

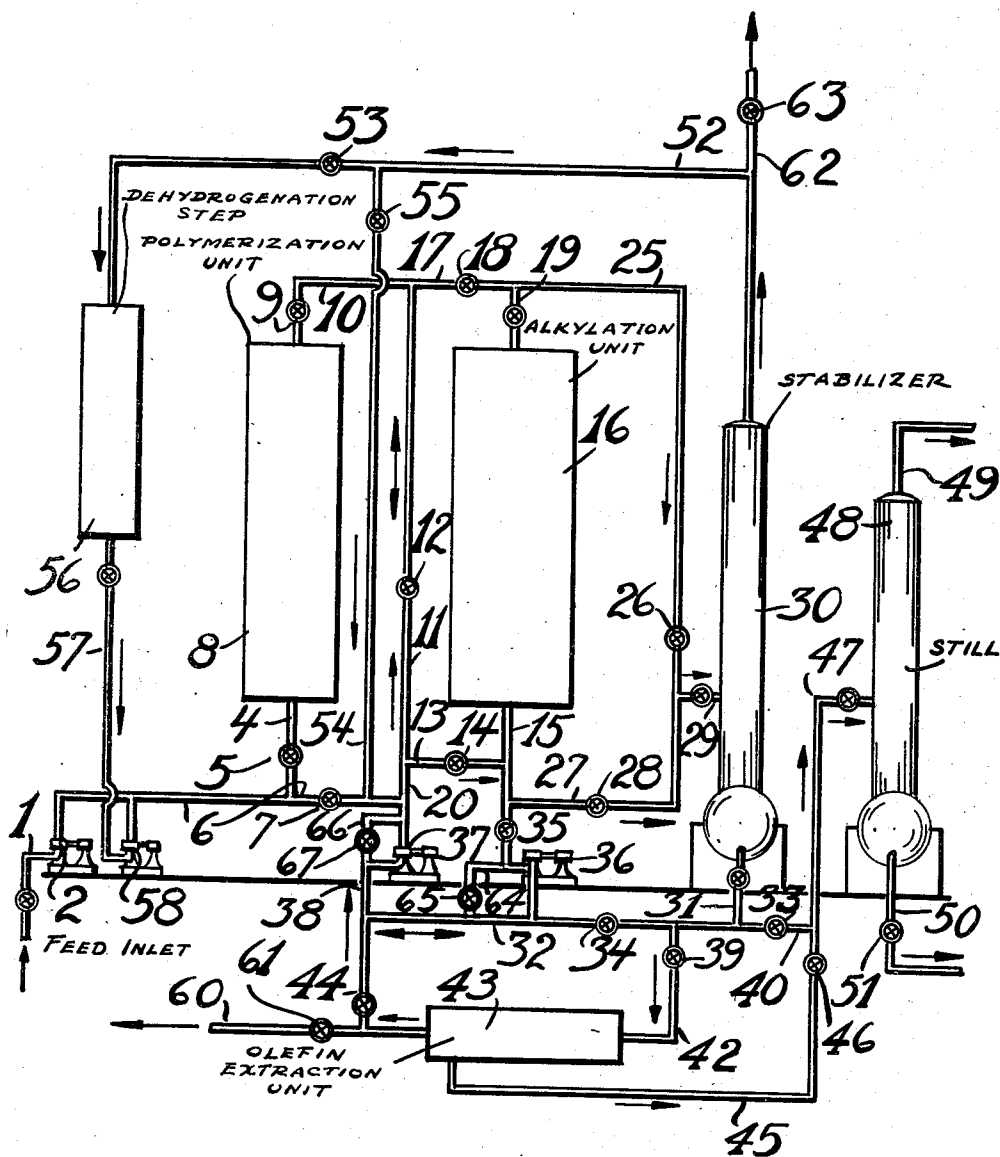
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PRODUCTION OF LIQUID SATURATED HYDROCARBONS

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PRODUCTION OF LIQUID SATURATED
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This invention relates to improvements in the production of highly desirable components of motor fuels and pertains particularly to the production of relatively low boiling saturated aliphatic hydrocarbons which have been found to be useful in the preparation of gasolines.

