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ISOMERIZATION OF HYDROCARBONS

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This invention relates to the conversion of hydrocarbons and has to do particularly with the isomerization of straight chain hydrocarbons to form isomers.

The invention broadly contemplates a continuous process of isomerization of hydrocarbons wherein a stream of hydrocarbons undergoing conversion is passed at relatively high velocity through a mass of solid pulverulent isomerization catalyst maintained under isomerizing conditions, the reaction time being of sufficiently short duration to avoid substantial cracking of the hydrocarbons and deterioration of the catalyst.

More specifically, the invention contemplates isomerization of normal paraffin hydrocarbons such as normal butane by contact in the gas phase with a granular or solid pulverulent catalyst, such as a catalyst comprising aluminum chloride, maintained under isomerizing conditions such that substantial conversion to isoparaffins is secured. The hydrocarbons undergoing conversion are caused to flow in a continuous stream through the catalyst mass in the presence of a suitable promoter, and at a velocity which is at least sufficient to maintain turbulent conditions of fluid flow through the mass. In addition, a relatively short time of contact between the catalyst and the hydrocarbons is employed, for example, not in excess of about one and a half minutes and preferably in the range 30 seconds or less up to about 1 minute.

The invention is applicable to a continuous flow process of isomerization wherein a stream of hydrocarbons undergoing conversion is continuously passed through a reaction zone containing a mass of granular or pulverulent catalyst. A stream of reaction mixture is continuously withdrawn from the reaction zone and passed to a fractionating or separating zone wherein unreacted hydrocarbons are separated from the isomerized hydrocarbons, and unreacted hydrocarbons in part at least, continuously recycled through the isomerization reaction zone.

An important object of the invention is to maintain conditions within the catalyst mass such that a uniformly high rate of conversion to isomerized hydrocarbons is maintained without experiencing substantial formation of cracked products and without substantial catalyst deterioration.

It has been found that by maintaining a sufficiently high velocity of fluid flow through the catalyst mass, a uniformly high rate of conversion to isoparaffins can be maintained with a relatively short time of contact between the hydrocarbons and the catalyst and that this high conversion rate can be effected without substantial cracking or without substantial occurrence of objectionable side reactions. By avoiding cracking or other objectionable side reactions, deterioration of the catalyst is reduced to a minimum, so that it remains effective during continuous use over an extended period of time.

There appears to be a critical velocity below which the desired results are not realized and that is at relatively low velocities such that conditions of viscous flow rather than conditions of turbulent flow exist within the reaction zone. Under relatively low velocity conditions high rates of conversion to isoparaffin hydrocarbons may be realized but are accompanied by relatively high yields of cracked products with a contact time of the order of 3 minutes, for example. Moreover, under relatively low velocity conditions a reduction in the time of contact between the hydrocarbons and the catalyst results in reducing the yield of cracked products but is also accompanied by a corresponding reduction in the yield of isomerized hydrocarbons.

It has now been found, however, that by maintaining turbulent conditions of flow within the catalyst mass a reduction in the time of contact while substantially reducing the yield of cracked products does not reduce the yield of isomerized hydrocarbons. In other words, when operating under conditions such that turbulent fluid flow exists in the reaction zone, altering the time of contact within certain limits does not cause any substantial variation in the yield of isomerized hydrocarbons, but does materially affect the extent of cracking.

This is demonstrated when applying the process to the isomerization of normal butane in the gaseous phase by contact with a catalyst such as Porocel impregnated with aluminum chloride and effecting the contact, in the presence of anhydrous hydrogen chloride, at a temperature of about 210 to 220° F. and under a pressure of about 165 pounds per square inch gauge. The catalyst in question is prepared by drying Porocel of 4 to 8 mesh by heating in an oven at 580° F. for about 2 hours. The dried Porocel is then subjected to contact with aluminum chloride vapors at substantially atmospheric pressure for a period of 2 to 6 hours, at a temperature of about 440° F. The resulting impregnated catalyst has a free space of about 58% by volume when packed in a reaction tower, and contains about 18 to 23% aluminum chloride by weight.

The catalyst is supported in a vertical reaction tower through which a stream of normal butane in the gas phase is passed, the butane feed being heated sufficiently to maintain an average reaction temperature of about 210 to 220° F.

In one series of runs the linear velocity (calculated actual velocity through the free space of the catalyst mass) is varied from 1 to 2 feet to about 10 feet per minute while maintaining the same time of contact in each run, namely, about 2 minutes. The time of contact is maintained con-

stant by decreasing or increasing the depth of catalyst bed from run to run and adjusting the butane charge rate accordingly.

A parallel series of runs is made under similar conditions but maintaining a contact time of about 1 minute.

