

# United States Patent

[15] 3,674,681

Lyon

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[54] **PROCESS FOR ISOMERIZING  
HYDROCARBONS BY USE OF HIGH  
PRESSURES**

2,475,358 7/1949 Moore et al. ....208/26  
2,668,866 2/1954 Good et al. ....208/18  
3,308,052 3/1967 Ireland et al. ....208/18  
2,326,585 8/1943 Vesterdal.....260/683.15

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[58] **Field of Search**.....260/683.65, 683.7, 668 A;  
208/18, 141, 27

[56] **References Cited**

**UNITED STATES PATENTS**

2,220,090 11/1940 Evering et al. ....260/683.7  
2,399,927 5/1946 Howes et al. ....260/683.65

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[57] **ABSTRACT**

The propensity of hydrocarbons to crack, during isomerization, is minimized by use of high pressure. This process is shown to be especially useful when isomerizing high molecular weight hydrocarbons, such as those found in the residues from petroleum and also highly branched hydrocarbons, both of which cannot be isomerized efficiently by use of prior art methods. In a preferred embodiment the hydrocarbon which is a slack wax is isomerized in a substantially inert solvent, at a pressure of at least 10,000 psi, and in the presence of a Lewis acid catalyst to produce lubricants characterized by their high viscosity index and low pour point.

**7 Claims, No Drawings**

## PROCESS FOR ISOMERIZING HYDROCARBONS BY USE OF HIGH PRESSURES

### FIELD OF THE INVENTION

This invention relates to an improved process for isomerizing hydrocarbons which, because of their high molecular weight and/or their branched structure, are subject to cracking with the resultant formation of undesirable, low molecular weight fractions. More specifically, this invention relates to the isomerizing of hydrocarbons which are susceptible to cracking, by contacting said hydrocarbon with a Lewis acid catalyst, at an elevated temperature and a pressure of at least 10,000 psi; the pressure serving to minimize cracking, while increasing the reaction rate. In a particularly preferred embodiment the reaction is run with both the hydrocarbon and the catalyst dissolved in a substantially inert solvent.

### PRIOR ART

The isomerization process is subject to the undesirable side reaction known as cracking. Cracking, in effect, means that the molecules are breaking down into lower molecular weight fragments instead of following the desired course of molecular rearrangement. Cracking has been minimized by various techniques well known in the prior art; they include conducting the isomerization reaction under mild conditions, i.e., low activity catalyst, low temperatures, and low conversions; and addition of chemical suppressors, such as hydrogen, naphthenes and aromatics. These techniques are subject to inherent difficulties, including the unattractive economics of running at low conversions, and are not at all effective in a process for isomerizing highly branched and/or high molecular weight hydrocarbons, i.e.,  $C_{20}$  and greater hydrocarbons.

Various by-products of the petroleum industry can be theoretically modified by isomerization to give highly desirable products. One example is the isomerization of slack wax, a low quality by-product of the petroleum industry, to a high quality lubricating oil. Slack wax has an excellent viscosity index (V.I.), but because of its essentially nonbranched structure, slack wax is composed primarily of high molecular weight normal and very slightly branched hydrocarbons having a carbon number range of 20 to 50, it solidifies at relatively high temperatures, that is, it has a poor pour point. The isomerization of the hydrocarbons in slack wax to give more highly branched structures would increase the pour point while maintaining the V.I., thus resulting in an improved lubricating oil. Due to the high molecular weight of the hydrocarbons, however, the cracking reaction predominates over the isomerization reaction, thereby resulting in a very low yield of lubricating oil.

The prior art processes have attempted to solve the problem of isomerizing high molecular weight, essentially unbranched hydrocarbons by the use of hydrogen to suppress cracking, and running under conditions that lead to low conversions. For example, see the process described in U.S. Pat. No. 2,668,790, wherein the patentee describes a process for isomerizing paraffin wax to produce a lubricating oil by use of hydrogen and a platinum catalyst. The patentee discloses that the reaction must be run under conditions that result in no more than 25 percent of the feed being cracked to low molecular weight products. The patentee also recognizes the need for removal of the cracked products to produce an improved V.I. lubricating oil. It should be noted that patentee discloses operation at pressures of from 50 to 3,000 psi, well below the range of the instant application.

Isooctane is another product that can be produced by an isomerization process. Isooctane is a desirable product because of its excellent performance as a fuel for automobiles. In the prior art process, normal octane is isomerized over a conventional isomerization catalyst such as  $AlCl_3$ ,  $AlBr_3$  and other Lewis acids. The desired branched isomers of octane, however, are subject to cracking with the resultant formation of low molecular weight fragments such as isobutane, isopentane, etc.

