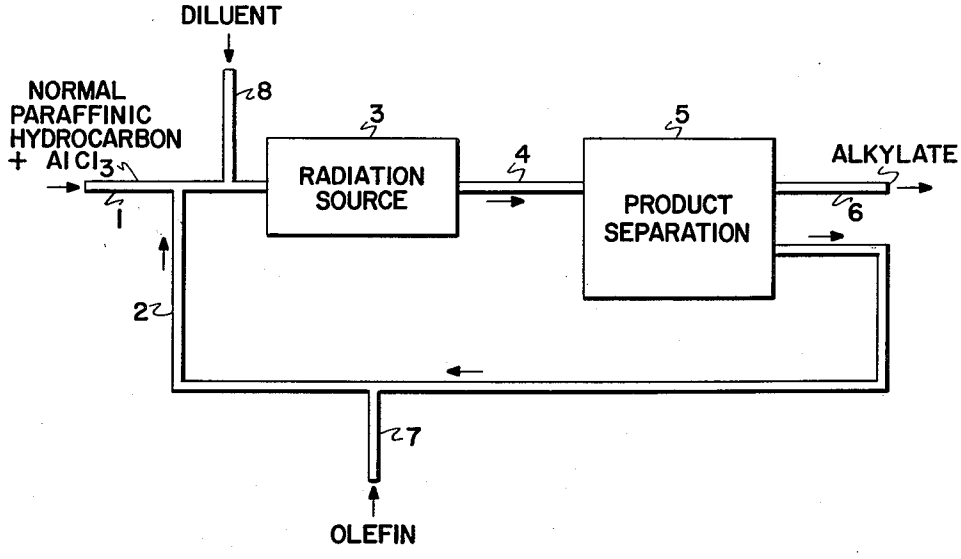
April 4, 1961 C. E. HEATH, JR., ET AL 2,978,397

RADIOALKYLATION OF NORMAL PARAFFINS

Filed April 29, 1957



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United States Patent Office 2,978,397 Patented Apr. 4, 1961

2,978,397

RADIOALKYLATION OF NORMAL PARAFFINS

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Filed Apr. 29, 1957, Ser. No. 655,911

12 Claims. (Cl. 204—162)

This invention relates to the alkylation of hydrocarbons and more particularly to the production of saturated branched-chain hydrocarbons by the reaction of straight-chain paraffinic hydrocarbons with olefins, in particular, mono-olefins having at least three carbon atoms per molecule in the presence of a Friedel-Crafts type catalyst, in particular, aluminum chloride, by exposing the reactants to high energy ionizing radiation. The products are normally liquid, saturated branched-chain hydrocarbons boiling chiefly within the motor fuel boiling range, i.e. 85° to 440° F. and are extremely useful for upgrading refinery gases and light virgin naphtha to high octane gasoline components.

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 straight-chain 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 useable in motor fuels. Often for such purposes particular alkylation products are necessary. It is known that isoparaffinic hydrocarbons are alkylated with olefins at low temperatures in the presence of various alkylation catalysts, promoters and activators. Reaction conditions have varied considerably depending upon the specific catalyst employed. Heretofore, however, it generally has not been possible to successfully alkylate straight-chain paraffinic hydrocarbons by these conventional processes. The present invention provides a novel alkylation process which obviates this and other disadvantages of prior art processes.

Normal paraffins having from 4 to 12 carbon atoms per molecule can be alkylated in a single step with olefins having from 3 to 12 carbon atoms per molecule by reacting the components in contact with a catalyzing amount of aluminum chloride at a temperature in the range of about 40° to 300° F. at about from 1 to 30 atmospheres' pressure.

This invention proposes a novel process for upgrading refinery gases and light virgin naphtha to high octane gasoline components by reacting mono-olefins with straight-chain paraffinic hydrocarbons by subjecting a mixture of these hydrocarbons in contact with aluminum chloride to high energy ionizing radiation. Specifically, the present process comprises irradiating a paraffinic hydrocarbon having from 4 to 12 carbon atoms with high energy ionizing radiation in the presence of a catalyzing amount of aluminum chloride and a small amount of a mono-olefin having at least 3 carbon atoms, for example, a normal paraffin-mono-olefin mixture wherein the paraffin/olefin molar ratio is in the range of from 3:1 to 100:1 in contact with about from 10 to 250 wt. percent, based on the weight of paraffin, of aluminum chloride

until at least about 1×10^{-6} kwh. of radiation energy per pound of hydrocarbon feed has been absorbed. The surprising discovery is that straight-chain paraffinic hydrocarbons can be alkylated according to this invention with radiation yields of the order of 250 molecules produced/100 e.v., and selectivities of at least 40% based on hydrocarbon feed reacted. An overall radiolysis conversion to alkylate is obtained which is equal to at least 100 wt. percent based upon the weight of olefin in the feed.

