

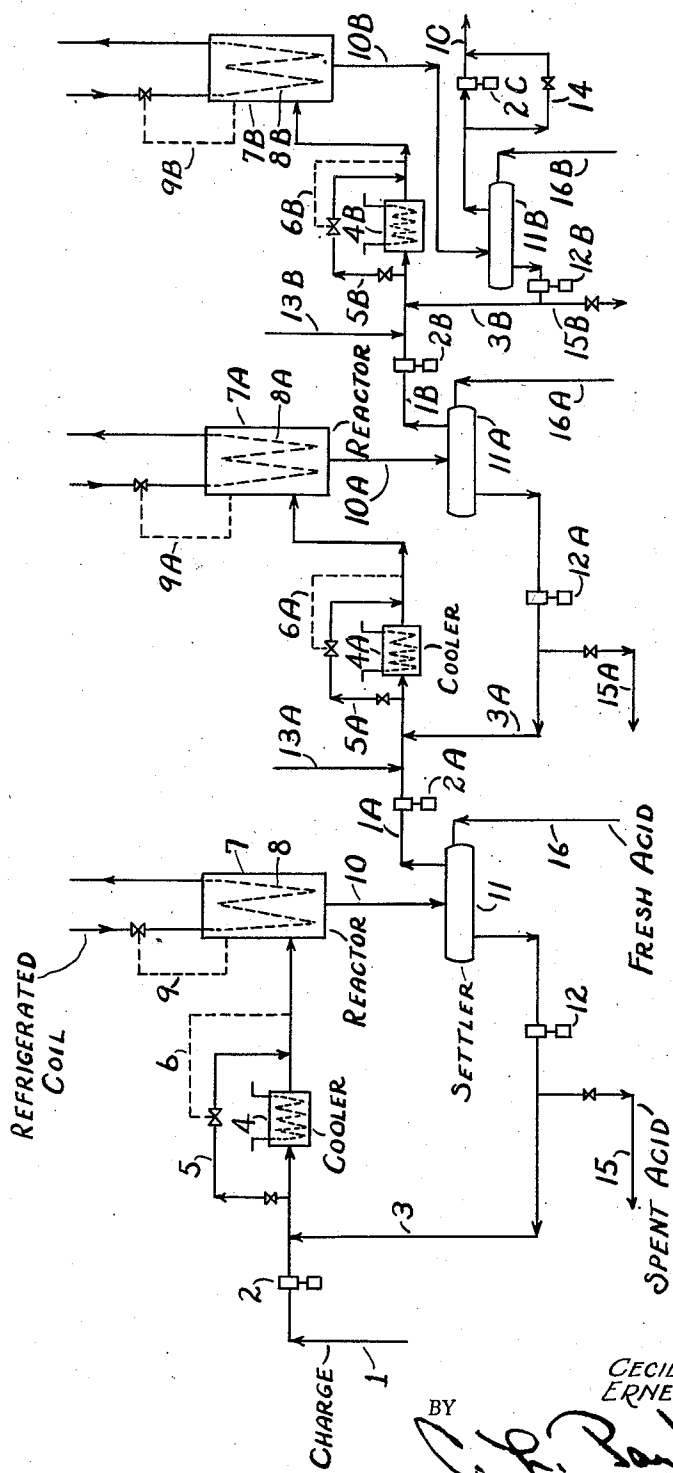
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MULTIPLE STAGE CATALYTIC ALKYLATION PROCESS

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MULTIPLE STAGE CATALYTIC ALKYLATION
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This invention relates to a method and means for producing a superior grade of aviation fraction gasoline of 88-96 octane number from a catalytic reaction which effects the junction of an isoparaffin and an olefine hydrocarbon molecule to form a product boiling in the gasoline range.

Another object of this invention is to produce a higher overall yield of aviation fraction of the total alkylate from the progressive low temperature and low pressure operation.

A further object of this invention is to maintain flexible control of the reaction system which allows two or more olefines, i. e., butene and pentene in reaction zones under conditions of temperatures and pressures which are conducive to optimum results for each specific reaction. These and other objects will be apparent from the following description.

