Patented Feb. 12, 1946 2,394,743

UNITED STATES PATENT OFFICE

2,394,743

BLENDING FUELS

Ingolfur Bergsteinsson, El Cerrito, Calif., assignor to Shell Development Company, San Francisco, Calif., a corporation of Delaware

No Drawing. Application August 4, 1941, Serial No. 405,409

5 Claims. (Cl. 260—676)

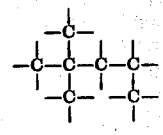
The present invention relates to the production of high octane number volatile blending fuels. A particular aspect of the invention relates to the production of neopentane.

As is well known, there is a great demand for motor fuels of high octane number. These fuels are usually prepared by blending certain selected stocks and then adding tetraethyl lead. Thus, for example, a highly aromatic base stock having an octane number of about 78 may be blended with iso-octane or alkylate having an octane number of, for example, 96 and then 3 cc. tetraethyl lead added per gallon. This method of producing these fuels is limited by several factors, one of the most important of which is the matter of volatility. It is necessary to maintain a certain balance of hydrocarbon constituents in such fuels in order to have a suitable volatility. Therefore, the amount of iso-octane or alkylate which can be added is strictly limited. If, in preparing premium gasolines, large amounts of iso-octane or alkylate are employed, some lower boiling hydrocarbons must be added to produce the desired volatility. There is, however, no good available supply of a material suitable for this purpose. Most of the lower boiling hydrocarbons have octane numbers much below 100 and their use in appreciable concentrations greatly reduces the octane number of the blend. One material which is ideally suited for this purpose is neohexane. It has the desired volatility, high octane number and high lead susceptibility. This material is, however, not readily available. There is therefore a great demand for high octane number blending stocks having the desired volatility and lead susceptibility.

As stated above, there are available considerable quantities of iso-octane and alkylate having 8 carbon atoms and limited quantities of neohexane having 6 carbon atoms. According to the process of the invention, high octane blending stocks consisting largely of hydrocarbons having 5 and 7 carbon atoms are produced. These materials in combination with neohexane and iso-octane and alkylate afford to the gasoline manufacturer a complete range of high octane blending stocks with which motor fuels of any desired volatility may be produced without sacrificing octane number.

The high octane blending stocks are produced according to the process of the present invention by a combination of processes comprising polymerization, hydrogenation and selective cracking. The first step in the production of these blending stocks according to the invention is to polymerize isobutylene to high boiling polymers. Although it is preferred to form the true polymer of isobutylene, i. e. that formed by the union of two or more isobutylene molecules, the isobutylene may also be interpolymerized with other olefines such as ethylene, propylene, alpha butylene, beta butylene and the like. These various polymers, whether produced from isobutylene alone or by interpolymerization of isobutylene with other olefines, are referred to hereinafter as "isobutylene polymers." The polymerization may be effected by any one of the numerous well known polymerization processes such as the so-called hot acid, cold acid, phosphoric acid, aluminum chloride and boron fluoride processes. In general, in these processes mixtures of polymers having various degrees of polymerization are formed. Some of these polymers are excellent fuel components per se or may be readily converted into valuable fuel components. For instance, di-isobutylene may be hydrogenated to iso-octane. These polymers may be fractionated from the higher boiling polymers and treated separately or may be separated after hydrogenating the total polymer product. The polymers preferably employed for the production of the present blending stocks are those having above 8 carbon atoms such, for example, as a fraction boiling between about 170° C. and 250° C.

These polymers are, according to the process of the invention, then substantially completely hydrogenated. Thus, the total polymers may be hydrogenated or the material may be first fractionated and the 170° C.–250° C. fraction hydrogenated. If the total polymer is hydrogenated, the hydrogenated product is preferably fractionated to separate a fraction boiling above about 170° C. which is employed for the production of the blending stocks. These polymers produced using isobutylene and boiling in this range are particularly rich in hydrocarbons containing the structural grouping:



I have found that these saturated hydrocarbons containing this structural configuration when subjected to a selective cracking treatment may be cracked unsymmetrically to produce large percentages of neopentane and that when these hydrocarbons of the described boiling range are subjected to such treatment there is also pro-

duced highly branched high octane paraffinic hydrocarbons having 7 carbon atoms.