Upon comparing the yields obtained in these two series of runs it is found that at a velocity of about 2 feet per minute the per cent isobutane is about 54% by volume with a contact time of 2 minutes, but is only about 46% with a contact time of 1 minute. The yields of cracked products obtained are 9 and 5%, respectively, under the same conditions, the cracked products including hydrocarbons both lower and higher in molecular weight than butanes. On the other hand, with a velocity of about 4 to 5 feet per minute the yield of isobutane is about 58% with either a 1 minute or a 2 minute time of contact. With these higher velocities the yield of cracked product is about 12% by volume for a 2 minute contact time and about 8% for a 1 minute contact time. However, the per cent yield of isobutane continues to remain at about 58% for both times of contact at lineal velocities as high as 10 feet per minute through the catalyst mass. Whereas, over the same velocity range the per cent yield of cracked product continues to remain about 4% greater with a 2 minute time of contact than with a 1 minute time of contact.

By reducing the time of contact still further while maintaining a high lineal velocity the yield of cracked products is correspondingly reduced. Thus, by employing a time of contact of 30 seconds or less the yield of cracked product will not exceed about 2 or 3% by volume, while a uniformly high per cent conversion to isobutane is realized, namely, in the range about 58 to 60% by volume, provided that turbulent flow conditions are maintained within the reaction zone.

The relationship between lineal velocity and other factors in order for turbulent flow to exist through a catalyst mass can be expressed by means of the formula for determination of Modified Reynolds Numbers described in an article entitled "Pressure drop in packed tubes" by Chilton and Colburn, Industrial and Engineering Chemistry, August, 1931, vol. 23, No. 8, pages 913 to 919. The formula is as follows:

$$\text{Modified Reynolds Number} = \frac{D_p U P}{Z}$$

where

D_p is diameter of catalyst particles in feet;
U is velocity in feet per second of fluid based on total cross-sectional area of the tube;
P is density in pounds per cubic foot of fluid under the operating conditions of temperature and pressure;
Z is viscosity in pounds per foot per second under the operating conditions of temperature and pressure.

The values of Z for butanes can be determined by reference to the data in an article entitled "Effect of pressure on viscosity of normal butane and isobutane" (published by Sage, Yale and Lacey, Industrial and Engineering Chemistry, February, 1939, vol. 31, No. 2, pages 223 to 226) as correlated in a subsequent article entitled "Viscosity of gas and vapors at high pressures (published by Comings and Egly, Industrial and Engineering Chemistry, vol. 32, No. 5, pages 714 to 718).

As indicated in Fig. 1 of the above mentioned Chilton and Colburn article, turbulent flow exists in a packed tube when the Modified Reynolds Number as determined by the above formula has a value of about 40 and above.

By this method of calculation it is found that in the case of a tube having an internal diameter of 1.5 inches packed with the previously described catalyst, the relationship between lineal velocity and Modified Reynolds Number when normal butane is passed through the tube at about 212° F. and under a pressure of about 165 pounds per square inch gauge is approximately as follows:

Lineal velocity [1] in feet per minute	Modified Reynolds No.
4	39.3
6	59
8	78.6
10	98.4

[1] Velocity through the catalyst mass.

As set forth in the formula the lineal velocity necessary in order to maintain conditions of turbulent fluid flow throughout the catalyst mass will depend upon the particle size and shape of the catalyst as well as other factors such as the viscosity of the hydrocarbons undergoing treatment and the conditions of temperature and pressure maintained within the reaction zone. Generally speaking, suitable catalysts will have a free space in the range about 45 to 65% by volume of the reactor space occupied by the catalyst mass, and under such conditions the lineal velocities of hydrocarbons through the catalyst mass should be in the range 4 or 5 feet to 10 feet per minute and above, sufficiently high in other words to maintain conditions of turbulent flow within the reaction zone.

Any granular or solid pulverulent type of isomerization catalyst may be employed. Suitable catalysts include metallic halides such as aluminum chloride, zirconium chloride, etc., alone or supported upon supporting materials such as alumina, carbon, pumice, silica gel, etc. The catalyst may be of the impregnated type wherein a relatively inert supporting material is impregnated with the active catalyst material.

Metallic halide catalysts are advantageously employed in conjunction with suitable promoters including anhydrous hydrogen halide such as hydrogen chloride.

The isomerization reaction may be effected in a single reaction zone or in a plurality of reaction zones through which the hydrocarbons undergoing conversion flow in series. For example, the reaction may be effected in a tower packed with the catalyst in the form of a single bed or a plurality of successive beds. On the other hand, a plurality of separate reaction towers may be employed.

Instead of employing series flow through a plurality of separate reaction towers, parallel flow of feed hydrocarbons may be employed.

A temperature gradient may be maintained throughout the reaction zone or zones such that relatively mild temperature conditions are maintained during the initial portion of the reaction, more severe conditions being permitted in the later stages of the reaction. For example, in the isomerization of normal butane a temperature of about 180 to 200° F. may be maintained during the initial stage of the reaction and a temperature of about 220 to 240° F. in the final stage. Generally speaking, the preferred range of temperature is about 210 to 220° F.