Among the advantages of the present process may be listed a higher yield of aviation fraction gasoline which is obtained over the yield in a single stage operation. An additional and greater advantage of this process is that two or more olefine bearing hydrocarbon streams may be processed to an advantage in the reaction zone whose temperature is most suitable for optimum yields, i. e., iso-butane and butene may be alkylated or reacted in stage one where the temperature is maintained in the range of from -10° to 20° F., thus producing approximately 10% more aviation fraction of 2 to 4 octanes higher than if reacted at a higher temperature as is used in stage 3. And similarly a hydrocarbon stream carrying ptenenes as the olefine to be reacted with iso-butane can be satisfactorily treated in the reaction zone operated at a temperature range of 20° to 40° F., or even at 40° to 70° F., in the 3rd stage. Ptenenes do not require as low an operating temperature for optimum alkylation yields as do butenes or propene when alkylated or reacted with iso-butane. Two or more olefines, i. e., butane and pentene, may be reacted in alkylation zones where the temperatures and iso-paraffin concentrations are suitable to each reaction.

A further advantage from this multiple stage operation is that a higher yield of aviation fraction of the total alkylate results from the progressive low temperature operation, and also that different olefines may be injected at intermediate points in the alkylation system to avoid excessive olefine concentrations in the first or second reaction zones.

To make this invention easily and more fully

understood, an explanation will now be made with reference to the drawing which illustrates a schematic flow arrangement in a simplified form. In the drawing the same reference characters are used to denote parts having duplicate forms and functions, the subscripts A and B denote the second and third stages respectively.

In the apparatus system illustrated, the hydrocarbon stream carrying iso-paraffin and olefine in molecular proportions in the range of 2 to 10 molecules of iso-paraffin per molecule of olefine charged through pipe 1 by pump 2 is joined with a cold acid recycle stream passed from pipe 3 and then passed to the first stage refrigeration cooler 4 where the temperature of the hydrocarbon and acid is further cooled to the desired low temperature level, for example, -10° to 20° F. Cooler 4 may have a by-pass 5 with a temperature controller 6 to regulate and maintain the temperature of the stream entering the first stage reaction zone 7.

This stream flows to the first stage reaction zone 7 where a portion of the iso-paraffins and olefines are reacted in the presence of a catalyst such as concentrated sulfuric acid (H₂SO₄) to form high anti-knock compounds boiling in the gasoline range. The exothermic heat of reaction which is liberated by the joining molecules is controlled by a separate closed refrigerated coil 8 in the reaction zone itself. The temperature controller 9 regulates the flow of refrigerant into the refrigerated coil 8. The effluent from the first stage reaction flows through line 10 to the first stage acid settler drum 11 where the hydrocarbon and acid layers separate. The acid fraction is recycled by pump 12 back through pipe 3 to be joined and mixed with the hydrocarbon charge entering the system. The hydrocarbon fraction from the acid settler 11 is pumped by pump 2A or flows (if no pump is necessary) through line 1A together with cold acid from line 3A to the second stage refrigeration cooler 4A where the temperature level for this zone is maintained at a higher temperature in the range of 20° to 40° F., depending upon which hydrocarbon it is desired to react. Cooler 4A may also have a by-pass 5A with a temperature controller 6A. A separate closed refrigerated coil 8A having a temperature controller 9A maintains the desired temperature level in the second stage reaction zone 1A by controlling the flow of refrigerant to coil 8A in a manner similar to that described in the first stage reaction zone 7. The effluent from the second stage reaction zone flows through line

10A to the second stage acid settler 11A whose object is analogous to the first stage settler.

The hydrocarbon fraction from the second stage acid settler 11A is pumped by pump 2B and flows through line 1B jointly with cold acid from line 3B to the third stage reaction zone 7B. Cooler 4B may be by-passed entirely through line 5B, depending on the operating temperature required in zone 7B. Reaction zone 7B is also equipped with a separate internal refrigerated coil 8B having controller 9B for temperature control. The effluents from the third stage reaction zone flow through line 10B to the third stage acid settler 11B in which the acid fraction is separated and returned by line 3B and pump 12B to the third stage system. The temperature level in the third stage reaction zone is maintained in the range of 40° to 70° F. The hydrocarbon effluents from settler 11B flow to the fractionating system (not shown) where the various products are separated.

Provisions are also made for the introduction of additional olefines in intermediate stages of the process. Pentenes and hexenes require higher iso-paraffin to olefine ratios than butenes and propene to produce high quality aviation alkylate. Therefore, as the olefine in the first stage is reduced the pentene or hexene olefines with or without additional iso-paraffin may be injected into the second or third stage charge lines 1A and 1B through lines 13A and 13B respectively, thus insuring adequate iso-paraffin olefine ratios in these reaction zones. When pentene and hexene olefines are to be alkylated, superior quality alkylate is derived with high iso-paraffin olefine ratios in the order of magnitude of 7 to 10 iso-paraffin molecules to one olefine molecule for optimum results.