It has heretofore been proposed to produce motor fuel constituents according to a number of well known processes, such as thermal and catalytic cracking of heavier hydrocarbons, polymerization of normally gaseous olefins, followed by hydrogenation, treating of crude and straight run gasoline cuts with olefins to improve their octane number by alkylating the aromatic constituents thereof with normally gaseous olefins, etc. It has been found possible to react paraffinic hydrocarbons with olefins to produce saturated hydrocarbons boiling within the motor fuel range. This reaction has been denoted as alkylation. It is therefore readily apparent that a saturated branched chain normally liquid paraffin may be produced directly by alkylating a normally gaseous branched chain paraffin, for example isobutane, by treating such a compound with a normally gaseous mono-olefin without the necessity of including a hydrogenation treatment in the process as would be the case where a polymerization process had been used.

Another advantage of the use of an alkylation process in contrast to the well known polymerization process lies in the fact that the petroleum industry is constantly seeking methods whereby it may be possible to utilize by-products of the industry and in this respect, alkylation is a distinct advance in the art. Large supplies of field butanes, refinery C₄ cuts from cracking units, debutanizer units, etc., each containing substantial quantities of gaseous olefins and paraffins, both straight and branched chain, are available. Such gaseous mixtures have heretofore been fed to polymerization processes which are able to utilize only the olefinic content of the mixtures. As a consequence, the industry has found it expedient to dehydrogenate the inert paraffinic gases coming from such units, to convert them to olefins and to then refeed these gases to the polymerization processes. Such a procedure is unnecessary in a comparable alkylation process, and the expensive dehydrogenation of paraffins and subsequent necessary hydrogenation of the condensation products is eliminated, yet a gasoline of substantially the same or higher octane value is produced.

It is an object of the present invention to provide a process for the production of premium

grade motor fuels by the reaction of isoparaffins boiling below the desired gasoline range or mixtures thereof with monomeric mono-olefins boiling below the desired gasoline range, dimers, trimers, tetramers, etc. of said monomeric mono-olefins or mixtures thereof.

It is a further object of the invention to so carry out the alkylation of the isoparaffins that it is possible to obtain substantially twice as large a yield of premium grade gasoline based upon the amount of olefins reacted as would be obtained in the conventional olefin polymerization processes.

To accomplish such objects, it is a feature of the present invention to carry out the reaction under optimum reaction conditions in the presence of alkylation catalysts which have been found to be particularly effective in promoting the desired reactions. It is obvious that the optimum reaction conditions will vary for each particular catalyst employed. In general, it may be said that alkylation conditions predominate when the feed rates are adjusted to provide longer contact time than would be used in corresponding polymerization reactions. Better yields of saturated products are obtained, however, where the olefin concentration is somewhat lower than in the corresponding polymerization reactions.

Likewise it was found that the more intimate the contact between the reactants, the higher the yields of alkylated products. The feed stock is preferably introduced into the reaction zone through jets, porous thimbles, turbo-mixers and the like.

It was sometimes found to be advantageous in the production of high octane saturated fractions suitable for motor fuels to return to the reaction zone the heavier alkylated fractions and the fractions boiling intermediate the reactants and the desired motor fuel fraction removed from the system as the final product. It is sometimes desirable to leave the products formed intermediate the reactants and the C₈ cut in the final product since the C₅, C₆ and C₇ saturated hydrocarbons are readily volatilized and have excellent anti-knock properties. Likewise any unreacted reactants are separated from the desired fraction and returned to the reaction zone. Increased yields of the desired fraction result whether this recycle step is carried out continuously or intermittently, whether only part or all of the recycle stock is fed into the alkylation zone together with the fresh feed.

