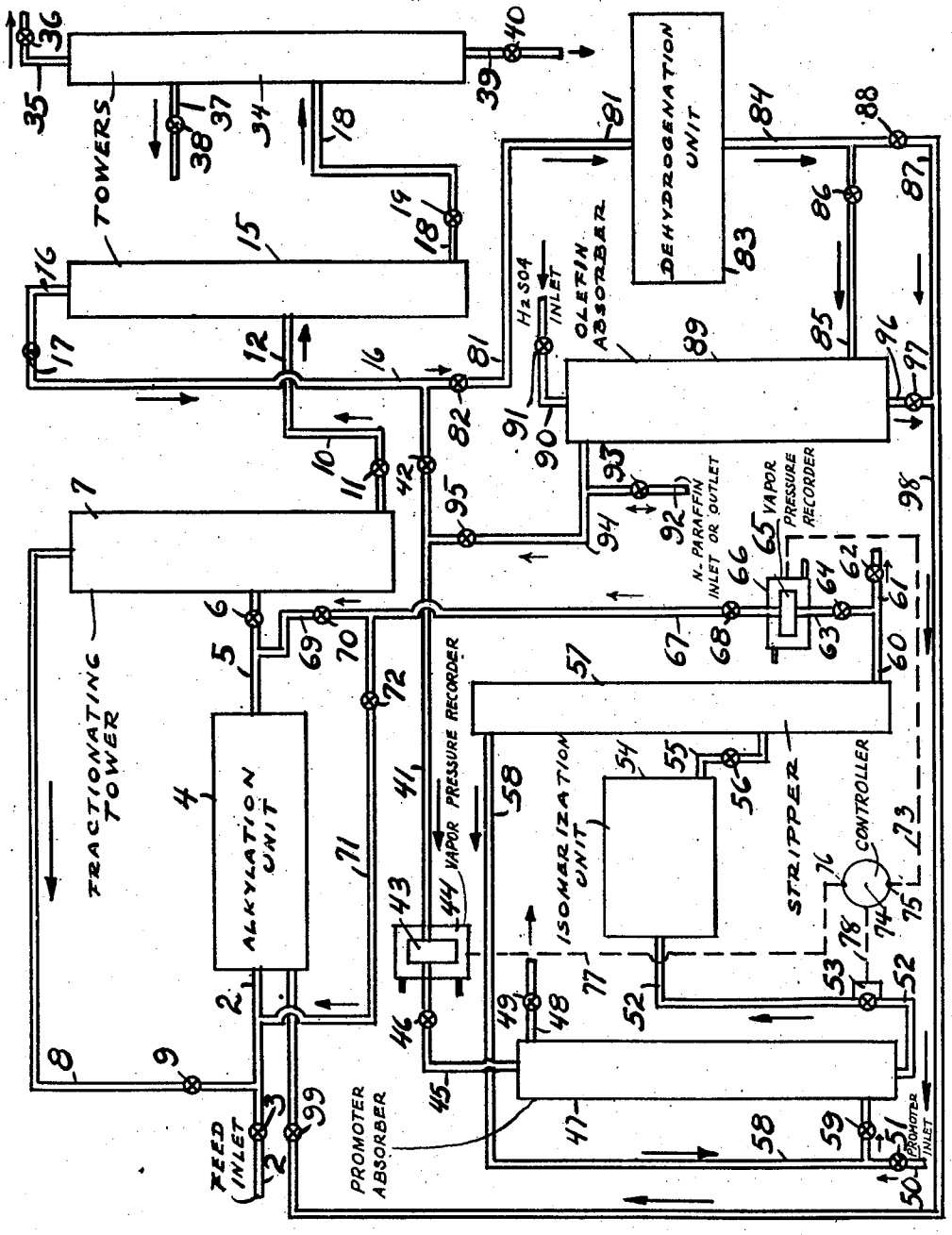
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HYDROCARBON SYNTHESIS

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HYDROCARBON SYNTHESIS

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The present invention relates to the production of hydrocarbons by catalytic means, said hydrocarbons being highly useful in the supplying of motor fuels or in the production of motor fuels made by alkylation processes. A more particular aspect of the present invention resides in a combination process in which feed stocks containing isoparaffins, normal paraffins and olefins, both straight and branched chain, are subjected to catalytic alkylation reactions to produce alkylate boiling within the motor fuel range in which the relatively inert normal paraffins are separated from the reaction mixture, subjected either to an isomerization to produce further quantities of isoparaffins for alkylation or to a catalytic dehydrogenation to produce further quantities of olefins which are likewise useful in alkylation, or the normal butanes are split, a portion going to a catalytic isomerization reaction and the remainder going to a catalytic dehydrogenation reaction.