While catalytic 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 seldom been achieved with any degree of success by the conventional process. The present invention is of particular importance because it provides a method of alkylating normal paraffinic hydrocarbons which have never been in as great demand as the more useful isoparaffinic hydrocarbons. Other advantages of the present process over prior conventional alkylation reactions are readily apparent. Generally, alkylation has been carried out in the presence of concentrated sulfuric acid and complicated alkylate separation and recovery processes have been required. The radioalkylation process of the present invention avoids contamination of the alkylate product and acid corrosion of alkylation equipment. With conventional alkylation processes at temperatures where equilibrium is favored and pressures required are moderate, reaction initiation is slow. On the other hand, at temperatures where initiation of reaction is rapid, equilibrium is unfavorable, and pressures on the order of 1,000 atmospheres are required. According to the present invention, high energy ionizing radiation is employed to carry out the reaction at temperatures low enough that excessive pressures are not needed. In a preferred process, alkylation is carried out according to the present invention at a temperature in the range of about 40° to 250° F. at about 1 to 30 atmospheres pressure with a total radiation dose of between about 10^{-6} and 10^{3} kwh. per pound of hydrocarbon feed.

Broadly, any normal paraffin can be alkylated with mono-olefins according to the present invention. Particularly, the process is applicable for the conversion of straight-chain paraffinic hydrocarbons having from 4 to 12 carbon atoms. Most interesting are the normal paraffins having from 4 to 8 carbon atoms, mixtures of these, and feed stocks comprising essentially one of the above paraffins and mixtures thereof.

Olefinic reactants for the present process comprise mono-olefins having at least 3 carbon atoms. Particularly, normal paraffins can be alkylated according to the present invention with mono-olefins having from 3 to 12 carbon atoms. Most advantageously, the mono-olefin constituent is selected from the group consisting of propene, butenes, pentenes, hexenes, heptenes, and mixtures thereof. Cyclic olefins also can be employed. From an economic standpoint it is often desirable to employ normal paraffins and olefins which are normally gaseous. Normally liquid olefins as well as paraffins are, however, preferred for the novel process of this invention. Mixtures of two or more of the above-mentioned olefins can also be used.

Suitable paraffinic streams are field butanes, n-butanes from catalytic cracking and light virgin naphthas. Such streams are composed of 80 to 100% C_4–C_6 paraffins, boiling in the range of 40° to 200° F. Suitable olefinic streams comprising propylene and butylene are found in olefin concentrates from catalytic cracking, coking, or thermal cracking. Such feeds contain 50 to 100% C_3–C_4 olefins. Particularly advantageous for the present process in a refinery feed boiling in the range of about from 10° to 200° F. containing at least 75 wt. percent of a

normal paraffin/mono-olefin mixture wherein the normal paraffin/mono-olefin molar ratio is about from 3:1 to 100:1.

It is desirable, although not necessary, to employ a substantial molar excess of the normal paraffinic component or components of the feed stock, as it has been found that increased yields of the desired saturated products are obtained thereby. This molar excess of normal paraffin with respect to the mono-olefins of the reaction can range from about 3:1 to as high as 100:1 or even higher. Advantageously, molar ratios of normal paraffin to mono-olefin of from 10:1 to 50:1 are employed.

The process of the present invention equally as well applies to the treatment of mixtures of hydrocarbons predominantly composed of straight-chain paraffinic constituents, for example, straight run naphthas of lower octane number preferably those having narrow boiling ranges, for example 90° to 200° F., can be alkylated according to the process of the present invention to improve their octane number markedly and to bring about other desirable changes in their characteristics. Likewise normally gaseous paraffinic mixtures such as fuel butanes, paraffinic mixtures resulting from the removal of olefin constituents of refinery C_4 cuts, waste gases of paraffinic nature evolved from thermal or catalytic alkylation processes and similar sources of mixed paraffinic hydrocarbon material can be utilized as suitable feed stocks in the present process.

