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RADIOETHYLATION OF PARAFFIN HYDROCARBONS

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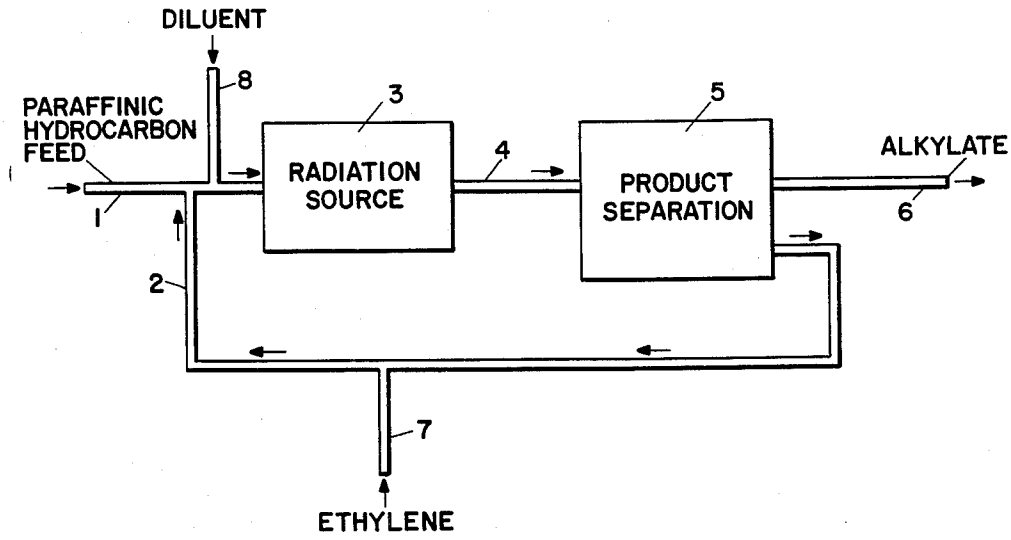

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RADIOETHYLATION OF PARAFFIN HYDROCARBONS

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This invention relates to the radiation conversion of hydrocarbons and more particularly to the production of saturated branched-chain hydrocarbons by the reaction of paraffinic hydrocarbons with ethylene in the presence of high energy ionizing radiation. The products are normally liquid saturated branched-chain hydrocarbons boiling chiefly within the motor fuel boiling range, i.e. 65° to 430° F. and are extremely useful for upgrading refinery gases and light virgin naphtha to high octane gasoline components.

This application is a continuation-in-part of copending applications, Serial Nos. 655,909 and 655,910, both filed Apri 29, 1957, by the present inventors, and are now abandoned.

In commercial operations petroleum refineries have large quantities of light hydrocarbon mixtures available. However, there recently has sprung up a greater demand for the isoparaffinic hydrocarbons than for the normal paraffinic hydrocarbons, making it necessary to incorporate new facilities in the ordinary refinery in order to obtain increased amounts of the isoparaffins which serve not only as blending agents for the normal paraffins but also as intermediates and reactants in the preparation of normally liquid hydrocarbons which are also useful in motor fuels. Often for such purposes particular alkylation products are necessary.

Generally, the conversion of paraffin-olefin mixtures has been carried out in the presence of various alkylation catalysts, promoters and activators, and complicated separation and recovery processes have been required to obtain the desired alkylate product. Heretofore, however, it generally has not been possible to successfully alkylate normal paraffinic hydrocarbons by these processes. Apart from troublesome problems caused by introduction of contaminants into the alkylate product, the foregoing operations result in major corrosion in alkylate fractionating columns, reflux accumulators, in transfer lines, and in charge storage tanks. Further, at temperatures where equilibrium is favored and pressures required are moderate, reaction initiation has been slow. On the other hand at temperatures where initiation of reaction is rapid, equlibrium has been unfavorable and extremely high pressures have been required.

Photochemical initiation of paraffin-olefin reactions also has serious drawbacks. Common resonance lamps suffer from instability and need continued maintenance. Optical heterogeneity, opacity of the particular medium, and the relatively low penetrating power of ultra-violet rays are also problems. Photochemical initiation is possibly only near atmospheric pressure with monomers which absorb in the regions of the spectrum for which intense sources are available and can never be used for processing requiring high-pressure, thick walled reaction vessels.

The present invention provides a novel hydrocarbon conversion process which obviates these and other disadvantaegs of prior art methods for reacting paraffins with olefins. In brief, this invention proposes a process for upgrading refinery gases and light virgin naphtha to high octane gasoline components by reacting ethylene with paraffins by subjecting a mixture of these hydrocarbons to high energy ionizing radiation. Specifically the preferred process of the present invention comprises irradiating a paraffinic hydrocarbon having from 2 to 8 carbon atoms with high energy ionizing radiation, in the presence of a small amount of ethylene, preferably about from 0.1 to 30 weight percent, based upon the total weight of paraffin and ethylene in the feed, until at least about 1×10^{-6} kwh. of radiation energy per pound of hydrocarbon feed has been absorbed, and recovering, as a product of the reaction, a higher molecular weight branched-chain homologue with a yield in the range of about from 200 to 10,000 molecules per 100 electron volts absorbed.

In the preferred process, conversion is carried out at a temperature in the range of about 500–800° F. at about 150 to 600 p.s.i.g. pressure with a total radiation dose of between about 10^{-4} and 10 kwh. per pound of hydrocarbon feed.

While free radical alkylation of isoparaffins with feed olefin has been one of the promising ways of making branched paraffins for use in high octane fuels, alkylation using normal paraffins has never been achieved by the conventional commercial process. The present invention is of particular importance because it provides a method of converting, to higher molecular weight branched-chain homologues, normal paraffinic hydrocarbons which have never been in as great demand as the more useful isoparaffinic hydrocarbons. The present discovery is, however, even more surprising in that it has new been found that an important product of the present process is the branched-chain isomer of the normal paraffin reacted. For example, the irradiation of normal butane with high energy ionizing rays in the presence of a small amount of ethylene results in a surprisingly high yield of both isopentane and isobutane. The reaction thus utilizes the less valuable normal paraffins in a novel radiolysis process and yields both "alkylate" and the corresponding isomeric isoparaffin with product selectivity in the range of about from 40 to 70 wt. percent.