In the petroleum industry it has often been difficult to adequately balanced feed stocks suitable for alkylation so as to produce from given quantities of recycle gases available the highest yields of aviation gasoline or high octane number motor fuels by the alkylation method. Particularly in small refinery operations there may be an apparent scarcity of some particular component required in the alkylation reaction. Thus, for example, isoparaffins or the olefin, or both, may be relatively scarce although large quantities of basic materials from which these prospective reactants may be produced are available. It is therefore desirable, particularly to the small refinery, to have available a process which utilizes to a most economical advantage the refinery gases available and to produce from these refinery gases the highly desired alkylate above described. The present process is designed to fully utilize existing refinery gases and to accomplish this utilization in a most economical and advantageous manner. As will be seen from a fuller understanding of the process of the present invention, considerable flexibility in the operation of these units is possible without departing from the general principles of the invention as herein more fully outlined. The problem has always been to improve overall yields of desired products while utilizing existing materials from refining operations. Therefore, any practical method for the manufacture on a commercial scale of high octane blending agents for use in the preparation of 100 octane number and higher aviation fuels is a welcome improvement in the art.

In describing the process, reference will be made chiefly to a cracked refinery C_4 cut and one or more of its components, but it is distinctly to be understood that the present invention is not restricted to such a feed stock, it being entirely possible to use field butanes which have been augmented with olefins from extraneous sources, to use combined C_4–C_5 refinery fractions from cracking operations, or to use C_5 fractions alone which contain isopentane, normal pentane, and the straight and branched chain C_5 olefins.

The operation of the combined isomerization-alkylation process is such that the two processes function substantially as a single unit although the reaction conditions in each of the two processes are independent of one another. After the feed stock containing iso and normal paraffins and olefins is subjected to alkylation the reacted mixture is fractionally distilled to remove a fraction rich in isoparaffin reactant, a fraction rich in unreacted normal paraffin, and an alkylate. The operation of the fractional distillation may be so controlled as to vary the composition of the normal paraffin fraction, leaving in it more or less of the isoparaffin which is ordinarily returned or recycled to the alkylation unit. This is carried out for the reason that when this normal paraffin fraction is conducted to the isomerization unit, control of the degree or amount of isomerization in the present invention is carried out in a novel manner, as follows:

The normal paraffin feed stock is heated to a substantially constant predetermined temperature, usually about 100° F., and its vapor pressure is measured. The feed stock then passes through a valve of variable orifice which controls the rate of flow or addition of the feed stock to the isomerization unit. The reacted effluent from the isomerization unit is maintained at substantially the same temperature as that of the incoming feed stock to that unit and its vapor pressure is likewise determined. A device is employed which is actuated by the difference in the vapor pressure of the incoming feed and the outgoing reacted mixture, and depending upon the increase in the percentage of isobutane contained in the reacted mixture, the valve through which the feed stock is introduced into the isomerization unit is either opened or closed by means of the pressure differential actuating means in order to control the extent of conversion of normal to iso butane, so that a substantially constant amount of isoparaffin is intro-

duced back into the alkylation unit so as to maintain a substantially constant source of supply to that unit of isoparaffin reacted with olefins to form alkylate. This replacement of reacted isoparaffins is therefore dependent upon the composition of the incoming feed stock because the rate of introduction of that feed stock is controlled by the vapor pressure differential means heretofore described. It is therefore readily understood that one method of controlling that means, or, in other words, of increasing or decreasing the differential in vapor pressure, is by permitting small or large aliquot portions of isoparaffin to be admixed with the normal paraffin going to the isomerization unit, and this is accomplished by a variation in the fractional distillation conditions maintained in the isoparaffin-normal-paraffin fraction distillation tower. As will be more fully described hereinafter, the effluent from the isomerization unit goes directly to the alkylation unit or may be returned to and admixed with the alkylated mixture going to the fractional distillation tower for effecting the separation of isoparaffin from normal paraffins and from alkylate.

