Patented May 2, 1944 2,347,790

UNITED STATES PATENT OFFICE

2,347,790

ALKYLATION PROCESS

Arlie A. O'Kelly, Woodbury, N. J., and Dale P. J. Goldsmith, Cambridge, Mass., assignors to Socony-Vacuum Oil Company, Incorporated, New York, N. Y., a corporation of New York

No Drawing. Application March 15, 1940, Serial No. 324,085

17 Claims. (Cl. 260—683.4)

This invention relates to the alkylation of paraffin hydrocarbons with olefine hydrocarbons. The invention particularly relates to the production of high anti-knock motor fuel by the catalytic alkylation of paraffins with olefines.

Alkylation of paraffins with olefines to produce motor fuels of high anti-knock value is known. By proper selection of the paraffins and olefines, motor fuels may be synthetically built-up which are composed of isooctanes or paraffinic compounds which approximate isooctanes in structure and thereby yield high grade motor fuels such as aviation grade. For this reason and the fact suitable gaseous starting materials are a by-product of the industry, there has been considerable activity along these lines in the last few years. As a result of the activity several processes have been suggested. For instance, Morrell U. S. P. 2,169,809 discloses a low temperature process for alkylating isoparaffins with olefines using sulfuric acid as a catalyst and keeping the temperature between about —10° and +20° C. Again Ipatieff et al. U. S. P. 2,112,847 disclose an alkylation process for isoparaffins and olefines using aluminum chloride in combination with hydrogen chloride as a catalyst and keeping the temperature at or below 0° C. In these catalytic processes only isoparaffins are alkylated, normal paraffins being unaffected. It has also been proposed to alkylate paraffins with olefines at high temperatures. However, such latter proposals have usually been concerned with non-catalytic processes, for example, Frey, U. S. P. 2,002,394 discloses that paraffins and olefines may be joined thermally at high temperatures and pressures.

It is an object of our invention to provide a high temperature catalytic alkylation process for alkylating paraffin hydrocarbons with olefine hydrocarbons.

A more specific object of our invention is to provide a process for the production of a high grade motor fuel by alkylating suitable paraffins with suitable olefines.

A most important object of our invention is to provide a process for alkylating paraffins with olefines which will alkylate normal paraffins in substantial amounts.

Our invention comprises alkylating paraffinic hydrocarbons which may be either normal or iso-paraffins or both with olefinic hydrocarbons at relatively high temperatures and pressures in the presence of certain catalysts.

The catalysts which we have discovered may be used in our invention are the metal chlorides and fluorides which are solid, stable compounds under the conditions of our process. It appears all such truly solid, stable metal chlorides and fluorides are operative. We, at present, particularly prefer such chlorides and fluorides of the metals of group II of the periodic table, and of these preferred catalysts we especially prefer catalysts consisting of or containing alkaline earth chlorides or fluorides. Our catalysts may be either a single pure compound, e. g., CaF_2 or $CaCl_2$; a mixture of our fluorides or chlorides or both, e. g., CaF_2 plus MgF_2 or $CaCl_2$ plus $BaCl_2$ or CaF_2 plus $CaCl_2$; or the catalyst may comprise metal fluorides or chlorides which are complexes or double salts of two fluorides, chlorides or both, e. g., $CaF_2.BaF_2$ or $ZnF_2.CaF_2$ or activated cryolite. In practice when employing complex or double salts, we usually use salts which are equimolecular in concentration; however, our experiments indicate that variation of one component makes no difference in the results obtained. Accordingly, in the claims where we use the term "associations" we mean to include both mixtures and compounds.

It is important to note that in the case of the metal fluoride catalysts, the conventional fluoride products obtained in commerce, except fluorspar, were generally found not to be particularly active compared to the chlorides. However the relatively inactive fluorides may be activated so that their activity is of the nature of the fluorspar and is, in general, higher than the activity of the chlorides. Activation of the relatively inactive fluoride catalysts may be accomplished, for example, by re-precipitation whereby the catalyst is produced largely in a much greater degree of subdivision than when commercially prepared. The re-precipitated catalysts thus present, if not a different, at least more active surface of contact. This activation of the fluorides by re-precipitation may be carried out, for instance, by precipitating such fluorides in dilute solution by means of sodium fluoride, drying the precipitated fluoride and then igniting it at temperatures up to about 500° C. Again activation of the complex fluoride, cryolite ($AlF_3.3NaF$), may be accomplished, for example, by digesting same in powder form with dilute hydrochloric acid or the like to remove a part of the sodium fluoride. This latter activation may be somewhat analogous to activation of clays by acids. Removal of some sodium fluoride may leave a more active surface or may leave more active surface or both.