In another specific embodiment of the present invention, isobutane is reacted in admixture with ethylene under the influence of high energy ionizing radiation to produce a high yield of isopentane.

Broadly, any paraffin, that is, any saturated, aliphatic hydrocarbon having two or more carbon atoms can be reacted with ethylene according to the present invention. Particularly the process is applicable for the conversion of paraffinic hydrocarbons having from 2 to 12 carbon atoms. Most intersting are the paraffins having from 2 to 8 carbon atoms and mixtures of these. Cyclic paraffins with alkyl or aryl side chains can likewise be converted according to the present process. Mixtures of two or more of these hydrocarbons can also be alkylated.

Various refinery gases such as ethane, propane. C_4 and C_5 cuts from thermal or catalytic cracking units, field butanes which have been subjected to prior isomerization

or partial dehydrogenation treatment, and spent gases and liquid products from catalytic polymerization processes are also useful as feed stocks for the present invention. It is only essential that the feed stocks to the process contain at least one paraffinic hydrocarbon and also contain an initial concentration of ethylene, present in an amount between about 0.1 and 30 weight percent, based upon the total weight of paraffin and ethylene in the feed. By the irradiation of the paraffin alone one cannot achieve the novel results of this invention.

Particularly advantageous for the present process is a refinery hydrocarbon feed boiling at a temperature in the range of from about 10° to 200° F. containing at least 75 weight percent of a paraffin-ethylene mixture wherein the concentration of olefin is equal to that given above, i.e. between about 0.1 and 30 weight percent. Furthermore, the presence of hydrogen is not deleterious to the reaction. Therefore, an unpurified refinery gas stream is suitable for use in the reaction. A particularly useful feed stock for the present process is Arabian virgin naphtha which has a high concentration of C_5, C_6 and C_7 paraffins.

As has already been stated it is desirable to employ a substantial molar excess of the paraffinic component of the feed stock. Further, according to this invention, ehtylene in amounts in the range of about 0.1 to about 30 weight percent is added to a feed comprising a paraffin and the mixture exposed to high energy ionizing radiation of an intensity and for a duration sufficient to convert at least one weight percent, based on total feed, of the paraffin. Most preferably, from about 0.5 to about 10 weight percent of ethylene is utilized, and the radiolysis of the feed mixture is carried out by exposing it either continuously or batchwise to the radiation. The unconverted constituents can be then returned to the reaction zone in an ordinary recycle process.

The surprising feature of the present discovery is that the novel radiolysis process does not result simply in addition of paraffin to olefin but, rather, results in a surprising amount of disproportionation. For example, for the "alkylation" of the butanes with ethylene according to this invention, the paraffin is converted to the next higher branched-chain homologue (one additional carbon atom) and with a product selectivity of at least 30 weight percent based on total product. This is truly a surprising discovery.

Advantageously the process of this invention is carried out in the vapor phase. For the vapor phase conversion in the presence of high energy ionizing radiation, the reaction occurs in the temperature range of 300 to 1000° F. at a pressure between about 10 to about 1000 p.s.i.g. Preferably the radiolysis of paraffins and ethylene is carried out at a temperature of between about 500° and 800° F. at a pressure of between about 150 and 600 p.s.i.g.

The radioethylation reaction of the present invention is carried out by exposing the paraffin or paraffin mixture in contact with small amounts of ethylene to high energy ionizing radiation, that is high energy quanta (radiation wave length less than 50 A.), neutrons, and charged and uncharged particles of atomic and sub-atomic nature having energies greater than about 30 electron volts. Types of radiation suitable for the purposes of invention include high energy electro-magnetic radiation such as gamma and X-rays, high velocity electrons as well as beta rays, alpha particles, protons, deuterons, fission fragments and neutrons. These types of radiation can be supplied by radioactive materials, nuclear machines or by common neutron sources. Fission by-products of processes generating atomic power or fiissionable materials which emit high energy gamma rays also afford a highly desirable and most abundant source of radioactivity suitable for the purposes of the invention. These by-products include those with atomic numbers ranging from 30 to 63 and their compounds. They are formed in the course of converting uranium and thorium and other fissionable materials in an atomic reactor.

In one embodiment of the invention, the irradiation with gamma rays and neutrons can be carried out most conveniently, particularly on a commercial scale, by employing an atomic pile, that is, a nuclear reactor. This particular source of radiation can be utilized on either a batch or continuous basis. More specifically, for example, a batch reaction can be carried out simply by irradiating the material in a container. In carrying out a continuous process the material to be irradiated can be pumped through pipes disposed in the atomic pile. Generally, the radiation from an atomic pile will consist primarily of neutrons and gamma rays. The neutron flux existing in these atomic piles generally will be in the range of about 10^{11} to 10^{14}, usually about 10^{12} to 10^{13} neutrons per centimeter squared per second and gamma ray dosage will generally be from about 10^4 to 10^8, usually about 10^6 to about 10^7 roentgens per hour. Conventional moderators can of course be used, such as water, carbon, and hydrocarbons. Radiation fields in the range of 10^5 to 10^9 rep./hr. are employed. In some cases the feed stream itself can serve as a moderator. Materials made radioactive by exposure to neutron irradiation such as radioactive cobalt-60, which emits gamma rays, can likewise be used with radiation fields in the range of 0.1 to 10^7 rep./hr. Suitable sources of high velocity electrons are the beams of electron accelerators such as the Van de Graaff electrostatic accelerator, resonant transformers and linear accelerators. For example, radiation intensities of the order of 4×10^6 rep./sec. are obtained with electron beams.

In general, however, high velocity electrons, high energy gamma rays, and neutrons are preferred for the purposes of this invention mainly because of the high penetrating power of the rays and the availability and ease of application of these sources of high energy ionizing radiation. By high energy ionizing radiation is meant the ionizing radiation from controlled terrestrial sources of sufficient energy that the dose rate is at least 1×10^{-4} kwh. per pound of hydrocarbon reactant per hour, and capable of penetrating through 0.1 millimeter of lead sheet. This excludes radiations such as cosmic and ultraviolet, which are ineffectual for the purposes of this invention.