In addition to the quality of product the acid consumption is somewhat less than when high iso-paraffin olefine ratios are maintained in the reaction zone. The octane number of the aviation fraction of the alkylate is from 2 to 4 octane numbers higher where the above conditions have been maintained in the reaction zones.

The effluents from the third stage reaction zone are pumped by pump 2C or by-passed through line 14 to the fractionating system (not shown) where separations are effected in the degree necessitated by the design conditions for each specific charging material. A stream high in isobutane content, say 85%, is separated in the fractionating system and recycled back to the alkylation system in sufficient quantity to maintain the desired iso-butane olefine ratios in the reaction system. Any propane present and the normal butane, aviation alkylate fraction and heavy alkylate fractions are each separated in their respective fractionating systems.

The catalyst employed in this invention is concentrated sulfuric acid of 95 to 98+ % (H_2SO_4). As the reaction progresses the acid concentration becomes diminished to the point where it is not economical to continue its use in the system. Therefore, periodically or continuously a quantity of the reduced concentrated acid is withdrawn from the bottom of the acid settlers through lines 15, 15A and 15B, and replaced by a sufficient quantity of fresh concentrated acid through lines 16, 16A and 16B respectively, to maintain the degree of concentration desired for economical operation. The used or spent sulfuric acid which has been withdrawn from the system may be pumped to storage for revivification or concentration and this acid is suitable for

reuse in the alkylation system. Certain inorganic salts such as silver salts have been found to be promoters or aides in catalysis when added to concentrated sulfuric acid, therefore this invention covers the use of promoters such as described.

An example of the advantage to be gained by this multiple stage reaction system is indicated as follows:

	Single stage	Multiple (3) stages
Volumetric yield..... per cent.....	82	96
Octane C. F. R. M.....	90	96

The pressures which are employed in the present process are to be sufficient to allow maintenance of the hydrocarbon materials in the liquid phase for the temperatures indicated. In general this pressure in the reaction vessels may be as low as 5 or it may in some cases be as high as 100 lbs., or more.

Any of the well known refrigerants may be used in the cooling coils, such as propane, nitrous oxide, carbon dioxide, ammonia, etc.

While specific embodiments of the invention and systems for carrying them into practice have been explained by way of illustration, it is to be understood that this invention is not to be confined by the exact steps, pressures, temperatures, proportions or particular devices mentioned heretofore as typical. The exact size of apparatus and conditions depend upon the analysis of the charging stock, quantities to be processed and specifications of the final products desired. Instruments, valves, pumps, temperature and pressure indicators, recorders and controllers, meters and other such engineering equipment are not all shown but it is to be understood that they will be used as required and as understood in the art.

Although the present invention is described and illustrated as a three stage alkylation process in the specification and drawing, it is also to be understood that the scope of this invention is not to be limited to a three stage process as it may be more desirable to use two stages for certain charging stocks and more than two stages may be desirable for other charging stocks.

Having described our invention what we claim and desire to secure by Letters Patent is as follows:

1. A process for producing aviation fraction alkylate which comprises reacting 3, 4, and 5 carbon atom olefine hydrocarbons with iso-paraffin hydrocarbons in ratios of 2 to 10 iso-paraffin molecules to 1 olefine molecule in the presence of a concentrated sulfuric acid catalyst at temperatures in the range of -10° to 20° F., passing said reacted hydrocarbons to a separating zone for separation of hydrocarbon effluents from said acid catalyst, subjecting said hydrocarbon effluents to a second catalytic reaction in a second reaction zone in the presence of an additional concentrated sulfuric acid catalyst at temperatures in the range of 20° to 70° F., injecting additional pentens and hexenes into the second reaction stage with said hydrocarbon effluents in higher iso-paraffin to olefine ratios than the butenes and propene in the order of magnitude of 7 to 10 iso-paraffin molecules to 1 olefine molecule, passing said reacted hydrocarbons to a second separating zone, separating and recycling said additional acid catalyst to the initial point

of entry of said second stage, and fractionating the hydrocarbon effluents to produce aviation fraction alkylate.

2. A multistage alkylation process for producing aviation motor fuel alkylate, which comprises admixing in an initial stage olefines of 3 to 5 carbon atoms and isobutane with a circulating stream of concentrated sulfuric acid made up of recirculated acid catalyst and fresh acid catalyst, reacting predominantly 4 carbon atom olefines in said first stage at a temperature in the range of -10°F. to 20°F. , separating treated hydrocarbons from the catalyst, admixing said treated hydrocarbons with a second circulated stream of sulfuric acid catalyst containing fresh and recirculated sulfuric acid, and adding additional hydrocarbons containing olefines of 5 carbon atoms and iso-paraffins, reacting a remaining portion of olefines and isobutane in said second stream at 20°F. to 40°F. , separating treated hydrocarbons from the catalyst in said second stream, admixing treated hydrocarbons separated from said second stream with a third circulated stream of sulfuric acid catalyst containing fresh and recirculated sulfuric acid, reacting remaining olefines and isobutane in said third stream at 40°F. to 70°F. , and recovering the treated hydrocarbons from said third stream.