The chloride and fluoride catalysts of our invention may be used by themselves in suitable form, e. g., granular, or, if desired or necessary.

these catalysts may be supported by suitable inert or relatively inactive carriers of a refractory nature in order to assure proper contact of the hydrocarbon gases with the catalysts in the catalytic chamber. Typical examples of refractory carriers suitable for use with our catalysts in the present invention comprise ordinary cryolite, clay, alumina, magnesium oxide, bauxite and zinc oxide. It is to be understood that when we use the term catalyst herein, we mean the actual catalytic material, viz., the chlorides or fluorides, and not the composite mass of our catalysts with refractory carriers.

The amount or proportion of our catalysts that may be used can vary over rather wide limits. In most of our operations we prefer to employ aroundt 25% to around 50% by weight with respect to the hydrocarbon charge. However amounts of 100% or even more may be used, if desired. Accordingly, it is to be understood the invention is not restricted to these amounts which are stated for illustrative purposes but rather to the general use of the catalysts to give our improved results.

In carrying out our process, we prefer, for practical operations, to use temperatures between about 600° F. and about 1000° F., although higher temperatures may be used if adequate pressures are provided, and we particularly prefer temperatures between about 800° F. and about 1000° F. The pressures at which our process is conducted should be upwards of about 2000 lbs. per sq. in., the most suitable pressure being more or less dependent upon the particular hydrocarbons and temperature involved. For instance, as it is more difficult to react the propyl radicals than higher radicals, the pressure should not be below about 3000 to 3500 lbs. for alkylating propane with propylene, and, in fact, for temperatures of 800° F. to 1000° F. we prefer to use pressures of 3000 lbs. or more for all alkylations. In general the higher the pressure the better the result. For most practical operations at the present time a pressure between about 2000 and about 5000 lbs. per sq. in., will be found to be suitable. However higher pressures may be used, for example, up to say 20,000 lbs. per sq. in., the upper limit on pressure being dictated merely by the feasibility of maintaining such pressure.

An important feature of the present invention is the fact that, contrary to many prior catalytic processes which are only capable of alkylating isoparaffins, our process is capable of alkylating normal paraffins in substantial amounts, and, in fact, normal paraffins are alkylated more efficiently by our process than are isoparaffins. Accordingly while the prior art has known highly efficient catalytic processes for alkylating isoparaffins, our process furnishes for the first time a highly efficient catalytic process for alkylating normal paraffins. The alkylation is more effective when using isoolefines, however normal olefines may be used. It is also to be understood that while the process is particularly outstanding for the alkylation of normal paraffins, the process is not limited thereto since isoparaffins are also efficiently alkylated by the process.

The paraffins and olefins to be used in our process may be derived from any suitable source as is known in the art and may be in either the pure state or in admixture with other constituents not undesirable. In order that the resulting alkylation product in the preferred operation of manufacturing motor fuels, will not be too heavy, the paraffins and olefines usually employed will be the normally gaseous paraffins and olefines, as is well understood in the art. It is preferred to use the normally gaseous paraffins and olefines of 3 or 4 carbon atoms, namely, butane, isobutane, propane, isobutylene, butylene, and propylene. Ethylene, however, may be used with any of the above paraffins or isoparaffins. A convenient and preferred source of these paraffins and olefines is the fixed gases obtained around petroleum refineries, such as the butane-butene fraction from a cracked gasoline stabilizer. These fixed gases of the refineries may furnish substantially all the desired paraffins and olefines or it may be necessary or desirable to obtain additional sources, all as is well known in the art.

As pointed out above the present process is particularly important for alkylating normal paraffins. However, there is an additional advantage in the fact that both n-paraffins and isoparaffins may be alkylated by our process. Normal paraffins and isoparaffins may be, and usually are, found in admixture with each other, therefore, it is particularly noteworthy that by our process both components of the mixture are alkylated rather than having one component (n-paraffins in the usual processes) go through the reaction as an inert diluent.