The amount of aluminum chloride to be used in the present process varies widely depending upon the particular hydrocarbon which is to be converted, the amounts ranging from about 10% to about 250% by weight based on paraffin present in the reactor. The catalyst can be produced in situ by the reaction of a metal such as aluminum with chlorine or a compound chemically reacting as the equivalent of free chlorine under the conditions of the reaction, or can be added to the feed stock as chemically pure anhydrous aluminum chloride, or as a commercial product. Advantageously, a catalyst bed can be made up of Porocel or some other suitable highly porous alumina. The catalyst mass can be formed by mixing granules of aluminum chloride with the desired quantities of dehydrated Porocel and the mass heated while passing through a stream of inert vapor.

The radiolysis of the feed mixture is carried out by exposing it either continuously or batchwise to the radiation. Any temperature below the critical temperature of the feed stock can be employed, although it is preferable to use a reaction temperature in the range of from about 40° to 250° F. Most advantageously, temperatures of from about 60° to 120° F. are employed at a pressure of from about 10 to 18 atmospheres. Sufficient superatmospheric pressure can be employed to maintain the reactant as well as the reaction products in the liquid phase under the reaction conditions obtained. In particular, liquid phase operations are conducive to the production of ultimate high yields and to carrying out the process in a continuous manner. It is to be understood, however, that the process is not only applicable to continuous operations, but it is contemplated to carry out the same in batch-type apparatus for single batch operation. The catalyst can be employed as a slurry or mechanical suspension of catalyst in the hydrocarbon medium and a mechanical agitator propelled by an external means inserted into the reactor can be used. On the other hand, where a bed-type catalyst is employed, it is well to force the liquid hydrocarbon feed into the reactor under pressure.

The alkylation process of the present invention is carried out by exposing the reactants 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 electromagnetic radiation such as gamma rays and X-rays and high velocity electrons, as well as beta rays, alpha particles, and neutrons. These types of radiation can be supplied by naturally occurring radioactive materials or by common neutron sources. Fission by-products of processes generating atomic power or fissionable materials which emit high energy gamma rays afford a highly desirable and most abundant source of radioactivity suitable for the purposes of invention.

Irradiation can also be obtained from nuclear reactors such as atomic piles. In this form of the invention wherein neutrons are used, it is preferred that the neutron flux in the radiation zone be about 10^8 neutrons/cm.^{2}/second besides maintaining an appreciable gamma-ray dosage. Conventional moderators can, of course, be used, such as water, carbon, and hydrocarbons. 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. Suitable sources of high velocity electrons are the beams of electron accelerators such as the Van de Graaff electrostatic accelerator. 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 these rays and the availability and ease of application of these sources of energy. By high energy ionizing radiation is meant, the radiation from terrestrial sources of sufficient energy that the dose rate is at least 1×10^{-4} kwh. per pound of hydrocarbon reactant per hour. This excludes radiation such as cosmic and ultraviolet which are ineffectual for the purposes of this invention.

The alkylation of normal paraffinic hydrocarbons, for example, normal butane with propylene to produce a high yield of alkylate product can according to the present invention be carried out utilizing a radiation dose in the range of, for example, about from 10^{-6} to 10^3 kwh. per pound of reactant. Advantageously, a total energy absorption of from about 10^{-4} to about 10 kwh. per pound of reactant is employed.

According to the present process, for example, normal butane in admixture with propylene (butane/propylene ratio of from 3:1 to 100:1) and aluminum chloride present in an amount in the range of 10 to 250 wt. percent, based on the weight of paraffin, at a temperature of from 60° to 120° F., is exposed to high energy ionizing radiation at a rate of at least about 1×10^{-4} kwh. per hour per pound of feed until at least 1×10^{-6} kwh. of radiation energy per pound of feed has been absorbed. Under these conditions, an overall radiolysis conversion to an alkylated product in the range of from 100 to 230 wt. percent based on olefin in the feed is obtained according to this invention. The product containing substantial amounts of higher molecular weight branched-chain paraffins can be separated from the reaction medium and fractionated within the desired boiling range. The unreacted normal paraffin can then be returned to the reactor to be further alkylated to more useful products. Advantageously, mixtures of normal paraffins and mono-olefins are fed into a radiation zone in a continuous feed system 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 reaction, contact time can be from about one-half hour to about 200 hours or more. In general it is desirable to convert only a portion of the normal paraffin-mono-olefin 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 zone in an ordinary recycle process. In this way the probability that the alkylate product will be cracked by continuing the radiation reaction after the product is formed is reduced. Advantageously, only about 1 to about 50% of the reactant

is converted in the radiolysis process per pass, and the unreacted reactant is returned for another processing following the separation of the desired alkylate product.