The problems in isomerizing octane have been recognized previously, for example see U.S. Pat. No. 3,301,917, which claims a process for the isomerization of  $C_4$ - $C_8$  paraffins in the presence of hydrogen. The patentee has recognized, in lines 23-33 of column 9, that the high molecular weight paraffins hydrocrack rather than hydroisomerize as temperatures are increased; therefore, higher paraffins are hydroisomerized at low temperatures, resulting in decreased reaction rates. Patentee discloses utilization of pressures of about 600 psi which, again, is well below the pressures disclosed in the instant application.

### SUMMARY OF THE INVENTION

According to this invention, it has been unexpectedly found that by isomerizing hydrocarbons under pressures of at least 10,000 psi, in the presence of a Lewis acid, and with or without the use of hydrogen, cracking can be minimized. Preferably pressures of from 10,000 psi to 100,000 psi are utilized, and most preferably the pressure range is from 40,000 psi to 60,000 psi. Many reactions that cannot be run without high ratios of cracking to isomerization, at pressures of from 0 to 5,000 psi can be effected easily at pressures of 10,000 psi, or greater. Another advantage of the instant invention is that reactions can be run at high temperatures, thereby increasing the rate of conversion without increasing the ratio of cracking to isomerization.

While not wishing to be bound by any particular theory, it is believed that the rate of the cracking reaction, wherein one molecule splits into two molecules, is decreased as the pressure is increased to 10,000 psi and above. The isomerization reaction rate, on the other hand, does not decrease, but instead increases. The result of increasing the reaction pressure to at least 10,000 psi, therefore, is that the ratio of isomerization to cracking is maximized.

It is contemplated that this invention may be of use in isomerizing not only essentially normal hydrocarbons, but can be used to isomerize branched hydrocarbons when more highly branched isomer distributions are desired. This invention is especially contemplated for isomerizing essentially linear hydrocarbons containing more than five carbon atoms in the chain. Also, this invention can be used with feed stocks containing only minor amounts of isomerizable hydrocarbon, on up to feed stocks that are 100 percent isomerizable hydrocarbon. This invention will also be used when the isomerizable hydrocarbon chain is attached to other groups such as aromatics, cyclic hydrocarbons, halogens, nitrates, sulfides, etc. As previously mentioned, the feed stocks of the petroleum industry, such as naphtha, straight run gasoline, kerosene, gas oils, residual oils, etc. are contemplated for use in this invention.

Naphtha, kerosene and slack wax, of the petroleum industry feed stocks are preferred for use in the process of this invention. Naphtha may be characterized as the product that is isolated from the distillation of crude oil and having a boiling point of from 60° to 200° F. at atmospheric pressure. Naphtha may be further characterized as a mixture of essentially unbranched hydrocarbons having a carbon number range of from 6 to 10. Kerosene is also isolated from crude oil by distillation, and boils between 200° and 300°F. at atmospheric pressure. Kerosene consists essentially of unbranched hydrocarbons having a carbon number ranging from nine to 16. Slack wax is available from the residue of the crude oil after distillation, deasphalting, hydrocracking, and separation from the hydrocracked oil. A typical slack wax would have a gravity, °API, of 35.2 and the following distillation spectrum: Weight percent boiling at 750° to 900°F., 15.7; 900° to 1,000°F., 18.9; and above 1,000°F., 65.4. As noted previously, the product would be characterized as having a poor pour point.

In the process of this invention, naphtha would be converted to a mixture of highly branched hydrocarbons boiling in the 50° to 200°F. range. This product, being structurally similar to isooctane, that is, both products are highly

branched, would make an excellent automobile fuel. In general, straight chain hydrocarbons are poor automobile fuels because of their tendency to preignite during the compression stroke of the cylinder. The result is knocking and is measured by octane number. 2,2,4-trimethylpentane, known as isooctane, has little tendency to preignite and is given an octane rating of 100 on the Octane Scale. In contrast, normal heptane, which has extremely poor anti-knock properties, is given a 0 rating on the Octane Scale. The highly branched hydrocarbons produced from the use of naphtha as the feed stock in the process of this invention will have high octane ratings. Products produced include: 2,2,3-trimethylpentane; 2,2,4-trimethylpentane; 2,2,3-dimethylbutane; 2,2,3-trimethylbutane; 2,2,3,3,-tetramethylbutane; 3,3,4-trimethylpentane; 2,2,3,4-tetramethylpentane; and various other highly branched hydrocarbons.

Kerosene would also be converted to a product having improved fuel value by the process of this invention. Slack wax as noted previously, would be converted into a product having a low pour point and a high viscosity index and therefore, useful as a high quality lubricant.

The use of naphtha or slack wax as the feed stock for the process of this invention is especially preferred, with slack wax the most preferred.

The reaction is run in the liquid phase and can be run neat, that is, with no solvent, but preferably solvents are used to dissolve the catalyst and/or the hydrocarbon that is to be isomerized. Solvents should be appreciably nonreactive under the conditions of the reaction and include trichlorobenzene, other halogenated aromatics, propane, butane, isobutane, neopentane and other inert hydrocarbons.