Furthermore it may be found desirable to combine the present process with one of the known processes for alkylating isoparaffins. Thus a paraffinic fraction containing substantial amounts of both normal and isoparaffins, such as a butane cut from a stabilizer, might be passed through a known "cold sulfuric acid" alkylation process whereby substantially all the isoparaffins would be efficiently alkylated, and then the unreacted n-butane, and any other normal paraffins, could be separated out and passed through our alkylation process in order to alkylate these normal paraffins or vice versa. Suitable amounts of olefines could be added in either or both steps if, and as, needed, and likewise paraffins.

In our process it is important, as in the known paraffin-olefine alkylation processes, to keep the concentration of the olefines relatively low during reaction in order to eliminate as much olefine polymerization as possible. It is advisable to maintain the olefine concentration in the charge below about 25% by liquid volume and preferably between about 10% and about 20% by liquid volume, and this may be done conveniently by slowly adding the olefines to the reaction mixture.

In order to further illustrate our invention the two following specific examples are given showing the results of alkylating (1) without a catalyst and then (2) with one of our chloride catalysts, namely, calcium chloride.

EXAMPLE I

A charge composed of 80% butane and 20% butylene by volume was processed through a high pressure continuous still at 960° F. and under 3000 pounds pressure. The synthetic-crude so produced was distilled through a packed column and the normally gaseous hydrocarbons contained with the normally liquid hydrocarbons refluxed in such a manner as to completely stabilize the synthetic-crude without material losses of the normally liquid hydrocarbons. A total yield of 95.3% with respect to olefine charged was obtained; 76.9% of this material boiled below 320°

F. and had a specific gravity of 0.695 and iodine number of 115. This aviation cut, up to 320° F., was redistilled carefully to a top temperature of 150° C. (302° F.) and the resulting product gave an octane number of 77.2 (CFR motor method) and acid heat of 92° F. The yield is 3.74 gallons per 1000 cu. ft. of charge per pass.

EXAMPLE II

The above process was repeated except that the reaction chamber of the still was packed with 4-mesh calcium chloride, U. S. P. grade and operated at 940° F. A total yield of normally liquid hydrocarbons of 129% with respect to the olefine used was obtained, 76.6% of which boiled below 320° F. The redistilled fraction boiling between 25 and 150° C., (up to 302° F.), had a specific gravity of 0.685 and an iodine number of 50. The octane number by the CFR motor method was 78.7. Acid heat was 68° F. The yield per 1000 cu. ft. of C_4 mixture is 5.14 gallons per pass.

Accordingly the two above examples show very clearly the advantages of our process. Thus it will be noted that by alkylating by our process a very substantial increase in yield is obtained, and, furthermore, it will be seen that the product obtained is substantially superior.

The following Table I shows further results obtained in alkylating n-butane with a butylene fraction (70% olefine) by our process under various exemplary conditions of operation, using various suitable catalysts (see runs 1–9), and how the results are superior over processes carried out under similar conditions but in the absence of a catalyst (see runs 10–13).

Table I

Run No.	Total charge	Olefine	Catalyst with respect to charge	Nature of catalyst	Reaction time	Reaction temp.	Reaction pressure lbs./sq. in. gauge
	Parts by volume	*Per cent*	*Per cent*		*Minutes*	°F.	
1	1,000	15	40	Anhyd. $CaCl_2$	30	800	3,300
2	800	15	25	do	30	850	2,650
3	850	20	25	do	30	875	3,300
4	850	15	25	do	30	875	3,150
5	800	15	50	do	15	900	3,250
6	800	15	50	do	30	900	3,350
7	800	16.2	40	Anhyd. $BaCl_2$	30	875	3,100
8	800	16.2	25	Anhyd. $SrCl_2$	30	875	3,000
9	850	15.0	25	Anhyd. $MgCl_2$	30	875	3,200
10	1,600	15.6	None	None	30	800	2,800
11	900	15.0	None	do	30	875	3,075
12	800	15.0	None	do	30	900	2,950
13	900	20.0	None	do	30	875	3,175