No special type of apparatus is required for carrying out the novel alkylation process of this invention. 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 aluminum chloride is mixed with the normal paraffinic hydrocarbon to be converted and admitted to the process by line **1**. The mono-olefin is supplied to line **2** by line **7**.

The mono-olefinic component added to the normal paraffinic feed mixture is controlled in order to obtain high yields of alkylate product. The amount to be added can be determined in any convenient manner, as by observing the composition, distribution, or yield of the product, or by monitoring the admixture entering the reaction zone. This can be done by continuous analysis, for example, by continuously measuring the product quality or continuously measuring by spectroscopic techniques the olefin concentration of the feed mixture. Preferably, the normal paraffin/mono-olefin molar ratio in the mixture is in the range of 1 to 10.

The resultant mixture is then exposed to high energy ionizing radiation in the radiation zone **3**, for example, this source can comprise an atomic pile, and the admixture can simply be passed through the pile in suitable conduits. It can flow around or through the core of the reactor, and in some cases the hydrocarbon material 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.

The radiation zone can advantageously comprise a cobalt-60 source. Electron accelerators of the linear type and Van de Graaff generators can also be employed as a source of high energy electrons. The electrons are directed through a thin, reinforced window into the hydrocarbon mixture.

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

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 absorbed. The pores may vary in diameter from 3 or 4 A. to about 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. 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. A large number of 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 3 to 10 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. Conditions maintained in the molecular sieve treatment in adsorption zone **5** are flow rates of about 0.1 to about 5 v./v./hr., 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 absorbed while the isoparaffinic product is not, but instead is passed by line **6** to suitable product containers. Unconverted normal paraffinic constituents can be recovered readily by the utilization of molecular sieves and returned by recycle process to the reactor by line **2** as indicated.

In some instances it may be desirable to employ 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 reaction zone. Generally, any common diluent which is substantially inert to high energy ionizing radiation is suitable for this purpose, for example, highly refined mineral oil, such as white oil, advantageously can be employed.

To further illustrate the invention, the following example is presented:

EXAMPLE I

A mixture of 42 gms. of n-butane and propylene (10/1 mole ratio) and 100 gms. of Isocel (14% $AlCl_3$ on Porocel) was pressurized to 30 atms. with N_2. This mixture was then irradiated with gamma rays from Co^{60} for one hour at 98° F. in a batch system. The total radiation dose was 1 megaroentgen or 1.06×10^{-3} kwh. per pound of hydrocarbon. A clear alkylate was produced which consisted of highly branched paraffins with high octane values. The yield based on total hydrocarbon feed was 8% or 165% based on the propylene consumed. Substantially all of the olefin was consumed.

In the absence of radiation a similar product was obtained but in substantially reduced yields. Thus a mixture of hydrocarbon and catalyst similar to that above was allowed to react at 98° F. for one hour. A clear liquid was produced having a similar composition to that described above. However, the yield was 5% on the feed or 117% based on olefin consumed.

It is seen that the first reaction has a significantly increased reaction rate. The radiation yield for the reaction described is 260 molecules of alkylate/100 e.v. of radiation absorbed.

The composition of the alkylate is given in Table I.

Table I

Product	Wt. Percent on Total Product
Isobutane	31.4
Isopentane	3.1
2 Methyl pentane; 2,3 dimethyl pentane [1]	4.2
3 Methyl pentane	2.6
2,4 Dimethyl pentane; 2,2 dimethyl pentane [1]	2.6
2,3 Dimethyl pentane; 3,3 dimethyl pentane [1]	7.6
2 Methyl hexane; 3 methyl hexane [1]	2.2
2,5 Dimethyl hexane	7.4
2,4,4 Trimethyl pentane	7.5
Other C_8 paraffins or naphthenes [2]	3.3
Other C_8 paraffins or naphthenes	.5
2,24 Trimethyl hexane	4.8
C_9 Paraffins or naphthenes (8) [2]	22.8

[1] Analysis by Gas-Liquid Partition Chromatography does not distinguish between these compounds.
[2] Not identified by GLPC.

