing the flux to below 4×10^6 but at least 10^4 equivalent roentgens per hour and continuing the radiation until the total energy absorbed exceeds at least 120 B.t.u.'s per lb., and recovering a product from the irradiated material. 15

4. The process of claim 3 wherein the radiation comprises neutrons and gamma rays obtained from fissionable material. 20

5. The process of claim 3 wherein the radiation is obtained from a radioisotope and comprises essentially gamma rays. 25

6

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