Although the invention is not restricted to any particular method of accomplishing the alkylation reaction, the isomerization reaction and/or the dehydrogenation reaction, for purposes of illustration it may be stated that the alkylation can be carried out in the presence of sulfuric acid of from 90 to 100% concentration, at a temperature between about 20 and about 75° F., under sufficient superatmospheric pressure to maintain liquid phase operation; that the isoparaffin should be present in substantial molar excess over the olefins being reacted, and that the mixture should be vigorously agitated to maintain a thorough contacting for a sufficient period of time to bring the reaction to substantial equilibrium. In the case of the isomerization reaction, a suitable method of carrying it out is to employ aluminum chloride, and in the case of normal butane isomerization to use temperatures of between about 200 and about 400° F. Likewise, a halogen-containing promoter is desirable and this may be selected from any one of a number of suitable substances, hydrogen chloride being the preferred one. Liquid or vapor phase reaction may be employed and the aluminum chloride may be deposited on a suitable carrier such as Porocel or other highly porous substance for greater contacting with the feed stock. In the case of the dehydrogenation unit, the operation may be carried out using a catalyst of chromia and alumina gels at atmospheric pressure and under a temperature range of from 1000 to 1400° F., at a throughput of from 100 to 1200 volumes of feed stock per volume of catalyst per hour. Each of these types of reactions are well known and the specific details, specific catalysts and reaction conditions form no part of the present invention other than in the combination as shown. As will be more fully explained, the invention lies in the subsequent isolation and treatment of the effluent from the alkylation unit to condition the inerts and unreacted portions of the feed thereto for further use in alkylation.

Referring to the accompanying drawing, which is a more or less diagrammatic representation in sectional elevation of a plant designed for carrying out the process of the present invention, the feed stock employed will be, for illustrative purposes only, described as a cracked refinery C_4 cut containing isobutane, normal butane, normal butylenes and isobutylene.

Such a feed stock is introduced into line 2 by means of open valve 3 and pumps not shown into alkylation unit 4 where it is contacted with sulfuric acid or other suitable alkylation catalysts. The reacted effluent, substantially free of acid, emerging therefrom through line 5 is fed through open valve 6 into fractionating tower 7 operating under such conditions of temperature and pressure wherein a substantially pure fraction of isobutane and any lighter boiling hydrocarbons present is passed overhead through line 8, controlled by valve 9, and recycled back to the feed line 2 for further use in the alkylation unit. It may be necessary at times to purge part of the stream in line 8 in order to prevent appreciable build-up of C_3 and lighter components in the reactor by means not shown. A bottoms from this tower 7 which consists of normal butane and alkylate, together with small amounts of isobutane, is then passed by means of line 10, controlled by valve 11, into line 12 and then into fractionating column 15 which is operated under conditions effecting a separation of main quantities of normal butane from the alkylate, it being understood of course that any quantities of isobutane not taken overhead from fractionating column 7 are removed with the normal butane overhead from fractionating column 15. The normal butane is then, by means of line 16 and open valve 17, conducted to either line 41 controlled by valve 42 or line 81 controlled by valve 82, or both, depending upon the openings set in valves 42 and 82.

The alkylate, together with any small amounts of normal butane which have not been taken overhead to line 16, is withdrawn through line 18 controlled by valve 19 and conducted into the final fractionating tower 34 for the removal of light alkylate through line 35 controlled by valve 36, medium cut alkylate through line 37 controlled by valve 38, and the heavy bottoms through line 39 controlled by valve 40.

In operating the alkylation unit, a single stage circulating stream emulsion type of reactor or a two-stage operation in which the olefins are first absorbed in sulfuric acid and the isoparaffin then contacted with the olefin extract under alkylation conditions may be employed. This latter type is advantageous particularly in cases wherein the feed stock does not contain only a single olefinic hydrocarbon but may contain C_2, C_3, C_4 and C_5 olefins and the like, in which case it may be desirable to selectively extract only the C_4 olefin or only the C_3 olefin, as the case may be, or both, leaving unabsorbed the undesired olefin. As stated, two-stage alkylation is preferable in such an instance.

