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2,332,321

UNITED STATES PATENT OFFICE

2,332,321

PRESSURE ALKYLATION PROCESS

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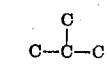
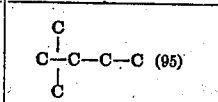
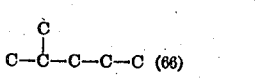
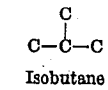
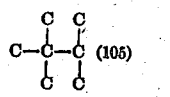
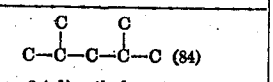
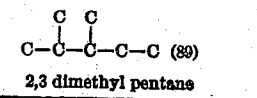
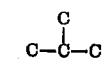
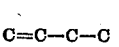
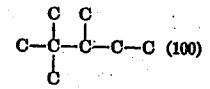
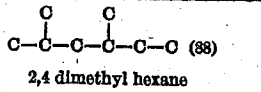
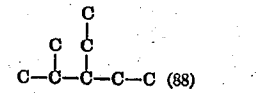
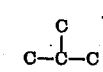
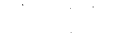
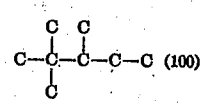
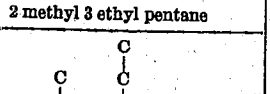
No Drawing. Application October 21, 1941, Serial No. 415,937

7 Claims. (Cl. 260—683.4)

This invention relates to a process for the production of alkylated hydrocarbons. More specifically the invention relates to the products obtained by reacting olefins and isoparaffins or olefins and aromatics under a high pressure and in a substantial absence of a catalyst.

At the present time alkylated hydrocarbons are produced by reacting low boiling isoparaffins with low boiling olefins in the presence of a catalyst, such as concentrated sulphuric acid. For example, isobutane and isobutylene react to form isooctane in the presence of concentrated sulphuric acid. This process, however, has some disadvantages. For example, low yields of alkylated hydrocarbon are produced for the amount of sulphuric acid catalyst employed. A large amount of sludge also results from the process which always is a nuisance in any refining operation. Furthermore, the sulphuric acid catalyst actually blocks the formation of alkylated hydrocarbons having highest knock rating. For example, the table shows skeleton structures of the theoretically possible and actually observed products of catalytic alkylation using isobutane and various olefins.

Table

Isoparaffin	Olefin	Product of alkylation reaction	
		Theoretically possible [1]	Actually observed [1]
 Isobutane	 Ethylene	 2,2 dimethyl butane	 2 methyl pentane
 Isobutane	 Propene	 Triptane	(1)  2,4,dimethyl pentane (2)  2,3 dimethyl pentane
 Isobutane	 Butene 1	 2,2,3 trimethyl pentane	(1)  2,4 dimethyl hexane (2)  2 methyl 3 ethyl pentane
 Isobutane	 Butene 2	 2,2,3 trimethyl pentane	(1)  2,4 dimethyl hexane (2) All products not determined yet but average octane only 88-90

[1] Numbers in parentheses are octane numbers.

Another process employed for the production of alkylated hydrocarbons is to react isoparaffins with olefins in the presence of hydrofluoric acid. This process is subject to criticism by reason of the fact that hydrofluoric acid must be handled with care as it is corrosive and dangerous. Furthermore, hydrofluoric acid is hazardous to health, and, as has been explained above with respect to the use of sulphuric acid as an alkylation catalyst, the hydrofluoric acid functions in a similar manner to block the reaction between olefins and isoparaffins in the production of the highest knock rating hydrocarbon such as triptane, isooctane, neohexane and other compounds.

Another process for the production of alkylating hydrocarbons consists in reacting isoparaffins with olefins in the vapor phase at temperatures above the critical and in the order of 1000° F. under a moderate pressure of 3000–5000 pounds per square inch. This method requires expensive equipment for safe operation. Furthermore it is not possible to produce alkylated hydrocarbons having the highest octane value by this method. The process is also disadvantageous from the

standpoint of operation since it is carried out in the vapor phase and, therefore, the rate of production of the alkylated product is extremely slow and capacity of equipment is, therefore, limited.