Run No.	Yield of liquid product	Yield with respect to olefine	Liquid product boiling below 320° F.	Sp. grav. of cut boiling below 320° F.	Iodine number of cut boiling below 320° F.	Gallons conversion per 1,000 cu. ft. of charge
	Parts by volume	*Per cent*	*Per cent*			
1	115	76.6	78	0.683	42	3.01
2	159	132	81	0.684	40	5.22
3	210	123.5	80.9	0.687	35	6.44
4	195	150.0	83.0	0.683	35	6.02
5	176	146.6	80.0	0.690	38	5.77
6	200	166.6	80.0	0.690	38	6.56
7	186	143.0	80.6	0.685	38	6.08
8	169	130.0	74.0	0.690	43	5.55
9	133	100.0	86.5	0.685	28	4.11
10	88	58.6	68	0.720	67	2.30
11	136	100.0	72	0.709	56	3.94
12	137	114.0	77	0.703	57	4.50
13	193	107.0	77	0.692	50	5.59

For purposes of still further illustrating our invention Table II is given below showing results obtained by our process under various exemplary conditions of operation using various suitable fluoride catalysts (see runs 1–9), and how the results are superior over processes carried out under similar conditions but in the absence of a catalyst (see run 10). All of the runs in Table II were made with normal butane and normal butylene except in run 4 where normal butane and isobutylene were used.

Table II

Run No.	Volume charge to bomb	Olefine	Catalyst with respect to charge	Nature of catalyst	Reaction time	Reaction temp.	Reaction pressure in lbs./sq. in. gauge
	Parts by volume	*Per cent*	*Per cent*		*Minutes*	°F.	
1	800	15	25	Fluorspar	30	875	3,350
2	800	15	25	Activated cryolite	30	875	3,300
3	800	15	21	Zinc cryolite	30	875	3,350
4	900	15	18	Fluorspar	30	850	3,500
5	800	15	21	Barium fluoride	30	850	3,450
6	800	15	21	$ZnF_2.CaF_2$	30	875	3,325
7	800	15	21	$CaF_2.BaF_2$	30	875	3,175
8	800	15	21	$CaF_2.SrF_2$	30	875	3,212
9	800	15	21	MgF_2	30	875	3,275
10	900	15	None	None	30	875	3,075

Table II—Continued

Run No.	Volume yield liquid product	Yield with respect to olefins	Liquid product boiling below 320° F.	Sp. grav. of cut boiling below 320° F.	Iodine number of cut boiling below 320° F.	Gallons conversion per 1,000 cu. ft. of charge
	Parts by volume	*Per cent*	*Per cent*			
1	178	148.3	81.4	0.685	46	7.02
2	150	125.0	80.0	0.685	38	5.81
3	177	147.5	81.9	0.686	42	6.96
4	205	151.1	87.8	0.685	20	7.18
5	172	143.3	87.2	0.685	30	6.77
6	185	154.1	82.1	0.684	35	7.28
7	177	147.5	81.9	0.684	35	6.96
8	188	156.6	79.9	0.684	35	7.32
9	156	130.0	76.9	0.684	35	6.14
10	136	100.7	72.0	0.709	56	4.75

We claim:

1. The process of alkylating paraffinic hydrocarbons with olefinic hydrocarbons which comprises contacting the paraffins and olefins under alkylating conditions in the presence of an active alkylation catalyst consisting essentially of solid material selected from the group consisting of compounds of the general type MX, and associations between such compounds, wherein M is a metal and X is chlorine or fluorine and wherein MX is a metal halide that is a solid, stable compound at 800° F., and controlling the concentration of olefins during reaction so that the principal reaction is said alkylation.

2. The process of claim 1 wherein at least a substantial portion of the paraffinic hydrocarbons which are alkylated are normal paraffins.

3. The process of claim 1 wherein M is a metal of group II of the periodic table.

4. In a process of synthesizing hydrocarbons of gasoline-boiling range by alkylating light paraffinic hydrocarbons with light olefinic hydrocarbons the improvement which comprises alkylating the light paraffins and olefins in the presence of an active alkylation catalyst consisting essentially of a member of the group consisting of alkaline earth metal chlorides and mixtures of said chlorides, and controlling the concentration of olefins during reaction so that the principal reaction is said alkylation.