The radiolysis of a paraffnic hydrocarbon, such as normal butane or isobutane with ethylene to produce a high yield of isopentane, can be carried out utilizing a wide radiation does range. The amount of feed converted in the process of this invention varies in a substantially linear fashion with time at a fixed radiation dose rate over a very wide range. This means that according to the present radiation process the conversion of the reactants varies substantially directly with time for a contsant rate of radiation energy absorbed over a wide concentration of unreacted reactant, for example, from 100–50 weight percent of unreacted reactants. As the total amount of conversion becomes large and the concentration of unreacted reactant becomes increasingly smaller, the rate of conversion naturally falls off. For radioethylation reactions in accordance with the present invention, a wide radiation dose range therefore can be employed. Preferable dosages are from about 10^{-6} to about 10^3 kwh. per pound of reactant.

(1 roentgen equals 1.06×10^{-9} kwh./lb.)

A total energy absorption of from about 10^{-4} to about 10 kwh. per pound of reactant produces as a conversion product a higher branched-chain paraffinic homologue with a product selectivity in the range of about from 30 to 70 weight percent based upon the total weight of paraffin and olefin present.

The production of higher molecular weight products from paraffin-ethylene mixtures by high energy ionizing radiation is somewhat dependent upon temperature. Suitable temperatures for the present process lie in the range

between 300° and 1000° F. For example, for the radiolysis of butane-ethylene mixtures, temperatures in the range of between about 600° F. and about 700° F. are employed most advantageously. The optimum operating temperature of course varies somewhat wtih pressure, that is, the higher the pressure, the higher the optimum temperature for high yields. Suitable pressures for conversion range between 10 and about 1000 p.s.i.g. Most advantageously pressures between about 150 and 600 p.s.i.g. are employed according to this invention. Conversion at higher temperatures is less desirable since increased cracking lowers the yield of alkylate. The lower temperature limit is set by the liquification temperature. The lower pressure limit is set by the amount of undesirable material (cracking) that is obtained. 20 p.s.i.g. will yield reasonable yields. The upper limit on pressure is set by the upper level of conventional pressure equipment.

According to the present invention small amounts of ethylene can be added to a paraffin or to paraffin mixtures and the resultant mixture subjected to high energy ionizing radiation of an intensity and for a duration sufficient to convert a substantial proportion of the mixture to a conversion product. This product containing substantial amounts of higher molecular weight branched-chain isomers can be separated from the reaction medium and fractionated within the desired boiling range. The unreacted paraffin can be then returned to the reactor to be further converted to more useful products. Advantageously mixtures of paraffin and ethylene are fed into an atomic reactor in a continuous feed system. Radiation does rate is determined by geometrical considerations and therefore total energy absorption is determined by feed rate. Contact times can vary from a fraction of a minute per pass up to an hour or more. In batch reactions contact time can be from about one-half hour to about 200 hours. In general it is desirable to convert only a portion of the paraffin-ethylene feed in a single pass through the radiation zone in the continuous system. The product can be recovered outside the reaction zone and the unreacted paraffin returned to the radiation reactor in an ordinary recycle process. In this way the probability that alkylate product will be cracked by continuing the radiation reaction after the product is formed is reduced. Advantageously only about 1 to about 50 percent of the reactant is converted in the radiolysis process and unreacted reactant is returned for further processing following the separation of the desired product.

No special type of apparatus is required for carrying out the novel conversion process of this invention. The usual alkylation equipment has been found to be entirely satisfactory. However, since the novel process avoids the use of the corrosive catalyst of the prior art it is unnecessary in order to preserve the equipment to construct the apparatus coming in contact with the reactants of the alkylation process out of acid resistant metals.

The novel features which are believed to be characteristic of the invention both as to its organization and method of operation will be understood more clearly and fully from the following description considered in connection with the accompanying drawing.

Referring to the drawing in detail, it will be seen that the paraffnic hydrocarbon to be converted is admitted to the process by line 1. Ethylene is supplied to line 2 by line 7.

The ethylene component added to the paraffinic feed can be controlled in order to obtain high yields of conversion product. The amount to be added is determined in any convenient manner as by observing the composition, distribution or yield of the products or by monitoring the admixture entering the radiation reaction zone. This can be done by continuous analysis, for example, by continuously measuring the product quality or continuously measuring by spectroscopic techniques the ethylene composition of the feed mixture. Preferably the ethylene content of the mixture is in the range of about 0.5 to about 10 weight percent.

The resultant mixture is then exposed to high energy ionizing radiation in a radiation zone using a conventional radiation source 3. For example, this source can comprise an atomic pile or nuclear reactor, and the mixture can simply be passed through in suitable conduits. It can flow around or through the core of the reactor and in some cases the hydrocarbon mixture can serve as a moderator. Suitable conditions of pressure and temperature are maintained during the alkylation.

Another suitable source of radiation comprises atomic "waste products" obtained from nuclear reactors or atomic piles. This material can be suitably enclosed or concentrated as in an underground storage area and the hydrocarbon mixture can be passed through or around the "waste material."

Electron accelerators of the linear type and Van de Graaff generators can be employed as a source of high energy electrons. The electrons are directed through a thin, suitably reinforced window into the hydrocarbon mixture.

The converted material is removed by line 4 and passed into a suitable product separation zone 5. This zone can comprise, for example, a distillation zone, several flash vaporization chambers, a solvent extraction zone, an absorption zone or a combination of any of these.

The desired products are removed from zone 5 by line 6 and preferably but not necessarily the unreacted paraffin and ethylene are recovered and removed by line 2 for recycle to the feed stream as indicated.