The above example shows that a hydrocarbon mixtube containing a normal paraffin having from 4 to 12 carbon atoms and a mono-olefin having from 3 to 12 carbon atoms, in contact with aluminum chloride present in an amount of about from 10 to 250 wt. percent

based upon the weight of paraffin can be converted in high yields to branched-chain alkylated products by exposure at a temperature of about 40° to 250° F. to high energy ionizing radiation until at least 1×10^{-6} kwh. of radiation energy per pound of hydrocarbon mixture has been absorbed.

It is to be understood that the above-described arrangements and techniques are but illustrative of the application of the principles of this invention. Numerous other arrangements and procedures may be devised by those skilled in the art without departing from the spirit and scope of the invention.

What is claimed is:

1. A hydrocarbon conversion process for producing an alkylate product rich in isoparaffins which comprises exposing a mixture of normal paraffin having 4 to 12 carbon atoms per molecule and a mono-olefin having 3 to 12 carbon atoms per molecule to from 10^{-6} to 10^{3} kwh. of high energy ionizing radiation per pound of said mixture in contact with aluminum chloride until said product is obtained.

2. A hydrocarbon conversion process to form an alkylate product rich in branched-chain paraffins which comprises exposing to from 10^{-6} to 10^{3} kwh. of high energy ionizing radiation per pound of a normal paraffin/mono-olefin mixture having a paraffin/olefin molar ratio in the range of from 3:1 to 100:1, said mixture consisting of a normal paraffin having from 4 to 12 carbon atoms and a mono-olefin having from 3 to 12 carbon atoms, said mixture being exposed to said radiation while in contact with aluminum chloride present in an amount in the range of from 10 to 250 weight percent based upon the weight of said paraffin until said product is obtained.

3. A process according to claim 2 wherein said mixture is exposed to said radiation at a temperature in the range of 40° to 250° F. at a pressure in the range of 1 to 30 atmospheres.

4. A process according to claim 2 wherein said normal paraffin is selected from the group consisting of n-butane, n-pentane, n-hexane, n-heptane, n-octane and mixtures thereof.

5. A process according to claim 2 wherein said mono-olefin is selected from the group consisting of propene, butene, pentene, hexene, heptene and mixtures thereof.

6. A process according to claim 2 wherein said ionizing radiation comprises gamma rays.

7. A process according to claim 2 wherein a converted alkylate product is recovered with an overall radiation yield which is at least 100 weight percent based upon the weight of mono-olefin in said mixture.

8. A process according to claim 2 wherein said mixture comprises a refinery feed boiling in the range of 10° to 200° F. having a total paraffinic-olefinic content of at least 75 percent by weight.

9. A hydrocarbon conversion process which comprises exposing a normal butane/propylene mixture having a paraffin/olefin molar ratio of 10/1 in contact with a catalyzing amount of aluminum chloride to gamma radiation in the range of 10^{-6} to 10^{3} kwh. per pound of said mixture and recovering an alkylated product with a radiation yield of about 250 molecules per 100 electron volts absorbed.

10. A hydrocarbon conversion process to form an alkylation product which comprises continuously passing into a radiation reaction zone a hydrocarbon feed boiling in the range of 10° to 200° F. which contains at least 75 percent by weight of a normal paraffin/mono-olefin mixture having a paraffin/olefin molar ratio in the range of 3:1 to 100:1, irradiating said feed in contact with a catalyzing amount of aluminum chloride with high energy ionizing radiation until at least 10^{-6} kwh. of radiation energy per pound of said feed has been absorbed to alkylate normal C_4–C_6 paraffins by C_3–C_4 mono-olefins in said feed, continuously removing resulting alkylation product from said radiation zone, separating unconverted feed from the alkylation product, recycling said unconverted feed to said reaction zone and continuously feeding a fresh supply of hydrocarbon feed to said radiation zone.

11. A process according to claim 10 wherein said alkylation product is separated by absorption on a molecular sieve.

12. A hydrocarbon conversion process for producing an alkylate product containing mostly C_4–C_9 hydrocarbons rich in isoparaffins, which comprises exposing a n-butane-propylene mixture of 10/1 mole ratio in contact with aluminum chloride to a megaroentgen of high energy ionizing radiation at 98° F. until the propylene in said mixture is substantially converted to higher boiling products.

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