The temperature conditions throughout the re-

action zone may be controlled by introducing a portion of the feed hydrocarbon at any desired temperature to intermediate and successive points in the reaction zone or zones. Thus, cool or preheated charge may be introduced at these intermediate points as may be found necessary.

The reaction may also be controlled by multiple injection of the promoter that is by injecting portions of the promoter at successive points or stages in the reaction zone. If desired increasing amounts of the promoter may be injected at successive points in the reaction. The amount of promoter added to the reaction may vary from about 0.5 to 10% by weight of the total charge. If desired, all of the promoter employed may be injected in the entering stream of feed hydrocarbon, in which case it may constitute 1 to 3% by weight of the hydrocarbon feed.

The foregoing provisions for maintaining relatively mild reaction conditions in the initial stage or stages of the reaction may also be employed to advantage where fresh catalyst is being employed in the reaction. Thus, when commencing an operation with a fresh catalyst charge, low temperature and hydrogen chloride concentration may be employed, gradually increasing the temperature and hydrogen chloride concentration until normal operating conditions are reached.

While the isomerization of normal butane has been specifically described it is contemplated that the process is applicable to the gas on vapor phase isomerization of other low boiling gasoline hydrocarbons including pentane, hexane and the like.

While the employment of a specific pressure has been described in connection with the isomerization of normal butane, nevertheless it is contemplated that other pressures may be employed in carrying out the reaction, but such that the hydrocarbons undergoing reaction are maintained in the gas phase.

The isomerization reaction may be effected in the presence of extraneous or diluent gases. For example, in isomerizing gasoline hydrocarbons such as pentane, hexane, etc., it is advantageous to add substantial amounts of isobutane to the feed as a means of still further inhibiting undesired side reactions. The resulting reaction mixture can be fractionated to segregate unreacted hydrocarbons and low boiling hydrocarbons which may be recycled, all or in part, through the reaction zone. In such case the recycled hydrocarbons may contribute materially in maintaining the desired velocity conditions within the reaction zone.

As previously mentioned multiple injection of the feed hydrocarbons to the reaction zone or zones may be employed. In such case the volume of vapor passing through the initial zone or stage may be considerably less than that passing through succeeding zones or stages. In order to maintain the desired high velocity in the initial stage a reaction chamber or vessel of narrower cross-sectional area may be employed for the first stage or if a single reaction vessel is used it may be of tapered construction, the feed hydrocarbons entering the vessel at the point of narrowest cross-sectional area.

A tapered reaction vessel with introduction of the charge at the point of taper is of advantage where it is desired to reduce the initial rate of conversion, since in this way relatively high space velocity with short contact time per unit depth of catalyst prevails near the charge entry point. Frequently, the maximum degree of catalytic action exists in the initial stage or at the point at which the fresh feed hydrocarbon comes into contact with the catalyst and before the hydrocarbons undergoing treatment have become diluted with products of reaction. Maintaining a relatively higher space velocity at this point thus tends to prevent the existence of excessively high rates of conversion in the initial stage of the reaction.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. In a continuous process for isomerizing low boiling straight chain hydrocarbons wherein a stream of hydrocarbon undergoing conversion in the gas phase is passed through a reaction zone containing a stationary mass of solid pulverulent isomerization catalyst at a temperature and under conditions such that substantial conversion occurs, the step comprising maintaining a relatively high lineal velocity of hydrocarbon flow through the mass in the initial stage of the reaction zone and progressively decreasing the lineal velocity of hydrocarbon flow as the hydrocarbons proceed through subsequent stages in the reaction zone such that a substantially uniform rate of conversion exists throughout the reaction zone.

2. In a continuous process for isomerizing hydrocarbons in the vapor phase, the steps which comprise passing vaporized feed hydrocarbons through a reaction zone containing a stationary mass of isomerization catalyst maintained under conditions such that substantial isomerization occurs, maintaining a relatively high lineal velocity of hydrocarbon flow through the mass in the initial stage of the reaction zone, and progressively decreasing the lineal velocity of hydrocarbon flow as the hydrocarbons proceed through subsequent stages in the reaction zone such that a substantially uniform rate of conversion exists throughout the reaction.

3. In a continuous process for isomerizing hydrocarbons in the vapor phase, the steps which comprise passing vaporized normal butane through a reaction zone containing a stationary mass of aluminum halide isomerization catalyst maintained in the presence of hydrogen halide under conditions such that substantial isomerization occurs, maintaining a relatively high lineal velocity of hydrocarbon flow through the mass in the initial stage of the reaction zone, and progressively decreasing the lineal velocity of hydrocarbon flow as the hydrocarbons proceed through subsequent stages in the reaction zone such that a substantially uniform rate of conversion exists throughout the reaction zone.

4. The process according to claim 3 in which the isomerization reaction is effected at a temperature of about 210 to 220° F.

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