The normal butane, unless removed from the alkylation system to compensate for the introduction of fresh quantities of normal butane, builds up indefinitely since it is inert in the alkylation unit, hence at least sufficient normal butane should be removed through line 16 for further processing so as to maintain the normal butane level at least constant in the alkylation unit and to compensate for the introduction of further quantities of normal butane in the feed stock in line 2. This normal butane, which may contain small or large amounts of isobutane, depending upon the fractionation conditions in fractionating columns 7 and 15, is conducted through line 41 controlled by valve 42 into a vapor pressure recording unit 43 having a constant temperature jacket 44. The vapor pressure is

usually measured for the purpose of the present invention, in the case of normal butane, at about 100° F. In other words, jacket 44 would be maintained about at 100° F. The effluent from the heater and constant temperature zone 43 passing through valve 46 and line 45 goes to absorber 47 and passes downwardly therethrough while simultaneously therewith there is passing upwardly by means of line 50 controlled by valves 51 and 58, hydrogen chloride which is introduced into this same absorber by means of recycle line 58, and any unabsorbed hydrogen chloride is released from the system through line 48 controlled by valve 49. The temperature and throughput maintained in the absorber are such as to give a hydrogen chloride concentration roughly of from 3 to 20% hydrogen chloride. This fat liquor, that is normal butane containing hydrogen chloride, is passed by means of line 52 through control valve 53 into the isomerization unit 54. The reacted mixture from isomerization unit 54 passes through line 55 through open valve 56 into the stripping tower 57 where the hydrogen chloride and any lighter degradation products which may have formed, such as ethane, methane, propane, are removed overhead and recycled to the absorber 47. The degradation products, together with any unabsorbed hydrogen chloride, are removed from the system through line 48 controlled by valve 49 as heretofore specified. The bottoms from the stripping operation and which consist primarily of normal and isobutane are passed through lines 60, 63 and open valve 64 into a temperature controlled vapor pressure recorder 65 similar to that of temperature controlled vapor pressure recorder 43 wherein the vapor pressure again at 100° F. is measured, the 100° F. temperature being insured by heating or cooling liquids in jacket 66. Vaper pressure recorders 43 and 65 are conventional pressure recorder mechanisms with a pneumatic device added which operates to produce an air pressure output of each recorder having a predetermined relation to the respective actual vapor pressures. Recorders 43 and 65 may be devices such as those described on pages 5, 6 and 7 of Bulletin #2 published by Industrial Engineers, Inc., of Los Angeles, California, entitled, "Graphical Vapor Pressure," with the recording pressure gauges substituted by an instrument such as described in Brown Instrument Company Catalogue #9400, page 4. By means of lines 73 and 77, these pneumatic outputs of recorders 43 and 65 are transmitted to pressure differential responsive device and controller 74 which is an adaptation of a conventional fluid flow controller as described in Brown Instrument Company Catalogue #2204, page 13, Figure 22, and Brown Instrument Company Catalogue #8902, page 20. The output of controller 74 is connected by means of air line 76 to a conventional control valve 53 such as, for example, the pneumatic diaphragm control valve type 57T as disclosed in Fischer Governor Company Catalogue #35, page F-24. A portion of the reacted effluent free of promoter may be withdrawn, if desired, through line 61, controlled by valve 62. This is usually done, however, only in cases where an excess of isoparaffin for the alkylation unit is produced in the isomerization unit. The reacted mixture is passed through line 67 by means of open valve 68 and may either be directly introduced with the reacted alkylate effluent, which is substantially acid-free, into fractionating tower 7 for separation of isobutane from the normal butane and alkylate by means of line 69, open valve 70, line 5 and open valve 6, valve 72 being closed, or valve 70 may be closed and the mixture of iso and normal butanes may be passed by means of line 71 and open valve 72 into the feed line 2 and the effluent from the isomerization unit 54 is thereby fed directly into the alkylation unit 4. Although no provision is made for the same in the drawing, nevertheless caustic treaters, driers, pumps, reboilers, and the like are employed as required. Usually a caustic treat of normal butane-isobutane effluent from the stripping column 57 is employed in order to neutralize any entrained aluminum chloride or hydrogen chloride contained therein. Any C_5 paraffins which have formed during the isomerization are removed from the system with the light alkylate as overhead from tower 34, without the necessity of including another fractionating tower in the isomerization section of the system.