Preferably, the product separation zone 5 comprises a molecular sieve having pore openings of about 5 A. It has been known for some time that certain zeolites, both naturally occurring and synthetic and sometimes termed molecular sieves have the property of separating straight-chain from branched-chain hydrocarbon isomers, as well as from cyclic and aromatic compounds. These zeolites have innumerable pores of uniform size and only molecules small enough to enter the pores can be adsorbed. The pores may vary in diameter from 3 or 4 A. to 15 A. or more, but it is a property of these zeolites or molecular sieves that any particular product has pores of substantially uniform size. The scientific and patent literature contains numerous references to the adsorbing action of the natural and synthetic zeolites. Among the natural zeolites having the sieving property may be mentioned chabazite. A synthetic zeolite with molecular sieve properties is described in U.S. Patent 2,442,191. Zeolites may vary somewhat in composition but generally contain the elements silicon, aluminum, and oxygen, as well as an alkali metal or an alkali earth metal. The naturally occurring zeolite, analcite, for instance, has the empirical formula $NaAlSi_2O_6.H_2O$. A large number of other naturally occurring zeolites having molecular sieve activity, that is the ability to adsorb a straight-chain hydrocarbon and exclude or reject the branched-chain isomers and aromatics because of differences in molecular size, are described in an article entitled, "Molecular Sieve Action of Solids," appearing in Quarterly Reviews, volume III, pages 293–320, 1949, published by The Chemical Society (London). Molecular sieves suitable for the present invention comprise sieves having pore openings in the range of from about 4 to 7 A. The molecular sieve heretofore described is arranged in any desired manner in the adsorption zone of separation zone 5. It can, for example, be arranged on trays or packed therein with or without support. A fluid bed of powdered adsorbent can also be used. Conditions maintained in the molecular sieve treatment in adsorption zone 5 are flow rates of about 0.1 to about 5 v./v./hour, temperatures of about 200° to about 350° F. and pressures from atmospheric pressure to several p.s.i.g. With molecular sieves of the indicated size of pores, the normal paraffins contained in the feed are readily adsorbed while the iso-

paraffins are not, but instead are passed by line 6 to suitable product containers.

The particular advantage of utilizing a molecular sieve separation zone can be seen by considering, for example, the present conversion process with, for example, normal butane and ethylene. The two major products are isopentane and isobutane. Because the conversion product, namely, isopentane is normally used for upgrading refinery gases and light virgin naphtha to high octane gasoline components, the presence of significant amounts of isobutane is extremely beneficial. Since ethylene may not be used up in the present process, this reaction results mainly in the conversion of low value normal paraffins in high yields to a product consisting essentially of branched-chain paraffins. Unconverted normal paraffinic constituents can be recovered readily by the utilization of molecular sieves and returned by a recycle process to the reactor.

In some instances it is desirable to employ radiation resistant diluents in the alkylation process in order to control the amount of conversion. These are introduced by line 8 into the feed prior to its entering the radiation zone. Gradually any common diluent which is substantially inert to high energy ionizing radiation is suitable for this purpose. For example, highly refined mineral oils such as a white oil advantageously can be employed.

In some instances it may be desirable to employ a combination process whereby the ethylene is produced either by a conventional process such as steam cracking or by high temperature radiation cracking followed by the vapor phase radiolysis reaction between ethylene and paraffin. In this manner, for example, a paraffinic hydrocarbon such as isobutane can be converted to the higher isoparaffinic homologue (one additional carbon atom) by the radiolysis of essentially that paraffinic hydrocarbon alone. However, in this instance a two-step process is necessary. The preliminary step can either be a mild cracking step to produce only the 0.1 weight percent of ethylene essential for the reaction or greater treatment to produce high yields of ethylene which can then be mixed with another paraffinic hydrocarbon stream to the desired ethylene concentration. In the latter embodiment of the present invention it is proposed to combine the two radiation zones. It should be noted that while reaction conditions can be chosen at which ethylene is produced, the addition of ethylene is always required to start the radioethylation reaction if a one step reaction is employed.

To further illustrate the invention the following examples are presented:

PILE IRRADIATION

Example 1

The major result from pile irradiation of isobutane-ethylene in vapor phase is the production of isopentane with high selectivity and high radiation yields. The neutron irradiations were carried out in the atomic pile at Brookhaven National Laboratory utilizing a radiation dosage of approximately 10^7 rep./hour. The reactor has been fully described in Brookhaven National Laboratory, Research Reactor Facility, Irradiation Services and Radioisotopes, published by Associated Universities, Inc., December 1955.

I (A) A typical run in a nuclear reactor:

(1) Operating conditions—	
Once-through flow equipment.	
Temperature, ° F	650
Pressure, p.s.i.g.	550
Contact time, minutes	2
Radiation energy absorbed, ev./gm	13×10^{18}
Material balance, weight percent	90.6
Reactor volume, cc	670
(2) Feed composition, weight percent on feed—	
Ethylene	2.5
Isobutane	97.5

I (A) A typical run in a nuclear reactor—Continued

Product yields, weight percent on feed—	
Ethylene	2.5
Isobutane	95.5
Ethylene free dry gas [1]	0.3
Butenes	0.2
Alkylate	1.6
	100.0
(3) Reaction selectivity, weight percent on feed reacted—	
Dry gas	14
Butenes	10
Isopentane	58
Alkylate, isopentane-free	18
	100
(4) Feed consumption, weight percent—	
Ethylene	0
Isobutane	2.0
(5) Radiation yields, molecules made/100 ev.—	
Dry gas	1,000
Butenes	25
Isopentane	90
Alkylate, isopentane-free	100

[1] Includes H_2, CH_4, C_2H_6, C_3H_8 and C_3H_6.

The composition of the alkylate product (containing 5 or more carbon atoms) is given in Table I:

TABLE I.—COMPOSITION OF PRODUCT (WEIGHT PERCENT)

Paraffins:	
Isopentane	76.0
n-Hexane	1.1
Branched C_6	1.3
Olefins:	
Hexenes	11.2
Heptenes	0
Octenes	0.2
Aromatics:	
Toluene	0.1
Xylene	0.1
Polymer:	
360° F.+	9.4

This example clearly shows that radiolysis of isobutane-ethylene mixtures in the vapor phase results in the production of isopentane with high selectivity and high radiation yields. The process illustrates disproportionation "alkylation" in a novel radiolysis process. The data clearly indicate that higher molecular weight branched-chain homologues can be produced from a paraffin alone by the addition of small amounts of ethylene and the radiolysis of the mixture at low pressures.