Isomerization reactors known in the art can be used for the practice of this invention, with consideration given to the fact that they must be able to withstand pressures of up to about 100,000 psi. Design of such equipment will be apparent to those knowledgeable in the art.

The catalysts that can be used in this invention are Lewis acid types. Lewis acids are molecules, ions or radicals that are electron deficient and, therefore, are capable of accepting a pair of electrons from a donor species. These include aluminum and boron halides, especially boron trifluoride, alu-

at least 10,000 psi with the range of 30,000 psi to 100,000 psi preferred, and 40,000 psi to 60,000 psi most preferred. As has been stated previously, hydrogen or any inert gas can be used but, unlike the prior art isomerization processes, hydrogen is not essential to reduce cracking. Pressure can also be generated by hydrostatic compression until the desired pressure is obtained. The reaction temperature will depend on the reactants and catalyst chosen. In general, the reaction temperature required is from 80° to 800°F., with the temperature range of from 100° to 400°F. being preferred.

The reaction time will vary according to the reaction rate of the feed stock under the reaction conditions used and also according to the degree of conversion desired. Contact times will usually vary from one second to 1,000 seconds.

A preferred embodiment of this invention is the production of novel lubricating oils from slack wax. A slack wax obtained from a first dewaxing of a petroleum residue stock will contain mostly normal paraffins with small amounts of slightly branched isoparaffins. This material has a very high pour point and a higher cloud point.

By isomerizing this slack wax, a hydrocarbon is obtained which has unique properties compared to lubricating oils produced by conventional methods, such as extremely high V.I. indices of from 125-155.

SPECIFIC EMBODIMENTS

To further illustrate this invention, the following examples are given.

EXAMPLE 1

Effect of Pressure on Cracking

One-third by volume normal hexane was dissolved in two-thirds by volume of a catalyst solution, which composition was 0.5 molar AlBr<sub>3</sub>, 0.1 molar H<sub>2</sub>O and 0.02 molar methyl t-amyl ether in 1,2,4-trichlorobenzene. The sample was placed in a high pressure vessel which was kept at 0°C. until the sample was under pressure. The vessel was brought to a reaction temperature of 40°C. and held for one hour. The vessel was again brought to 0°C. and the pressure was released. The reaction products were analyzed by gas chromatography and the results are included in Table I.

TABLE I

Percent reaction products	Run 1, 10 p.s.i.g.	Run 2, 25,000 p.s.i.g.	Run 3, 50,000 p.s.i.g.	Run 4, 68,000 p.s.i.g.	Run 5, 90,000 p.s.i.g.
i-C <sub>4</sub> H <sub>10</sub> .....	27.56	20.06	17.57	9.67	4.79
n-C <sub>4</sub> H <sub>10</sub> .....	1.16	1.28	2.46	1.23	0.55
i-C <sub>3</sub> H <sub>12</sub> .....	17.51	16.24	13.66	8.14	4.54
n-C <sub>3</sub> H <sub>12</sub> .....	1.68	0.71	1.52	1.31	0.31
n-C <sub>2</sub> H <sub>6</sub> .....	35.86	34.13	11.44	40.90	42.43
2-methyl pentane.....	6.24	11.05	17.10	14.43	17.06
3-methyl pentane.....	2.45	3.75	6.61	4.99	6.18
2,2-dimethylbutane.....	5.80	9.38	23.45	14.48	17.94
2,3-dimethylbutane.....	1.67	3.40	6.18	4.85	6.18
Total C <sub>4</sub> +C <sub>5</sub> (cracked products).....	47.91	38.29	35.21	20.35	10.19
Total C <sub>8</sub> (uncracked and isomerized products).....	52.08	61.71	64.78	79.65	89.79

minum trichloride, aluminum tribromide, etc.; organic and inorganic acids, such as H<sub>2</sub>SO<sub>4</sub>, HF, HCl, H<sub>3</sub>PO<sub>4</sub>, HSO<sub>3</sub>F, SbF<sub>5</sub>, sulfamic acid, etc.; with AlBr<sub>3</sub>, AlCl<sub>3</sub>, BF<sub>3</sub>, HF, H<sub>2</sub>SO<sub>4</sub>, HSO<sub>3</sub>F, and SbF<sub>5</sub> being particularly desirable and AlBr<sub>3</sub> most preferred. The catalyst is preferably soluble in the hydrocarbon or the hydrocarbon-solvent blend, but the use of heterogenous catalysts are not precluded from the scope of this invention.

If a homogeneous catalyst is used, its concentration must be appropriate to the mode of operation. If the expense of catalyst recovery and recycle are accepted, the catalyst concentration may be as high as 10 to 20 percent weight of catalyst per weight of feed. If catalyst is not recovered, the catalyst concentration may be 2 percent or less, even though this may lower the rate of reaction. The catalyst may be prepared by procedures well known in the art of isomerization.