The invention is not limited to the use of reactants from any particular source. Single paraffinic and olefinic hydrocarbons may be em-

ployed. However, it is commercially more feasible to use mixtures of hydrocarbons containing the necessary paraffins and olefins as part of their constituents. The reacted mixture from catalytic and thermal polymerization units, including the gaseous constituents thereof, may be directly introduced as reactants into the alkylation process of the invention. Gaseous mixtures evolved from catalytic and thermal cracking units may also be advantageously employed. It is an essential requirement in the practice of the invention that the feed stock contain at least one isoparaffin, preferably boiling below the boiling point of the desired final product fraction, and that the feed stock contain at least one mono-olefin. Partially dehydrogenated field butanes, refinery C₃-C₆ and C₄ cuts, saturated paraffinic mixtures containing isoparaffins and which have been enriched with mono-olefins from extraneous sources, etc. are suitable. The invention contemplates the reactions of isobutane, isopentane, etc. with ethylene, propylene, normal or isobutylenes, normal and branched chain amylenes, the dimers, trimers, tetramers, etc., codimers, cotrimers, cotetramers, etc., cross polymers, interpolymers, etc. of these olefins and the like. It is preferable, to insure high yields of alkylation products, to have between about 2 and about 12 mols of isoparaffin in the reactor per mol of mono-olefin present. Likewise, from 4 to 24 mols of isobutane should be contacted with each mol of diisobutylene, etc. This avoids excessive formation of high boiling compounds.

A particularly desirable catalyst is the metal halide-aluminum halide complex wherein the aluminum halide is present in from about 1.1 mols to about 2.5 mols per mol of metal halide. Specifically, AlCl₃-NaCl in varying molecular proportions has been found to be a particularly effective catalyst. Likewise catalysts composed of KBr-FeCl₃ or KBr-FeBr₃ complexes have been very effective in promoting alkylation. Other similar double salt complexes which are within the scope of the invention are lithium chlor-aluminate, antimony bromaluminate, sodium bromaluminate, mercury bromaluminate, potassium chloraluminate, etc. These complex double salts may be prepared by mixing the alkali metal halide, alkaline earth metal halide, or other corresponding metal halide, for example sodium chloride, with slightly more aluminum halide, for example, aluminum chloride, than is necessary for the catalyst of the desired mol ratio. The excess aluminum chloride is added in order to compensate for losses due to volatilization on heating. The mixture is heated in an open vessel until fusion occurs and a clear liquid results. At a temperature of 400-450° F. some solid sodium chloride usually is present and the liquid portion of the mixture is therefore poured off through a wire gauze.

Such a catalyst may advantageously be impregnated or deposited upon carriers either inert or activated with sulfuric, hydrochloric, and hydrofluoric acids or acidic gases such as HCl, SO₃, SO₂, HF, etc. Suitable aluminous and/or siliceous materials are activated alumina, silica gel, bauxite, fuller's earth, bentonite, kieselguhr, pumice, celite, Sil-O-Cel, infusorial earth, Montmorillonite, Marsil clays, Tonsil, Super Filtrol, activated Floridin, etc.

Where the double salt type complex is used as the catalyst, it has been found that they eventually lose their catalytic alkylation activity under the operating conditions of the invention.

Any suitable reactivation or regenerative process may be employed, for example, treatment of the catalyst mass with inorganic acidic gases such as the hydrogen halides, HCl, HBr, or the free halogens, Cl₂ and Br₂, or by treatment with heat and pressure to free the pores of the catalyst mass of residual heavier hydrocarbon compounds and decomposition residues.

In general, for best results, it may be stated that where the double salt complexes are employed as catalysts, all other conditions remaining substantially the same, the higher the pressure used, the more critical the changing of rate of feed becomes and the more change in the composition of the final product results. The feed rate may vary between about 0.5 to about 20 volumes/volume/hour but preferably it is maintained between about 0.7 and about 6.2 volumes/volume/hour. All other things being the same, and using a double salt complex as a catalyst, the higher the pressure, the more saturated the product becomes and the higher the yield based upon the olefinic content of the feed. Pressures ranging from between about 100 and about 3000 lbs./sq. in. gauge have been tried but pressures of from 1000 to 3000 lbs./sq. in., preferably between about 1800 lbs./sq. in. gauge and about 3000 lbs./sq. in. gauge are most advantageous. Using the double salt complex as catalysts, temperatures of from about 300 to about 500° F. and total reaction times of from about 5 minutes to about 1 hour are employed, but it is preferred to use temperatures of about 400° F. and total reaction times of about 7 minutes to about 45 minutes. In general, the longer the contact time that is maintained the better the yield that will be produced. Olefinic concentrations of from about 5% to about 40% of the total hydrocarbon content of the feed stock are contemplated. Ordinarily, it is desirable to employ a relatively small concentration of olefins since the problem of heat dissipation from the exothermic reaction becomes more easily solved thereby and also by such means undesirable polymerization reactions are inhibited.