That portion of the normal butane in line 16 which goes to the dehydrogenation unit is passed through line 81 by means of open valve 82 into the dehydrogenation unit 83 and the resulting mixture of olefins and paraffin content may be either selectively or non-selectively absorbed in sulfuric acid of alkylating strength at 20–50° F. and at the proper acid to olefin ratio in absorber 89 by passing the effluent from line 84 into the absorber 89 by means of line 85 controlled by valve 86, or the absorber may be by-passed and the reacted effluent fed direct to an alkylation unit 4 by means of lines 87 and 98 controlled by valves 88 and 99. If absorption of olefin is desired, the sulfuric acid is fed into absorber 89 through line 90 controlled by valve 91 and the feed extract is withdrawn through line 96 controlled by valve 97 and by means of line 98 and valve 99 fed into the alkylation unit so that in effect a two-stage alkylation is carried out thereby. The normal butane-isobutane or unabsorbed portion of the effluent from the dehydrogenation unit 83 is passed by means of line 94 controlled by valve 95 to the isomerization unit 54 by means of line 41, etc., as previously described. Further quantities of normal butane may be added to the effluent from the absorber 89 by means of line 92 controlled by valve 93, or if desired some or all of the unabsorbed effluent from absorber 89 may be discarded from the system through line 92 controlled by valve 93, valve 95 being partially or completely closed. In cases where the effluent from dehydrogenation unit 83 goes to the alkylation unit 4 by way of lines 84, 87 and 98, it is desirable to first subject the effluent to stabilization (not shown in the drawing) in order to substantially free the effluent of hydrogen, methane, ethane, etc., up to and including the C_3 hydrocarbons, both paraffinic and olefinic, prior to introducing the same into alkylation unit 4.

Obviously there are many modifications and deviations, variations and the like, of the invention as hereinbefore set forth which may be made without departing from the spirit and scope of the present invention, and the appended claims indicate only such limitations as should be imposed in order to adequately define the invention.

What is desired to be secured by Letters Patent is:

1. A process for the production of high boiling normally liquid isoparaffins which comprises alkylating a hydrocarbon mixture containing low boiling isoparaffin, low boiling normal paraffin, low boiling monoolefin, under alkylation reac-

tion conditions in the presence of an alkylation catalyst to produce normally liquid isoparaffins, separating the unreacted normal paraffin from the alkylate produced, isomerizing sufficient of said low boiling normal paraffin to isoparaffin and returning the same to the alkylation unit so as to compensate for and replace the isoparaffin reacted in the alkylation reaction by subjecting the said normal paraffin to isomerization in the presence of an aluminum halide and a halogen-containing promoter, the rate of throughput of the normal paraffin being correlated with the amount of isoparaffin required for the alkylation reaction by measuring the vapor pressure of said low boiling normal paraffin at a predetermined temperature, measuring the vapor pressure of the isomerized mixture substantially free of catalyst and promoter at substantially the same predetermined temperature and directly controlling the throughput of the feed stock through the isomerization reaction zone by means of the vapor pressure differential between the two vapor pressure measurements and conducting the resulting isomerized mixture to the alkylation system.

2. A process for the production of high boiling normally liquid isoparaffins which comprises alkylating a hydrocarbon mixture containing low boiling isoparaffin, low boiling normal paraffin, low boiling monoolefin, under alkylation reaction conditions in the presence of an alkylation catalyst to produce normally liquid isoparaffins, separating the unreacted normal paraffin from the alkylate produced, isomerizing sufficient of said low boiling normal paraffin to isoparaffin and returning the same to the alkylation unit so as to compensate for and replace the isoparaffin reacted in the alkylation reaction by subjecting the said normal paraffin to isomerization in the presence of an aluminum halide and a halogen-containing promoter, the rate of throughput of the normal paraffin being correlated with the amount of isoparaffin required for the alkylation reaction by measuring the vapor pressure of said low boiling normal paraffin at a predetermined temperature, measuring the vapor pressure of the isomerized mixture substantially free of catalyst and promoter at substantially the same predetermined temperature and directly controlling the throughput of the feed stock through the isomerization reaction zone by means of the vapor pressure differential between the two vapor pressure measurements, conducting the resultant mixture to the alkylation system, and wherein at least a portion of the normal paraffin from the alkylation product is further diverted to a catalytic dehydrogenation unit operated under dehydrogenation conditions and in the presence of a dehydrogenation catalyst to obtain a product predominating in monoolefin and normal paraffin, introducing said product into the alkylation reaction zone at least in sufficient quantity to compensate for and balance the loss of olefin therefrom because of condensation with isoparaffin.