The process of this invention will be run under pressures of

It was seen that the concentration of products from the cracking reaction (C<sub>4</sub> + C<sub>5</sub>) decreased from 47.91 percent at 10 psig to 10.19 percent at 90,000 psig. It was thus demonstrated that the increased pressure tended to decrease the cracking reaction rate. It was also noted that the yield of the desired isomerization products 2-methylpentane; 3-methylpentane; 2,2-dimethylbutane; 2,3-dimethylbutane is 53.34 percent at 50,000 psig. For essentially straight chain hydrocarbons containing from four to 10 carbon atoms, pressures of about 50,000 psig appear to yield the best balance between conversion rate and cracking. Thus it is seen that using the pressures of the prior art, as indicated by Run 1 of Table I, 47.91 percent cracked products and 16.22 percent branched products are produced. At the preferred pressure of the instant invention, i.e., 50,000 psig, 35.21 percent cracked products and 53.34 percent branched products are produced, thereby demonstrating the superiority of the process of the instant invention over the process of the prior art.

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## EXAMPLE 2

Effect of Pressure on Cracking of Branched Hydrocarbons  
2,3,4-trimethyl pentane was subjected to the conditions described in Example 1. A total of 28 runs at various reaction pressures were made and the average ratio of i-butane to other trimethylpentane isomers, that is, the ratio of cracking to isomerizing, was calculated from the results.

Blank	Yield of isobutane (Wt. $iC_4H_{10}$ /Wt. 2,3,4 TMP initially charged)
0 psig	.04 ± .01
50,000 psig	0.20 ± .03
90,000 psig	.08 ± .01
	.057 ± .006

The blank shows that some cracking and isomerizing occurred during the time the sample was exposed to room temperature while mixing and prior to chilling and pressurizing. If the blank is subtracted from the results at other pressures, it can be seen that the cracking reaction is almost nonexistent at 90,000 psig. It should also be mentioned that the rate of isomerization increases by a factor of 50 between 0 psig and 50,000 psig. Hence the improvement in selectivity (ratio of isomerization to cracking) is in this example a factor of 200.

## EXAMPLE 3

A 200 gm. sample of  $nC_{24}H_{50}$ , a compound typical of the slack wax components which must be isomerized, is mixed with an equal weight of liquid propane solution of  $AlBr_3$  (1 weight percent) and benzene (1 weight percent). The mixture is allowed to react at 50,000 psi and 300°F. for 5 minutes and is recovered. The  $AlBr_3$  is deactivated by addition of water and the hydrocarbon mixture is analyzed by gas chromatography. The  $nC_{24}H_{50}$  is 90 percent converted. The reaction products are 85 percent isomerized  $C_{24}H_{50}$  and 15 percent cracked products, chiefly hydrocarbons boiling in the diesel fuel range with negligible amounts of light gases.

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## EXAMPLE 4

A sample of slack wax having a pour point of 30°C. and a V.I. of 125, is treated in the manner described in Example 3. The resultant oil (recovered in 73 percent yield) has a -20°C. pour point and a 135 V.I.

## EXAMPLE 5

The experiment of Example 3 is repeated using  $AlCl_3$  in place of  $AlBr_3$ . The results are substantially similar indicating that high pressures suitably control the cracking of high molecular weight hydrocarbons even in a process that utilizes a high activity catalyst.

The invention is not to be limited to the above examples since many variations will be apparent to those skilled in the art.

What is claimed is:

1. In an improved process for isomerizing slack wax, which comprises contacting said hydrocarbon at isomerization conditions with a catalyst comprising an aluminum halide, the improvement which comprises isomerizing said slack wax at a pressure of from 10,000 to 100,000 psig, for a time adequate to obtain the desired degree of isomerization.

2. The process of claim 1 wherein the temperature at which said process is carried out ranges from 80° to 800°F.

3. The process of claim 2 wherein said catalyst is  $AlBr_3$ .

4. The process of claim 3 wherein said catalyst further comprises  $H_2O$  and a hydrocarbon ether.

5. The process of claim 3 wherein said reaction takes place in a solvent.

6. The process of claim 5 wherein said solvent is a halogenated benzene.

7. In an improved process for isomerizing slack wax, which comprises contacting said hydrocarbon at isomerization conditions with a catalyst selected from the group consisting of  $AlCl_3$ ,  $AlBr_3$ ,  $BF_3$ ,  $HF$ ,  $H_2SO_4$ ,  $HSO_3F$  and  $SbF_5$ , the improvement which comprises isomerizing said slack wax at a pressure of from 10,000 to 100,000 psig for a time adequate to obtain the desired degree of isomerization.

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