Experimental evidence points to the theory that the mechanism of the alkylation reaction involves the intermediate formation of polymers or copolymers by the mono-olefins followed by the degradation of these higher polymers and copolymers into an active or nascent state which permits their reaction with the paraffins present. The same mechanism appears to hold true where the reaction occurs between a preformed polymer or copolymer and a paraffin. While the theory of the invention appears to be as described, it is to be distinctly understood that the invention is not limited to any theory of operation and is restricted only insofar as indicated by the appended claims.

No specially designed apparatus is necessary for the successful carrying out of the invention. Conventional apparatus now customarily used in effecting acid polymerizations is quite suitable. In the case of effecting alkylations under pressures of 1800 to 3000 lbs./sq. in. and temperatures of around 400-500° F., it has been found to be advantageous to introduce the reactants into the catalyst chamber from the top and allow them to flow through the reactor in a downward direction whereas in cases where the alkylation proceeds at room temperatures or slightly below and under substantially atmospheric pressure, it is advantageous to introduce the reactants into the catalyst chamber at the bottom and remove

the reacted mixture from the top of the reactor. The fractionation of the resultant products is accomplished in conventional fractionating towers. Any excess or unreacted reactants may be recycled to the catalytic reactor after first being mixed with the fresh feed just prior to its introduction into the catalyst chamber. If desired recycled reactants may be subjected to a dehydrogenation treatment prior to their mixing with fresh feed. It is apparent that the process and apparatus may be readily adapted to the carrying out of a continuous operation. Such a type of process and apparatus is familiar to those working in the art and it is to be understood that conventional and/or minor variations therefrom may be made without departing from within the spirit or scope of the present invention.

For illustrative purposes and not with the intention of restricting the invention thereto, there is shown in the accompanying drawing a diagrammatic illustration or flow sheet representing one specific process adapted to carrying out the invention. The process may be adapted to the use of liquid, gaseous, or solid catalysts as the exigencies of each particular case might require. It is to be distinctly understood, however, that the invention in its broader aspects is not restricted to any particular type of apparatus or to any particular flow plan, but that the flow plan hereinafter described is only intended to aid in a further understanding of applicants' invention.

Referring to the drawing, the olefins and paraffins to be subjected to alkylation are introduced into the system through charging line 1 by means of pump 2. The olefinic-paraffinic hydrocarbon mixture may then be passed through pipes 6, 20, 13 and 15 controlled by valves 7 and 14 directly into alkylation reactor 16 which is filled with the desired catalyst and provided with suitable heating or cooling jackets (not shown), or, if it is desired to polymerize a portion of the olefinic content of the feed prior to the alkylation reaction, valve 7 may be closed and the feed passed through line 4 controlled by valve 5 into any suitable conventional polymerization reactor. The olefinic portion of the feed is converted into polymers thereof while the paraffinic portion remains unchanged. The resultant mixture of polymers and paraffins exits through pipe 10 controlled by valve 9. Valve 18 is closed and the polymerized mixture enters the alkylation zone through lines 10, 13 and 15 controlled by valves 2 and 14.

The reacted mixture is discharged from the alkylation reactor through pipes 19 and 25 controlled by valve 26. Valve 28 is closed and the reacted mixture is passed into the stabilizer 30 by means of pipe 29.

It is sometimes advantageous from the standpoint of yields, quality of product, etc. to carry out the alkylation reaction by directing the reactants into the alkylation reactor so that they will flow through the catalyst in the opposite direction from that described above. In such a case, reactants not passing through polymerization zone 8 are flowed through pipe 6 controlled by valve 7 into pipes 20, 11, 17 and 19, valves 12 and 18 being open and valves 5, 9, 14 and 26 being closed. The reacted mixture discharged from the alkylation zone 16 passes by means of lines 15, 27 and 29 into stabilizer 30. If it is desirable to first subject the olefinic-paraffinic hydrocarbon mixture to a preliminary polymerization treatment, valves 7, 12, 14 and 26 remain

closed and valves 5, 9, 18 and 28 are opened so that the flow is through pipes 4, 10, 17 and 19 into the alkylation reactor 16.