The surprising feature of the present invention is well illustrated by the above example, namely that the radioethylation of isobutane with ethylene under the influence of high energy ionizing radiation results in the production of isopentane. The reaction is thus a disproportionation process and is markedly different from the conventional thermal alkylation. This is further illustrated by Example 2.

Example 2

A mixture of isobutane and ethylene (6.5 mol percent ethylene) was fed into the flow unit at Brookhaven National Laboratories at an average temperature of 550° F. and pressure of 550 p.s.i. with an average contact time of 3.8 minutes resulting in a yield per pass, weight percent on feed, of 1.72. The resulting products were gas, C_5—430° F. gasoline and heavy polymer. The radiation yield of these three fractions are as follows:

Component:	Radiation yield (molecular reacting per ion pair)
Gas	50
C_5—430° F. gasoline	270
Polymer	35

The major product of this reaction is isopentane. The complete yields after comparison of these products with conventional thermal alkylation is presented in the accompanying table. It is seen that the conversion reaction is

not direct alkylation but instead surprisingly results in a disproportionation reaction.

TABLE II.—COMPARISON OF PILE "ALKYLATION" WITH THERMAL ALKYLATION

[Feed: Isobutane-ethylene mixture]

	Pile reaction	Thermal alkylation
Mole percent ethylene	6.5	7.9
Temperature, ° F	550	940
Pressure, p.s.i.g	550	4500
Contact time, minutes	3.8	4.0
Yield, weight percent on feed	1.72	22.0
Component, weight percent on product:		
H_2	0.46	0.01
Paraffins:		
CH_4	1.54	4.4
C_2H_6	1.25	3.8
C_3H_7	0	9.8
n-C_4H_{10}	0.68	0.3
n-C_5H_{12}	0	3.8
i-C_5H_{12}	46.15	2.5
n-C_6H_{14}	1.71	0.8
2,2-dimethylbutane	0.06	33.8
2,3-dimethylbutane	0.06	0
2-methylpentane	0.02	8.8
3-methylpentane	0.03	
2,3-dimethylpentane	0.06	
3-ethylpentane	0.03	9.4
2,4-dimethylhexane	1.14	
Methyl cyclohexane	0.06	
C_8 naphthene	0.40	
Olefins:		
C_3H_6	0.91	2.6
C_4H_8	7.51	3.1
C_5H_{10}	6.26	3.8
C_6H_{12}	17.07	2.3
C_7H_{14}	0	1.5
C_8H_{16}	0.23	3.0
Aromatics:		
Toluene	0.17	0
Xylene	0.17	0
C_9H_{12}	0.04	0
Bottoms:		
Aromatics	2.28	0
Olefins	5.97	1.8
Saturates	5.75	3.2

The above examples show that high energy ionizing radiation can be used to react paraffins with ethylene in the vapor phase at milder conditions than those used in thermal alkylation. While the free radical (thermal) reaction requires 800–950° F. and 4500–6000 p.s.i.g., the radiolysis reaction can take place at 500–800° F. and at 150–60 p.s.i.g. Further, it is seen that the distribution of products from the neutron reaction differs greatly from that obtained thermally.

Example 3

Hydrocarbon mixtures consisting of straight-chain paraffins having about from 2 to 8 carbon atoms, and mixtures thereof have been irradiated in the presence of small amounts of ethylene with high energy ionizing radiation comprising neutrons to produce higher molecular weight branched-chain homologues with radiation yields in the range of about 200 to 1000 molecules per 100 ev. energy absorbed. Pile irradiation at an intensity of approximately 1.06×10^{-2} kwh. per pound of hydrocarbon reactant per hour was employed in all experiments reported in this example.

Irradiation temperatures for the various experiments were in the range of about 500° to 800° F. at pressures of about from 150 to 600 p.s.i.g. Feed compositions contained about from 0.5 to 10 mole percent of ethylene based upon total feed. For continuous runs, flow rates were of the order of 1400 cc. (liquid) per hour and contact times of the order of from 1 to 4 minutes. Typical conversion reaction data according to this invention for n-butane-ethylene mixtures at 550 p.s.i. are given in Table III. Conversions of only 2–5 wt. percent were employed in order to better evaluate the product.

TABLE III

Temp., ° F.	Feed comp., mole percent ethylene	Weight percent on feed		Molemules of alkylate product per 100 ev.
		Alkylate [1]	Gas [2]	
704	7.4	1.55	1.67	1,019
644	4.8	2.00	1.84	1,013
546	8.1	0.52	0.59	250
502	4.7	1.17	0.13	474

[1] Product having 5 or more carbon atoms.
[2] Ethylene free dry gas.

TABLE IV.—PRODUCTS MADE FROM PILE IRRADIATION OF n-BUTANE-ETHYLENE AT 550 P.S.I.

	Temperature, ° F.			
	502	546	655	704
Weight percent on total product:				
Hydrogen	1.6	1.5	0.6	0.2
Methane	2.2	5.0	12.8	4.9
Ethane	1.6	8.5	4.7	24
Propane	0.5	11.5	8.1	3.2
Propylene	1.1	3.0	0	3.2
Isobutane	20	41	40	16.6
Butenes	9.7	4.0	4.6	14.7
n-Pentane	0	1.0	0	0
Isopentane	46	15.5	26	25
Pentenes	2.2	1.0	1.4	4.7
n-Hexane	4.8	4.5	0	3.1
Hexenes	4.8	0	0	0
Liquid product [1]	4.8	4.0	2.0	0
Total conversion, weight percent on feed	1.85	2.00	7.03	4.69
Contact time, min	3.1	2.6	2.7	2.0

[1] C_6+ excluding NC_5 and NC_6=.

The above example clearly demonstrates the novel and surprising process which has been discovered. These data show that a hydrocarbon mixture consisting of at least one straight-chain paraffin having about from 2 to 8 carbon atoms can be irradiated in the vapor phase with high energy ionizing radiation at temperatures in the range of about from 500° to 800° F. in the presence of in the range of 0.5 to 10 mole percent of ethylene to produce a conversion product with radiation yields of about from 200 to 1000 molecules per 100 ev. absorbed. It is seen that in the radiolysis of, for example, n-butane-ethylene mixtures, isobutane plus isopentane make up 40–70 wt. percent of the total product. Product selectivity to isopentane was about from 15 to 46 wt. percent. Comparison of isobutane and isopentane yields is given in Table V.