According to the process of the present invention, the above-described hydrogenated polymers are subjected to a selective cracking treatment. This treatment requires the use of a particular class of catalysts. It is found that the type of catalyst ordinarily used for catalytic cracking of hydrocarbons, such as the clay-type silica-alumina catalysts, causes the cracking of these materials to take place in an entirely different direction, the hydrocarbon apparently being broken between different carbon atoms. The catalysts employed according to the process of the invention are those of the dehydrogenation type such, in particular, as the sulf-active oxides and/or sulfides of chromium, molybdenum and tungsten. A particularly suitable catalyst is, for example, chromium oxide, especially in combination with alumina. These various related catalysts are used for the dehydrogenation of hydrocarbons, the cyclization of paraffin hydrocarbons, and similar processes, and are well known. Generally speaking, any of the dehydrogenation catalysts used for these processes may be used in the present process.

As stated above, the catalysts used in the present process are the same as those ordinarily recommended for the cyclization of hydrocarbons, for example, the conversion of normal heptane to toluene. It is to be pointed out, however, that very little aromatic hydrocarbons are usually produced in the present selective cracking treatment, except as a side reaction simultaneous with the cracking. This is not, however, unusual since it is well established that the structure of hydrocarbons often greatly influences the type of reaction which can take place.

The selective cracking treatment is effected by contacting the hydrogenated polymer with a catalyst of the above-described type at a temperature in the order of from 425° C. to about 550° C. The pressure may be subatmospheric, atmospheric or superatmospheric. Very suitable pressures are, for example, from 1 to 10 atmospheres. The contact time depends upon the other operating conditions and may vary considerably. Suitable contact times are, for instance, between about 0.5 and 40 seconds. If desired, in order to increase the catalyst life, hydrogen or a hydrogen-containing gas may be recycled through the reaction zone. The conditions are, however, in no case sufficiently severe to cause destructive hydrogenation. The selective cracking step may be operated in any of the conventional manners such, for example, as by passing the hydrocarbon vapors through a chamber filled with a fixed bed of the catalyst and maintained under the desired reaction conditions, or by the recently developed recycled aerated catalyst process.

The product from the selective cracking operation is preferably fractionated to remove small quantities of lighter hydrocarbon gases, etc. Unreacted material and any higher boiling reaction products may also be separated. The unreacted material may, if desired, be recycled. The intermediate boiling material may, if desired, be employed as a blending stock per se or, if desired, may be fractionated into a plurality of fractions having different volatilities, which fractions may be separately blended into the motor fuel in the desired proportions. For example, the cracked product may be separated into a lower boiling fraction containing the neopentane and the higher boiling fraction consisting largely of branched chain paraffins having 7 carbon atoms. These fractions may then be blended with isooctane, neohexane and/or other fuel components to produce especially excellent fuels. In general, the amount of neopentane which may be utilized in gasoline type fuels is quite limited. It may therefore be that the present process will produce an excess of this material. In such cases, all or a part of the neopentane fraction may be used for other purposes, for example, as a starting material for special chemicals, etc. For such uses it is preferably carefully re-fractionated to recover this hydrocarbon in a substantially pure form.

The following example illustrates the production of suitable blending stocks according to a preferred embodiment of the present process.

Example

Isobutylene was polymerized with cold sulfuric acid by the conventional method to produce a mixture of polymers. The polymers were fractionated and a fraction boiling between about 176° C. and 199° C. was separated. This material was hydrogenated with a nickel catalyst in the conventional manner to produce a material having a bromine number of 5.6 gm. BR_2/100 gm. (Rosenmund). This material was fractionated to give a product boiling between 170° C. and 181° C. and having a bromine number of about 0.5. It was then selectively cracked by passing the vapors in contact with a chromium oxide catalyst supported upon alumina under the following conditions:

Catalyst	Cr_2O_3/Al_2O_3 (11% Cr)
Temperature	500° C.
Pressure	1 atmosphere
Liquid hourly space velocity	0.15

(Liquid hourly space velocity is defined as the volumes of liquid reactant contacted with a volume of catalyst per hour.)