5. In a process of synthesizing hydrocarbons of gasoline-boiling range by alkylating light paraffinic hydrocarbons with light olefinic hydrocarbons the improvement which comprises alkylating the light paraffins and olefins in the presence of an active alkylation catalyst consisting essentially of a member of the group consisting of fluorides of metals of group II of the periodic table and mixtures of said fluorides, and controlling the concentration of olefins during reaction so that the principal reaction is said alkylation.

6. In a process of synthesizing hydrocarbons of gasoline-boiling range by alkylating light paraffinic hydrocarbons with light olefinic hydrocarbons the improvement which comprises alkylating the paraffins and olefins at a temperature above about 600° F. and at a pressure above about 2000 pounds per square inch in the presence of an active alkylation catalyst consisting essentially of solid material selected from the group consisting of compounds of the general type MX, and associations between such compounds, wherein M is a metal and X is chlorine or fluorine and wherein MX is a metal halide that is a solid, stable compound at 800° F., and controlling the concentration of olefins during reaction so that the principal reaction is said alkylation.

7. In a process of synthesizing hydrocarbons of gasoline-boiling range by alkylating light paraffinic hydrocarbons with light olefinic hydrocarbons the improvement which comprises alkylating the paraffins and olefins at a temperature between about 600° F. and about 1000° F. and at a pressure above about 2000 pounds per square inch in the presence of an active alkylation catalyst consisting essentially of solid material selected from the group consisting of compounds of the general type MX, and associations between such compounds, wherein M is a metal and X is chlorine or fluorine and wherein MX is a metal halide that is a solid, stable compound at 800° F., and controlling the concentration of olefins during reaction so that the principal reaction is said alkylation.

8. The process of claim 7 wherein M is a metal of group II of the periodic table.

9. The process of claim 7 wherein normal paraffins are the predominant type of paraffinic hydrocarbons which are alkylated.

10. The process of claim 7 wherein the temperature is between about 800° F. and about 1000° F. and the pressure is above about 3000 pounds per square inch.

11. In a process of synthesizing hydrocarbons of gasoline-boiling range by alkylating light paraffinic hydrocarbons with light olefinic hydrocarbons the improvement which comprises alkylating the paraffins and olefins at a temperature between about 800° F. and about 1000° F. and at a pressure above about 3000 pounds per square inch in the presence of an active alkylation catalyst consisting essentially of a member of the group consisting of alkaline earth metal chlorides and mixtures of said chlorides, and controlling the concentration of olefins during reaction so that the principal reaction is said alkylation.

12. The process of claim 11 wherein normal paraffins are at least a substantial portion of the paraffinic hydrocarbons alkylated.

13. In a process of synthesizing hydrocarbons of gasoline-boiling range by alkylating light paraffinic hydrocarbons with light olefinic hydrocarbons the improvement which comprises alkylating the paraffins and olefins at a temperature between about 800° F. and 1000° F. and at a pressure above about 3000 pounds per square inch in the presence of an active alkylation catalyst consisting essentially of a member of the group consisting of fluorides of metals of group II of the periodic table and mixtures of said fluorides, and controlling the concentration of olefins during reaction so that the principal reaction is said alkylation.

14. The process of claim 13 wherein normal paraffins are at least a substantial portion of the paraffinic hydrocarbons alkylated.

15. The process of synthesizing hydrocarbons of gasoline-boiling range by alkylating light normal- and iso-paraffins contained in a hydrocarbon

mixture with light olefins which comprises alkylating the predominant portion of isoparaffins of said mixture in one step where alkylation of isoparaffins with olefins is the principal reaction and alkylating the predominant portion of normal paraffins of said mixture in a separate step at a temperature between about 600° F. and about 1000° F. and at a pressure above about 2000 pounds per square inch in the presence of an active alkylation catalyst consisting essentially of solid material selected from the group consisting of compounds of the general type MX, and associations between such compounds, wherein M is a metal and X is chlorine or fluorine and MX is a metal halide that is a solid, stable compound at 800° F., and controlling the concentration of olefins during reaction in said normal paraffin alkylating step so that the principal reaction in this step is said alkylation of normal paraffins.

16. The process of claim 15 wherein M is a metal of group II of the periodic table.

17. The process of claim 13, wherein the metal fluoride is an activated metal fluoride.

ARLIE A. O'KELLY.
DALE P. J. GOLDSMITH.