TABLE V

Temp., ° F.	Molecules made per 100 ev.	
	Isobutane	Isopentane
500	197	375
550	549	168
650	1,730	929
700	784	645

A further surprising feature of the present invention was the discovery that net ethylene consumption is often very low in the present process. Ethylene consumption as a function of temperature for pile irradiation of n-butane-ethylene at 550 p.s.i.g. is demonstrated by the data appearing in Table VI.

TABLE VI

Temp., ° F.	Contact time, min.	Gms. ethylene disappearing per 100 gms. fed	Gms. total product made per 100 gms. ethylene fed
700	2.4	+0.6	166
704	2.0	+2.3	126
655	2.7	−17.0	296
546	2.6	−3.1	49
502	3.1	−1.1	79

The above data show that at critical temperatures ethylene produced in situ from the butane is sufficient to carry the reaction once it has been initiated by the addition of ethylene to the reaction mixture.

The above example shows that light gasoline of high octane can be produced under the influence of high energy ionizing radiation from mixtures of butane and ethylene. Radiation yields of the order of 200–1000 molecules of product per 100 ev. can be obtained. The principal products of the reaction are isopentane, C_6 olefins, and other branched light hydrocarbons. The process is particularly useful for upgrading refinery gases and light virgin naphtha to high octane gasoline components.

The radioethylation reaction with propane has been carried out under a variety of conditions. Table VII displays the results of neutron irradiation of propane in the presence of 10 mole percent ethylene at 800° F. The mixture was pumped through the reactor in the manner described above. For a contact time of 1.5 minutes with a dose rate of 17 megarep. per hour the yield was 6.2 weight percent on feed. Total radiation yields observed were as high as 3224 molecules made per 100 ev.

TABLE VII

Product distribution	Weight percent (based on feed reacted)	
	150 p.s.i.g.	550 p.s.i.g.
Hydrogen	2.6	2.0
Methane		3.7
Ethylene	0	9.3
Propylene	8.4	
Butenes		11.6
Isobutane	79.5	30.4
n-Butane	2.3	
Isopentane	7.1	41.8
Pentenes		1.2

The above example shows that high energy ionizing radiation can be employed to convert propane in the presence of ethylene to form branched chain compounds with high selectivities. Very little cracking to hydrogen and methane was obtained. That conversions are optimized at temperatures in the range of 500° to 800° F. is apparent from the data presented in Table VIII for the propane-ethylene reaction at different temperatures.

TABLE VIII.—RADIATION YIELD—C_4 AND HIGHER PARAFFINS

[Molecules made per 100 ev.]

Pressure: 150 p.s.i.g.			Pressure: 550 p.s.i.g.			
502 ° F.	650 ° F.	806 ° F.	496 ° F.	601 ° F.	708 ° F.	818 ° F.
870	981	2,960	115	277	506	470

Typical pile irradiation conversion reaction data according to this invention for pentane-ethylene mixtures are given in Table IX. Radiation yields as high as 300 molecules per 100 ev. and selectivities up to 25 wt. percent on feed reacted have been obtained.

TABLE IX

Feed: Isopentane-ethylene (20/1 mol ratio)
Pressure, p.s.i.g.: 550
Contact time, 2–6 minutes

Temperature, ° F	513	524	649	655	791
Conversion, weight percent on feed:					
Ethylene-free cracked gas (H_2-C_4)	0.7	0.3	0.9	2.5	17
Ethylene	0.6	0.4	1.6	1.1	1
C_5's	2.1	1.0	0.2	2.3	3
C_7 alkylate	0.1	0.2	0.1	0.1	0.02
C_8 polymer	0.2	0 3	0 4	0.2	0
Total	3.7	2.2	4.2	6.2	21
Selectivity, weight percent on feed reacted:					
Ethylene-free cracked gas	19	14	45	40	81
Ethylene	16	18	38	18	5
C_5's	57	45	5	37	14
C_7 Alkylate	3	9	2	2	0
C_8 polymer	5	14	10	3	0
Radiation yield, molecules/100 ev.:					
Ethylene	77	413	1,951	1,232	1,263
C_7 alkylate [1]	22	60	21	27	86
C_8 + polymer	114	115	99	92	10

[1] Primarily 2,3 and 3,3 dimethyl pentane.

GAMMA IRRADIATION

Example 4

Gamma radioethylation reactions were carried out utilizing a Co^{60} radiation source. The facilities employed were of conventional type and have been fully described by J. F. Black et al., The International Journal of Applied Radiation and Isotopes 1, 256 (1957). To illustrate the present invention, the experimental data for the propane-ethylene system is given in Table X. The conversions were carried out at an intensity of 0.12 megarep/hr., at 55 atm. using 8/1 mole ratios of propane/ethylene. Material balances were better than 96 wt. percent and all radiation yields refer to experiments in which the blank (thermal) contribution was subtracted out if present. One hour batch exposure of the feed at 700° F. resulted in 23 wt. percent conversion of ethylene and a yield of branched chain paraffins (having 4 or more carbon atoms) of 300 wt. percent based on ethylene reacted. Radiation yields (G) in the range of 1000–10,000 have been recorded.

TABLE X

Product	Selectivity, weight percent on feed reacted	Molecules made per 100 ev. (G)
Hydrogen	0.06	0
Isobutane	52.3	4,950
Isopentane	6.7	481
Isohexane	2.9	160
Isoheptane	4.8	200
Isooctane	3.2	120

The above example shows that light hydrocarbons can be upgraded to high octane products with high radiation yields by irradiating a mixture consisting essentially of ethylene and a paraffin having from 2 to 8 carbon atoms with high energy ionizing radiation comprising gamma rays.

ELECTRON IRRADIATION

A High Voltage Engineering Corporation, model AK–S, 2 mev. Van de Graaff electron accelerator was utilized in a series of radioethylation reactions with different paraffin hydrocarbons. This is a conventional electron accelerator.

Example 5

The electrons were passed into the reaction cell through a 15 mil steel window with intensities in the range of 1 to 40 megarep./hr. Typical data for the radioethylation reaction of the present invention utilizing electrons is presented in Table XI.