3. A process for the production of high boiling normally liquid isoparaffins which comprises alkylating a hydrocarbon mixture containing low boiling isoparaffin, low boiling normal paraffin, low boiling monoolefin, under alkylation reaction conditions in the presence of an alkylation catalyst to produce normally liquid isoparaffins, separating the unreacted normal paraffin from the alkylate produced, isomerizing sufficient of said low boiling normal paraffin to isoparaffin and returning the same to the alkylation unit so as to compensate for and replace the isoparaffin reacted in the alkylation reaction by subjecting the said normal paraffin to isomerization in the presence of an aluminum halide and a halogen-containing promoter, the rate of throughput of the normal paraffin being correlated with the amount of isoparaffin required for the alkylation reaction by measuring the vapor pressure of said low boiling normal paraffin at a predetermined temperature, measuring the vapor pressure of the isomerized mixture substantially free of catalyst and promoter at substantially the same predetermined temperature and directly controlling the throughput of the feed stock through the isomerization reaction zone by means of the vapor pressure differential between the two vapor pressure measurements, conducting the resultant mixture to the alkylation system, and wherein a portion of the normal paraffin from the alkylation product is so diverted to a catalytic dehydrogenation unit operated under dehydrogenation conditions and in the presence of a dehydrogenation catalyst to give a product containing monoolefin and isoparaffin, absorbing the olefin content of the reacted effluent in sulfuric acid of alkylating strength and alkylating the resultant extract with isoparaffin, subjecting the unabsorbed portion of the reacted effluent from the dehydrogenation unit to a catalytic isomerization under isomerization reaction conditions and conducting the resultant isomerized mixture substantially free of halogen-containing promoter and catalyst to the alkylation reaction.

4. In a process of isomerizing normal paraffins of at least four carbon atoms per molecule under isomerization reaction conditions in the presence of an aluminum halide and halogen-containing promoter, the improvements comprising measuring the vapor pressure of the feed stock at a predetermined temperature, measuring the vapor pressure of the isomerized mixture substantially free of aluminum halide and halogen-containing promoter at substantially the same predetermined temperature, directly controlling the throughput of the feed stock through the isomerization reaction zone by means of the vapor pressure differential between the two vapor pressure measurements so as to regulate the amount of normal paraffin passing through the isomerization reaction zone and the amount of isoparaffin produced therein.

5. In a combination alkylation-isomerization process involving the alkylation of a cracked refinery C_4 cut containing butenes and butanes, the amount of isobutane present being adjusted so that it is in molar excess of the butenes, and wherein normal butane is separated from the isobutane by distillation from the alkylated reaction mixture, isomerized to isobutane and reintroduced into the alkylation reaction zone, the improvements comprising regulating the amount and rate of normal butane isomerization to isobutane by measuring the vapor pressure of the feed stock to the isomerization unit at a predetermined temperature, measuring the vapor pressure of the isomerized mixture substantially free of catalyst and promoter at substantially the same predetermined temperature, regulating the throughput of the feed stock through the isomerization reaction zone directly by means of the vapor pressure differential between the two vapor pressure measurements and introducing

the resultant mixture of isobutane and normal butane into the alkylation system.

6. In a process of normal paraffin isomerization wherein the normal paraffin contains at least four carbon atoms per molecule to produce isoparaffins under isomerization reaction conditions in the presence of a Friedel-Crafts type catalyst and a halogen-containing promoter, the improvement comprising regulating the rate and amount of normal paraffin fed through the isomerization unit and isomerized therein by measuring the vapor pressure of the feed stock at a predetermined temperature, measuring the vapor pressure of the isomerized mixture substantially free of Friedel-Crafts type catalyst and halogen-containing promoter at substantially the same predetermined temperature and directly controlling the throughput of the feed stock through the isomerization reaction zone by means of the vapor pressure differential between the two vapor pressure measurements.

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