About 0.87 mols of gas were formed by side reactions per each mol of feed. This gas consisted largely (68%) of isobutylene, the remainder being mostly propane (8%) and hydrogen. The debutanized liquid product consisted essentially of aliphatic hydrocarbons having 5, 7 and 8 carbon atoms, some aromatic hydrocarbons having 8 carbon atoms, about 30% of unreacted material, and some higher boiling material predominantly of aromatic character. There was no evidence of any appreciable amounts of hydrocarbons having 6 carbon atoms. The lower boiling material having 5 carbon atoms per molecule consisted exclusively of neopentane. This was separated and identified by its physical constants—M. P. —19.0° C., N_D^4 1.3490.

That the selective cracking of the hydrogenated polymers to form neopentane is dependent upon the use of catalysts of the above-described type is evidenced by similar experiments wherein portions of the same hydrogenated polymer were subjected to catalytic cracking with conventional cracking catalysts of the silica-alumina type. With catalysts of this type entirely different reaction products were produced and no evidence of the formation of neopentane was found.

That the above-described selective cracking is also dependent upon the treatment of the particular type of saturated hydrocarbon stocks described is evidenced by similar experiments wherein saturated alkylate of the same boiling range was treated with both the above-described Cr_2O_3/Al_2O_3 catalyst and the conventional crack-

ing catalysts. In neither case did the cracking take place to produce neopentane. The alkylate which was produced by the sulfuric acid alkylation of butylenes with isobutane is a highly branched material having an excellent octane number. It does not, however, have the same structural configuration as the above-described hydrogenated polymers. Also, it is essential that the polymer employed in the process be hydrogenated prior to subjection to the selective cracking treatment. If the olefinic polymer is cracked as described above, decomposition takes place almost exclusively to form isobutylene and no appreciable amount of hydrocarbons having 5 carbon atoms is formed.

I claim as my invention:

1. A process for the production of high antiknock volatile blending fuels which comprises forming an isobutylene polymer boiling within the range of about 170°–250° C., hydrogenating said polymer and passing vapors of the hydrogenated product in contact with a sulf-active dehydrogenation catalyst under conditions of temperature, pressure and contact time coordinated within the limits of 425° C. to 550° C., 1 to 10 atmospheres, and 0.5 to 40 seconds, respectively, such that cracking to lower molecular weight hydrocarbons is the predominant reaction and separating the product into a gaseous fraction consisting predominantly of isobutylene which can be re-polymerized, a fraction consisting largely of aliphatic hydrocarbons having 7 and 8 carbon atoms per molecule which is suitable as a gasoline fuel component, a higher boiling fraction consisting largely of unconverted feed which may be recycled, and a fraction consisting largely of neopentane.

2. A process for the production of high antiknock volatile blending fuels which comprises forming an isobutylene polymer boiling within the range of about 170° C.–250° C., hydrogenating said polymer and passing vapors of the hydrogenated product in contact with a chromium oxide-alumina catalyst under conditions of temperature, pressure and contact time coordinated within the limits of 425° C. to 550° C., 1 to 10 atmospheres, and 0.5 to 40 seconds, respectively, such that cracking to lower molecular weight hydrocarbons is the predominant reaction.

3. A process for the production of high antiknock volatile blending fuels which comprises forming an isobutylene polymer boiling within the range of about 170° C.–250° C., hydrogenating said polymer and passing vapors of the hydrogenated product in contact with a chromium oxide catalyst under conditions of temperature, pressure and contact time coordinated within the limits of 425° C. to 550° C., 1 to 10 atmospheres, and 0.5 to 40 seconds, respectively, such that cracking to lower molecular weight hydrocarbons is the predominant reaction.

4. A process for the production of high antiknock volatile blending fuels which comprises forming an isobutylene polymer boiling within the range of about 170° C.–250° C., hydrogenating said polymer and passing vapors of the hydrogenated product in contact with a sulf-active dehydrogenation catalyst under conditions of temperature, pressure and contact time coordinated within the limits of 425° C. to 550° C., 1 to 10 atmospheres, and 0.5 to 40 seconds, respectively, such that cracking to lower molecular weight hydrocarbons is the predominant reaction.

5. A process for the production of high antiknock volatile blending fuels which comprises forming an isobutylene polymer boiling within the range of about 170° C. to 250° C., hydrogenating said polymer, and passing vapors of said hydrogenated product in contact with a chromium oxide catalyst supported upon alumina at a temperature of about 500° C., substantially atmospheric pressure and a liquid hourly space velocity of about 0.15, and separating from the cracking products a fraction consisting largely of neopentane.

INGOLFUR BERGSTEINSSON.