TABLE XI.—ELECTRON RADIOETHYLATION $C_3/C_2^=$ STUDIES AT 150 AND 550 P.S.I.G.

Run No.	3	2	5	4
Mole percent	12	12	12.8	11.4
Temp., ° F.	650	650	650	650
Pressure, p.s.i.g.	550	550	150	150
Contact time, min.	1.5	1.5	1.0	1.0
Mrep/hr.	19	37.5	14	30
Conversion, weight percent on feed	2.6	3.6	1.0	1.3
Selectivity, weight percent on feed reacted:				
C_1	0.9	0	1.1	2.3
C_2	0.9	2.0	4.2	6.2
$C_3^=$	0	0	6.9	5.8
iC_4	27.0	24.1	16.1	15.0
$C_4^=$	17.6	13.8	20.0	18.4
iC_5	27.6	31.0	39.1	42.6
$C_5^=$	13.7	10.3	11.1	9.5
$C_6^=$	4.6	1.7		
$C_4^=$	0	0.4	1.5	0.2
Polymer	7.7	16.7		
Mol. made/100 ev.:				
C_1	37	0	32	47
C_2	18	30	65	68
$C_3^=$	0	0	77	46
iC_4	300	188	129	85
$C_4^=$	202	111	166	108
iC_5	246	194	252	195
$C_5^=$	125	66	74	45
$C_6^=$	35	9		
$C_4^=$	0	4	13	1
Polymer	33	50		
Material balance, percent recovery	94.0	86.2	101.4	97.7
Weight percent $C_4+/C_2^=$ reacted	161	158	156	179

TABLE XIII.—YIELDS AND SELECTIVITIES IN PILE RADIOALKYLATION OF $nC_5/C_2^=$ AT 550 P.S.I.G., 400/800° F., 2-3 MIN. CONTACT TIME

Temp., ° F.	400	451	492	553	647	756	801
Contact time, min.	3.2	3.9	3.1	2.5	2.7	2.6	2.8
Mol. percent $C_2^=$	4.3	2.7	4.6	4.0	4.6	4.9	5.6
Material val., weight percent	99	99	78	91	79	92	80
Conversion, weight percent on feed/min.	2.3	0.7	0.5	0.2	1.5	0.9	1.0
Radiation yields, molec./100 ev.:							
$C_4^=$ cracked prod.	440	610	392	189	824	506	12,000
$C_2^=$	319	445	270	(1)	(1)	(1)	(1)
C_3's	373	0	6	0	95	43	70
C_6+	700	130	38	53	83	126	[1] 270
Selectivity, weight percent on feed reacted:							
H_2	0.05	0.19		2.49	1.76	0.04	
C_1	0.06	0.47	4.76	0.73	3.79	2.71	5.91
$C_2^=$	9.04	43.30	46.58	13.06			
C_2	2.82	11.44		5.81	0.03	10.14	25.89
$C_3^=$		0.41	8.63	10.62		14.18	30.89
C_3		0.38	0.60	3.22	1.84	6.74	10.03
nC_4		3.07	6.21		67.51	22.98	6.70
iC_4			7.14				
$C_4^=$			0.30		1.84	0.77	10.59
iC_5	26.84					8.56	
$C_5^=$	0.32		2.68		10.54		0.9
$C_6^=$	0.05	0.09				3.75	3.46
nC_5	4.07	5.14			0.27		
2 MP, 23 DMB	35.44	0.66	0.10		1.75	0.07	0.6
3 MP	2.93	20.29	5.61		1.75	3.77	0.05
22 DMB	15.64						0.28
23 DMP, 33 DMP	0.02		0.29		5.32		
nC_7		4.44	5.61	14.04		11.26	
2 MH, 3 MH	1.32	5.01	11.31	33.35	1.79	7.51	0.37
3 EP	1.31	5.01	0.19	16.69	1.79	7.50	0.86
Other iso-heptanes	.03	0.13					

[1] Average of 2 experiments.

Example 6

Comparison of the radioethylation reaction with ordinary radiolysis of pure hydrocarbons.—The novel features of the present radioethylation process can be illustrated by comparing the irradiation reactions of paraffin-ethylene mixtures in accordance with this invention with prior irradiation processes involving pure hydrocarbons. Table XII illustrates these differences by giving, as an example, the results for the radiolysis of the butanes and also the ethylene-butane systems. Similar results for n-pentane and n-pentane-ethylene are recorded in Table XIII.

TABLE XII.—COMPARISON OF PILE IRRADIATION OF BUTANES AND BUTANE-ETHYLENE MIXTURES AT 650° F., 550 P.S.I.G.

Feed	Isobutane	Isobutane/ethylene 2.5 weight percent	n-Butane	n-Butane/ethylene 4.8 mole percent
Contact time, min.	2.6	2.0	4.5	2.7
Conversion, weight percent/min.	0.3	2.3	0.84	2.6
Material bal., weight percent	94	91	92	96
Molecules made/100 ev:				
Ethylene Free Dry Gas	470	1,000	720	3,500
C_5+	20	1,000	90	1,013
Ethylene	0	0	75	0
Selectivity, weight percent on feed reacted:				
Ethylene free dry gas	29.1	11.5	29.0	26.2
Ethylene	0	2.5	6.0	0
n-Butane	53.0	0	0	0
Isobutane	0	0	39	40
Butenes	5.6	10	7.3	4.6
Isopentane	13.0	58	16.4	26
Alkylate isopentane free)	0	18	2.3	3.4

PRODUCTS FROM PILE IRRADIATION (2.7 MIN.) n-PENTANE AT 550 P.S.I.G. AND 650° F.[1]

Product:	Selectivity, weight percent on feed reacted
H_2	0.77
C_1	7.38
$C_2^=$	2.64
C_2	26.41
$C_3^=$	15.10
C_3	46.17
$C_4^=$	1.53

[1] Material balance 94.1 weight percent.