I have discovered that isoparaffins, such as isobutane or isopentane and higher isoparaffins can be reacted with propylene, normal butylenes, amylenes, isobutylene, di-isobutylenes and other olefin polymers for the production of alkylated hydrocarbons by my process. Furthermore, I have discovered that aromatic hydrocarbons such as benzene, toluene, xylene, ethyl benzene, naphthalenes and the like may be reacted with the foregoing olefin hydrocarbons for the production of alkylated products by my process. My process consists in reacting the isoparaffinic hydrocarbons or the aromatic hydrocarbons with one or more of the foregoing olefins in the liquid phase under a pressure of substantially 1000 atmospheres to 2000 atmospheres or above although some olefins react at much lower pressures and at a temperature below the critical point so that the hydrocarbons in the reaction zone are in the liquid phase at all times and for a sufficient period of time to produce alkylated hydrocarbons. This reaction is carried out in the absence of catalysts. By contacting olefins and isoparaffins in the liquid phase under a pressure of between 1000 and 2000 atmospheres at a temperature below the critical point for a period of one to three hundred minutes it is possible to cause the olefins to react with the isoparaffins thereby producing alkylated hydrocarbons in the same fashion as alkylated hydrocarbons are produced by the sulphuric acid alkylation process, by the hydrofluoric acid alkylation process or by the high temperature process described above and, as has been previously described, aromatics may be reacted with olefins by the same method as for the production of alkylated hydrocarbons. In most instances a temperature between 70° F. to 350° F. or 400° F. has been found satisfactory. Lower temperatures may be employed with a corresponding increase in the time employed for the reaction.

At the pressure and temperature employed by my process olefins interact with each other to produce polymerized hydrocarbons. For this reason polymerization is a competing reaction with the alkylation reaction between olefins and isoparaffins or the olefins and the aromatics. When it is desired to favor alkylation and to repress polymerization a relatively high mol ratio of aromatics or isoparaffins to olefins should be employed. For instance if olefin polymerization is 10 to 100 times as fast as alkylation then 10 to 100 mols isobutane to one of olefin should be used in the reaction zone. If the polymerization is only twice as fast then only 2 mols isobutane to one of olefin may suffice although higher ratios of isoparaffin to olefin always favor alkylation over polymerization as can be predicted from mathematical equations. The ratio also depends upon the individual olefin or olefins being alkylated as some olefins polymerize faster than others. For instance, isobutylene polymerizes several hundred times faster than does propylene or the other butylenes. The ratio also depends on the isoparaffin or aromatic being alkylated. For instance, isobutane alkylates about five to ten times more easily than isopentane and about one hundred times more easily than iso-octane and several times more easily than benzene. In other words, I have found that a ratio of at least three parts of isoparaffin or aromatic to one part of olefin should be maintained in the pressure reaction zone in order to minimize the degree of polymerization and at the same time favor the degree of alkylation. In most instances it is desirable to maintain even higher ratios of isoparaffins or aromatics to olefins than three to one. In fact, I have observed and in general it may be stated that the higher the ratio of isoparaffins or aromatics to the olefins present in the reaction zone the greater the degree of alkylation and the lesser the degree of polymerization of the olefins. In other words, I find that it is desirable to maintain a ratio of aromatics or isoparaffins to olefins in the order of fifty parts of isoparaffin or aromatic to one part of the olefin and in many cases I have observed that a ratio of two hundred parts of the isoparaffin or aromatic to one part of the olefin gives very favorable results.

In carrying out the process a reaction chamber is usually completely filled with liquid isoparaffin or aromatic hydrocarbon. Into this reaction chamber there is pumped a liquid isoparaffin and olefin mixture in the proportion of their reacting ratios until the desired pressure is attained in the reactor. Thus in the reaction zone there exists a ratio of the isoparaffin or aromatic to olefin of at least three to one and preferably in the order of fifty to one to two hundred to one. From the reaction zone a volume of reaction product is withdrawn at a rate less than the rate of introduction of the olefins and isoparaffins into the system because of the diminution in volume attending the alkylation reaction. The rate of introduction of feed and removal of product is adjusted or controlled to maintain a constant pressure in the reaction zone. The product removed is fractionated to separate the unreacted isoparaffins or aromatics from the alkylated hydrocarbons and these unreacted isoparaffins or aromatics are returned directly to the pressure reaction zone or they are mixed with fresh olefinic feed stock and then this mixture is compressed and forced into the reaction zone.

It is, therefore, an object of this invention to react isoparaffins and/or aromatics with olefins in the liquid phase under a pressure of at least 1000 atmospheres up to 2000 atmospheres or above or in some cases below 1000 atmospheres while maintaining a ratio of aromatics and/or isoparaffins to the olefins sufficiently high to favor alkylation and to repress polymerization.

I have also found it possible in the course of my invention to react olefins with each other in the liquid phase non-catalytically to produce higher molecular weight olefin polymers under a pressure of at least 1000 to 2000 atmospheres, although higher or lower pressures may be used, and at temperatures below the critical point, so that a liquid phase is always present. In carrying out the polymerization process a reaction chamber is usually completely filled with liquid olefins or an olefin-paraffin mixture in which the mol ratio of olefin to paraffin is greater than 1 in order to favor polymerization over alkylation. The olefin feed mixture is then pumped into the vessel until the desired pressure is attained. Reaction product is now removed from the chamber at such a rate that the pressure does not fall below a reacting minimum. The product is fractionated to separate the desired polymers and unreacted olefin is returned to the olefin feed mixture to be recycled. By proper regulation of the reaction time, reaction pressure and reaction temperature it is possible to obtain any desired degree of polymerization from liquid olefins boil-

ing in the gasoline range through the lubricating oil range to those in the wax and grease-like solid range depending, of course, upon the olefin used as charging stock and the amount of recycling of product.