It is sometimes found advantageous to allow the ultimately complete alkylation reaction to proceed in small increments of the total final conversion and to recycle the reactants continuously through the alkylation zone 16 through the circuit of pipes 15, 19, 17, 11, 20, 38 and 32 provided with pump 37. Pump 36 is by-passed by allowing the flow through pipe 64 and valve 65. It is contemplated to so recycle whether the reactants are contacted with the alkylation catalyst downflow or upflow, pump 36 being provided for the reversed direction of flow from that above indicated. For downflow operation pump 37 is by-passed by allowing the flow through pipe 66 and valve 67. A portion of the reacted mixture so recycled is withdrawn either intermittently or continuously, the rate of withdrawal being adjusted to insure adequate time for substantial completion of the alkylation.

Any suitable method of dispersing the reactants into reactor 16 is contemplated, such as jets, turbo mixers, atomizers, porous thimbles, etc.

The reacted mixture enters stabilizer 30 through pipe 29. The temperature of the stabilizer is maintained at such a point as to insure the removal of normally gaseous hydrocarbons from the normally liquid hydrocarbons. The gases comprising paraffins, and at times some olefins, leave the stabilizer by means of pipe 52 controlled by valve 53. If desired, these gases coming from the stabilizer may be reintroduced directly into the fresh feed pipe 6 by closing valve 53 and opening valve 55 so that the gases are conducted to pipe 6 by means of pipe 54, or the gases may be bled from the system through pipe 62 and valve 63, valves 53 and 55 being closed. A compressor unit (not shown) is inserted in line 54 to liquefy the gases prior to their introduction into feed line 6. It is preferable, however, to close valve 55 and open valve 53 so that these gases which are predominantly paraffinic in character are passed to a dehydrogenation step 56 of any suitable conventional design, wherein the gaseous paraffins are converted into gaseous olefins either in whole or in part, the gases are liquefied, hydrogen, methane, C₂ and C₃ fractions are removed, and the remaining gases leaving the dehydrogenation step 56 by pipe 57 are pumped by means of pump 58 into the fresh feed line 1.

The normally liquid products leaving the bottom of stabilizer 30 by means of pipe 31 may be conducted directly to the gasoline still 48 through lines 40 and 47 by opening valve 33 and closing valve 46, conducted directly back to the alkylation unit 16 by means of pipe 32 by closing valves 33, 39 and 35 and opening valve 34, thereby effecting further conversion before final treatment, or conducted by means of pipe 42, closing valves 33 and 34 and opening valve 39, to an olefin extraction unit 43 wherein by any suitable conventional treatment, such as treatment with a solvent, for example, sulphur dioxide, any normally liquid olefinic polymers that might be present are removed. Free olefins from this unit may be removed to storage (not shown) through line 60 or they may be directly returned by means of pipes 44, 38 and 20 to the alkylation unit 16. It is to be understood that when the bottoms from stabilizer 30 are conducted back to the alkylation unit 16, only a portion of these bottoms are so recycled at any one time, the remainder

of the bottoms being treated according to any of the alternative methods above suggested.

The liquid paraffinic fraction is conveyed to gasoline still 48 by means of pipes 45 and 47 upon opening valve 46.

Gasoline still 48 is maintained at suitably controlled temperatures such that a desired gasoline fraction is removed to storage through pipe 49 and the heavier fraction removed through line 50 by opening valve 51.

The following table is a compilation of data from several experiments:

Table I

Example	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Catalyst	AlCl ₃ NaCl pum-ice	AlCl ₃ NaCl on celite												
Moles AlCl ₃ /Mol NaCl	1.1	1.1	1.7	1.1	1.2	1.7	1.8-2.0	1.1	1.8-2.0	2.0	1.8	1.1	1.7	2.0
Grams active catalyst/100 grams feed	3.5	13	13	21	40	25	6	25	30	14	10	18	18.4	19
Reaction time, hours	0.15	0.15	0.17	0.18	0.72	0.18	0.185	0.20	0.20	0.18	0.18	0.185	0.18	0.20
Temperature, °F	357	390	392	392	396	395	390-407	400	398	397	393	402	406	399
Pressure, lbs./sq. in., gauge	1000	1000	1000	1750	1800	1800	1800	1800	1800	1800	1800	3000	3000	3000
Throughput, v./v./hour	3.5	3.5	2.9	2.8	0.7	2.8	2.7	2.5	2.5	2.8	2.8	2.7	2.8	2.5
Reactant feed:														
Weight percent isobutylene	8.9	8.9	8.8	8.6	8.6	8.3	8.3	8.3	8.3	8.3	8.3	8.9	8.5	8.3
Weight percent n-butylene	1.1	1.1	1.4	1.1	1.1	1.2	1.2	1.2	1.2	1.2	1.2	1.0	1.6	1.2
Weight percent diisobutylene	90	90	89.8	90.3	90.3	90.5	90.5	89.4	89.4	90.7	88.5	90.1	87.6	90.5
Weight percent isobutane											11.5			
Weight percent ethylene													2.3	
Weight percent tert. butyl chloride														
Weight percent heavy reacted products														
Weight percent olefin reduction	91	89	89	100	100	98	94					98	100	98
C ₃ +product:														
Weight percent on isobutylene	116	145	145	170	201	201	184-200	139	125	175		193	207	206
Weight percent on diisobutylene														
Weight percent on ethylene														
Bromine No.	53	39	26	22	14	25	14	21	6	22	186	32	2.5	7
Weight percent saturates (total)	62	70	76	79	92	85	83	86	95	79	99	67	98	95
Weight percent C ₅ -fraction	5	15	9	23	22.5	35	28.3	18	32	20	22	21	34	28
Weight percent C ₆ -fraction	15	11	15	12	10	12	12.2	9	14	14	29	10	14	14
Weight percent C ₇ -fraction	15	11	9	9	10	9	9.8	7	9	8	9	8	12	10
Weight percent C ₈ -fraction	30	32	21	28	32.5	20	21.0	31	26	23	15	30	27	18
Weight percent C ₉ and higher	35	31	46	28	25	24	28.7	35	19	35	25	31	13	30
Octane No. C ₅ -C ₈							84							

Example 7 represents a composite run from four or five separate experiments run under substantially identical conditions and with substantially identical reactants. The products of the individual runs were combined and the properties and composition of the products described are of those composite products.

In some of the examples, where the bromine number has been stated to be one, it has experimentally been determined as being between 0.5 and 1.

The method of preparation of the NaCl-AlCl₃ on celite catalyst has been previously described. The mol ratio of AlCl₃ to NaCl indicates that 1.7, Example 3, is the best ratio for alkylation, all other conditions being the same. Celite also appears to be superior to pumice as a carrier for the double salt complexes.

At 1800 lbs./sq. in. the 1.7 ratio gives an increase in yield and degree of alkylation over the 1.1 ratio; a yield of 201% (85% saturated) as compared to 170% (79% saturated). Also more C₅-C₈ product was found using the higher ratio.

A temperature of around 400° F. has been found to be suitable when using the double salt complexes as catalysts. Higher yields are obtained as the pressures are increased within reasonable limits. A lower percentage of saturation is noted at the higher pressures but more than 99% of the products boiling below 260° F. was saturated in the higher pressure experiments.

From the above experimental data it appears that a rate of feed of about 1 v./v./hour is

required for maximum yields of saturated product when using a double salt complex lean in AlCl₃ whereas yields practically as good can be obtained at 2.8 v./v./hour using a double salt complex richer in AlCl₃.

It is to be understood that where mention is made of "double salt complexes", or the equivalent thereof, in the description and claims, it is intended to include the mixtures of metal halide-aluminum halide and metal halide-iron halide compositions containing other than the requisite molecular quantities of each component for

known compositions, although it is realized that such mixtures containing other than equimolecular amounts of each of the components may not be considered to be true double salt complexes but may be considered, at least partially, physical mixtures of the components thereof. The description and claims are to be construed in such a light for want of a more convenient term to cover the catalysts involved.

The above examples are intended to be but illustrative of the concept of the invention and they are not to be considered as limiting in any way the scope of the invention.