The above example shows that the irradiation with high energy ionizing radiation of a hydrocarbon mixture consisting essentially of a paraffin and ethylene results in the production of a higher molecular weight branched-chain homologue of the paraffin with a radiation yield in the range of about 200 to 1000 molecules per 100 ev. absorbed by the mixture. Little if any "alkylate" is produced by the radiation of pure paraffins under the same conditions. Comparison of the data in Table XIII shows that ethylene must be initially present to get any alkylation at all.

Example 7

Refinery feed stocks such as light virgin naphtha can be upgraded by exposure to high energy ionizing radiation in the presence of ethylene in accordance with this invention. In this example on Arabian light virgin naphtha (122/213° F.) was irradiated in a nuclear pile in the manner already described. The feed composition is given in Table XIV and shows the major components to be nC_5–nC_7 paraffins. The data obtained are given in Table XV.

TABLE XIV.—COMPOSITION OF ARABIAN 122/213° F. LVN USED IN PILE RADIOALKYLATION EXPERIMENTS

Gross (FIA):		
Saturates	volume percent	96.4
Olefins	do	0.7
Aromatics	do	2.9
Composition, weight percent (GLPC):		
nC_4		0.3
iC_5		2.7
nC_5		7.8
22 DMB		0.2
2 MP, 23 DMB		12.2
3 MP		8.6
nC_6		35.4
24 DMP, 22 DMP		7.5
C_6H_6		1.8
23 DMP, 33 DMP		7.5
2 MH, 3 MH		5.2
3 EP		2.5
nC_7		6.8
M CyH		0.9
C_7H_8		0.6
RON+3 cc.		76.0
Mercaptan No., mg./100 cc.		

TABLE XV.—PILE-INDUCED UPGRADING OF ARABIAN LVN BY 27 MIN. EXPOSURE AT 500 P.S.I., 6 MOL PERCENT C_2^-

Temperature, ° F.	502	650	800
Conversion, weight persent on feed	19.4	17.0	29.4
Selectivity, weight percent on feed reacted to—			
Dry gas	9.73	[1] 3.85	29.27
C_4	9.12	10.83	20.47
iC_5	5.10	15.26	12.15
iC_6		14.80	
iC_7	12.26	3.96	2.63
C_5/C_6 olefins	5.16	40.91	32.80
Other C_5+ (mostly unidentified C_8 paraffins)	58.63	40.91	32.80
G, molecules made per 100 ev.:			
Dry gas	165	80	850
C_5+ product	240	250	320
Feed cut (122/213° F.) inspections:			
RON+3 cc. TEL (unirradiated feed=76)		78.1	80.9
Mercaptan number (unirradiated feed=17.9)			3.2

[1] This number not considered reliable.

The above example shows that a hydrocarbon feed stock containing at least 75 percent by weight of a paraffin-ethylene mixture can be upgraded in quality. Alkylation yields in the range of 240–320 were observed. At 800° F. a most significant change was obtained in RON (3 cc.) TEL which was increased from 76 to 81 with only 29 wt. percent conversion of the feed.

What is claimed is:

1. A hydrocarbon conversion process which comprises subjecting a hydrocarbon mixture consisting essentially of a paraffin having from 2 to about 8 carbon atoms per molecule and in the range of 0.1 to 30 weight percent of ethylene to a total dosage of high energy ionizing radiation in the range of about 10^{-6} to 10^3 kwh. of radiation energy per pound of said hydrocarbon mixture at a temperature in the range of about 500° to 800° F. and a pressure in the range of about 150 to 600 p.s.i.g., and recovering a higher molecular weight branched-chain homolog of said paraffin with a radiation yield in the range of about 200 to 10,000 molecules per 100 ev. absorbed by said mixture.

2. A process according to claim 1 wherein said higher molecular weight homologue is recovered with a product selectivity of about from 30 to 70 weight percent.

3. A process for producing isopentane which comprises exposing a mixture of butane and ethylene at a temperature in the range of about 500° to 800° F. and a pressure in the range of about 150 to 600 p.s.i.g. to high energy ionizing radiation of an intensity and for a duration sufficient to produce isopentane with a yield in the range of about 200 to 1000 molecules per 100 ev. absorbed by said mixture said mixture containing in the range of from 0.1 to 30 weight percent of ethylene.

4. A hydrocarbon conversion process which comprises irradiating with high energy ionizing radiation a refinery hydrocarbon feed at a temperature in the range of about 500° to 800° F. and a pressure in the range of 150 to 600 p.s.i.g. until a total dosage of radiation energy in the range of from 10^{-6} to 10^3 kwh. per pound of said feed has been absorbed, said feed essentially consisting of about 0.1 to 30 weight percent of ethylene and paraffin having from 2 to about 8 carbon atoms per molecule, and recovering a higher molecular weight branched-chain homologue of said paraffin.

5. A hydrocarbon conversion process which comprises irradiating with high energy ionizing radiation a hydrocarbon mixture, in the vapor phase, at a temperature in the range of about 500° to 800° F. and a pressure in the range of 150 to 600 p.s.i.g. until in the range of 10^{-6} to 10^3 kwh. of radiation energy has been absorbed per pound of said mixture, said mixture consisting of about 0.1 to 30 weight percent of ethylene and a paraffinic component selected from the group consisting of paraffins having from 2 to about 12 carbon atoms per molecule and mixtures thereof, and recovering a converted product with a yield in the range of about 200 to 10,000 molecules per 100 ev. absorbed by said mixture.

6. A hydrocarbon conversion process which comprises continuously passing into a radiation reaction zone a hydrocarbon feed stock containing at least 75 percent by weight of a paraffin-ethylene mixture, said mixture consisting of about 0.1 to 30 weight percent of ethylene and at least one paraffin having from 2 to 8 carbon atoms per molecule, irradiating said feed stock with high energy ionizing radiation at a temperature in the range of about 500° to 800° F. and a pressure in the range of 150 to 600 p.s.i.g. until at least 10^{-6} kwh. of radiation energy per pound of feed stock has been absorbed, continuously removing a reaction product from said radiation zone, separating unconverted feed stock from the desired conversion product, recycling said unconverted feed to said reaction zone and continuously feeding a fresh supply of hydrocarbon feed stock to said reaction zone.

7. A process according to claim 6 wherein said unconverted feed stock is separated in a molecular sieve adsorption zone.

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