It is also possible and sometimes advantageous to use catalysts in the reaction vessel of the porous solid or powder type in order to hasten the reaction and thus increase the capacity of the unit. Materials of the following nature may be employed as catalysts: charcoal, activated charcoal, promoted active and unactivated charcoals and carbons, adsorbent clays and earths, powdered or porous solid metal oxides, metal salts, metal acid salts, organic and inorganic acids. These catalysts may also be employed in the manner described above to produce isoparaffins from normal paraffins. For example, normal butane or normal pentane may be converted into isobutane and isopentane, respectively, by the use of these catalysts under the pressure and temperature conditions previously described. Furthermore, when it is desired to produce alkylated hydrocarbons which do not have the maximum knock rating or octane value I find that olefins and isoparaffins may be reacted under the foregoing high pressure, in the liquid phase and in the presence of these catalysts with the result that a high yield of alkylated hydrocarbons is produced.

This invention has been described primarily in conjunction with the production of alkylated hydrocarbons of the lower boiling ranges, however, I do not wish to limit myself in this respect since alkylated hydrocarbons boiling as high as lubricating oil or above may also be produced by the proper choice of stock.

Furthermore, I have described the production of alkylated hydrocarbons by reacting isoparaffins with olefins in the liquid phase at high pressure and at temperatures below the critical temperature, however, I do not wish to limit myself with respect to the use of isoparaffins only since I have found that alkylated hydrocarbons may be produced by reacting normal paraffins such as propane, butane, pentane or normal paraffinic hydrocarbons of higher molecular weight with olefinic hydrocarbons under the conditions specified above.

I claim:

1. A process for the production of alkylated hydrocarbons which comprises reacting a hydrocarbon having a tertiary carbon atom with an olefin in the liquid phase under a pressure of at least 1000 atmospheres in a reaction zone while maintaining a high ratio of said hydrocarbon having the tertiary carbon atom to olefin in said reaction zone, said reaction being carried out in the substantial absence of a catalyst.

2. A process for reacting isoparaffins with olefins for the production of alkylated hydrocarbons without the aid of a catalyst which comprises commingling an olefin with an isoparaffin in the liquid phase in a reaction zone maintained at a pressure of at least 1000 atmospheres, maintaining a ratio of isoparaffin to olefin in said reaction zone of at least three parts of isoparaffin to one part of the olefin, withdrawing reaction product from said reaction zone and separating alkylated hydrocarbons therefrom.

3. A process for the production of alkylated hydrocarbons by the reaction of an isoparaffin with an olefin in the absence of a catalyst which comprises introducing a mixture of olefins and isoparaffins in the liquid phase into a reaction zone maintained at a pressure between about 1000 atmospheres and 2000 atmospheres at a temperature in the order of 75° F. to 200° F. while maintaining the ratio of isoparaffins to olefins in said reaction zone in the order of at least three parts of isoparaffins to one part of olefin, withdrawing reaction product from said reaction zone and recovering alkylated product therefrom.

4. A process for the production of alkylated hydrocarbons which comprises reacting a hydrocarbon having a hydrogen atom attached to a tertiary carbon atom with an olefin in the liquid phase under a pressure of at least 1000 atmospheres while maintaining a high ratio of said hydrocarbon having the tertiary carbon atom to olefins, said reaction being carried out in the substantial absence of a catalyst, withdrawing reaction mixture from said reaction zone, removing a portion of the reaction mixture from the alkylation system and returning another portion of said reaction mixture containing unreacted hydrocarbons to said reaction zone.

5. A process according to claim 4 in which the rate of removal of reaction mixture from the alkylation system is adjusted with respect to the feed so that a substantially constant pressure is maintained in the reaction zone.

6. A method according to claim 1 in which the reaction is carried out at a temperature below the critical temperature of the hydrocarbons undergoing reaction.

7. A method for the production of alkylated hydrocarbons which comprises reacting a normal paraffin with an olefin in the liquid phase at a pressure in excess of 1000 atmospheres and at a temperature below the critical temperature of the hydrocarbons undergoing reaction, said reaction being carried out in the substantial absence of a catalyst.

KARL KORPI.

Certificate of Correction

Patent No. 2,332,321. October 19, 1943.

KARL KORPI

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, in the table, third column thereof, in that portion of the first formula directly under the heading "Theoretically possible" for



and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 15th day of February, A. D. 1944.

[SEAL]

HENRY VAN ARSDALE,
Acting Commissioner of Patents.