The nature and objects of the present invention having been thus fully described, what is claimed as new and useful and desired to be secured by Letters Patent is:

1. A process for the production of a composition composed predominantly of saturated liquid hydrocarbons boiling in the gasoline range which comprises reacting a mixture containing at least one low boiling isoparaffin with at least one member of the group consisting of normally gaseous mono-olefins, dimers, trimers, tetramers and higher polymers thereof, co-, inter-, and cross-dimers, trimers, tetramers, and higher analogous polymers thereof, in the presence of a catalyst taken from the group consisting of a catalyst of the type QX.ZX wherein Q stands for a metal other than aluminum, Z stands for aluminum, the molar ratio of ZX to QX being greater than 1 to 1, and X is a halogen.

2. Process as in claim 1 wherein the isoparaffin

is present in a substantial molecular excess over the amount of olefinic constituents present.

3. Process as in claim 1 wherein the alkylation is conducted continuously and at least a part of any unreacted reactants are returned to the original alkylation reactions.

4. A process for the production of a composition composed predominantly of saturated normally liquid hydrocarbons boiling in the gasoline range which comprises reacting a mixture containing at least one low boiling isoparaffin with at least one member of the group consisting of normally gaseous mono-olefins, dimers, trimers, tetramers and high polymers thereof, co-, inter-, and cross-dimers, trimers, tetramers and higher analogous polymers thereof, in the presence of a catalyst QX.ZX wherein Q stands for a metal other than aluminum, Z stands for aluminum and X stands for a halogen, the ratio of ZX to QX being greater than 1 to 1, said catalyst being deposited upon a carrier.

5. Process as in claim 4 wherein the carrier is celite.

6. Process as in claim 4 wherein the alkylation is carried out at a temperature between about 300 and about 500° F.

7. Process as in claim 4 wherein the alkylation is carried out at a temperature between 300 and about 500° F. under a gauge pressure of between about 1000 and about 3000 lbs./sq. in. and the catalyst is carried on celite.

8. Process as in claim 4 wherein the alkylation is carried out at a temperature of between about 300 and about 500° F., the catalyst is supported on celite and the reactants are passed over the catalyst at a rate of from between about 0.5 and 7.0 volumes/volume/hour.

9. A process for the production of a composition composed predominantly of saturated liquid hydrocarbons boiling within the gasoline range which comprises reacting isobutane with a normally gaseous mono-olefin in the presence of NaCl-AlCl₃ double salt complex supported on celite, the mol ratio of AlCl₃ to NaCl being between about 1.1 and about 2.0 to 1, at a tem-

perature between about 300 and about 500° F. at a pressure between about 1000 and about 3000 lbs./sq. in. gauge at a throughput of between about 0.5 and about 7.0 volumes/volume/hour.

10. Process as in claim 9 wherein the olefin is isobutylene.

11. A process for the production of a composition composed predominantly of saturated liquid hydrocarbons boiling within the gasoline range which comprises reacting a low boiling isoparaffin with a dimer of a normally gaseous mono-olefin in the presence of NaCl-AlCl₃ double salt complex supported on celite, the mol ratio of AlCl₃ to NaCl being between about 1.1 and about 2.0 to 1, at a temperature between about 300 and about 500° F. at a pressure between about 1000 and about 3000 lbs./sq. in. gauge at a throughput of between about 0.5 and about 7.0 volumes/volume/hour.

12. Process as in claim 11 wherein the reactants are isobutane and diisobutylene and the isobutane is present in substantial molecular excess over the diisobutylene.

13. A process for the production of normally liquid saturated hydrocarbons, which comprises reacting an iso-paraffin with a mono-olefin in the presence of a catalyst of the type QX.ZX, wherein Q stands for a metal other than aluminum, Z stands for aluminum, the molar ratio of ZX to QX being greater than 1 to 1, and X stands for a halogen.

14. A process for the production of normally liquid hydrocarbon mixtures composed predominantly of saturated branched chain compounds boiling within the gasoline range, which comprises reacting at least one iso-paraffin with at least one mono-olefin in the presence of a catalyst of the type QX.ZX, wherein Q stands for a metal other than aluminum, Z stands for aluminum, the molar ratio of ZX to QX being greater than 1 to 1, and X stands for a halogen, under super-atmospheric conditions of temperature and pressure.

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