3. A multistage alkylation process for producing aviation motor fuel alkylate, which comprises admixing in an initial stage olefines of 3 to 5 carbon atoms and isobutane with a circulating stream of concentrated sulfuric acid made up of recirculated acid catalyst and fresh acid catalyst, reacting predominantly 4 carbon atom olefines in said first stage at a temperature in the range of -10°F. to 20°F. , separating treated hydrocarbons from the catalyst, admixing said treated hydrocarbons with a second circulated stream of sulfuric acid catalyst containing fresh and recirculated sulfuric acid, reacting a remaining portion of olefines and isobutane in said second stream at 20°F. to 40°F. , separating treated hydrocarbons from the catalyst in said second stream, admixing treated hydrocarbons separated from said second stream with a third circulated stream of sulfuric acid catalyst containing fresh and recirculated sulfuric acid, and adding additional hydrocarbons containing olefines of 5 and 6 carbon atoms and iso-paraffins, reacting remaining olefines and isobutane in said third stream at 40°F. to 70°F. , and recovering the treated hydrocarbons from said third stream.

4. The process for producing alkylation which comprises mixing hydrocarbons taken from the group of the 3, 4, and 5 carbon olefines with iso-paraffins in the presence of a concentrated sulfuric acid catalyst under alkylating conditions to form an alkylate by the alkylation of said iso-paraffins with said olefines and then contacting iso-paraffins admixed with said alkylate, with added olefines of a greater number of carbon atoms chosen from the group of the 5 and 6 carbon olefines in the presence of concentrated sulfuric acid catalyst, under alkylating conditions, to alkylate said iso-paraffins with said last named olefins and separating the catalyst from the alkylate thus formed.

5. A process for producing alkylates which comprises mixing olefines chosen from the group of 3, 4, and 5 carbon olefines with iso-paraffins, the molecular ratio of said iso-paraffins to olefins in the mixture being in excess of 1, in the pres-

ence of sulfuric acid catalyst and maintaining said mixture at a relatively low alkylating temperature, separating the alkylate thus formed from the acid catalyst and again contacting said alkylate containing iso-paraffins with olefinic hydrocarbons of a greater number of carbon atoms chosen from the group of the 5 and 6 carbon olefines, the molecular ratio of said iso-paraffins to olefines in said mixture being in excess of 1, in the presence of sulfuric acid catalyst under alkylating conditions at a temperature higher than said first named alkylating temperature to cause an alkylation of said iso-paraffins by said last named olefines and separating the alkylate thus formed from said acid catalyst.

6. A method for alkylation of iso-paraffin with olefines which comprises commingling iso-paraffins with olefines comprised predominantly of 4 carbon olefines with an alkylating catalyst under alkylating conditions whereby said 4 carbon olefines alkylate said iso-paraffins, and separating the catalyst from said alkylate fraction and contacting said alkylate fraction containing iso-paraffins with an alkylating catalyst in the presence of added olefine comprised predominantly of olefinic hydrocarbons of molecular weight higher than the said four carbon olefinic hydrocarbons, and alkylating iso-paraffins in said alkylate hydrocarbon fraction with said higher olefines and separating the alkylate thus formed from said alkylating catalyst.

7. A method of alkylation of iso-paraffin with olefines which comprises commingling iso-paraffins with low molecular weight olefines and with an alkylating catalyst under alkylating conditions whereby said low molecular weight olefines alkylate said iso-paraffins and separating said catalyst from said alkylate fraction and contacting said alkylate fraction containing iso-paraffins with an alkylating catalyst in the presence of added olefine of molecular weight higher than said low molecular weight olefines and alkylating the iso-paraffins present in said alkylate hydrocarbon fraction with said higher olefines and separating the alkylate thus formed from said alkylating catalyst.

8. A method of alkylation of iso-paraffin with olefines which comprises commingling iso-paraffins with four carbon olefines and with a liquid alkylating catalyst under alkylating conditions and alkylating said iso-paraffins with said four carbon olefines, separating the catalyst from said alkylate fraction and contacting said alkylate fraction with an alkylating liquid catalyst under alkylating conditions in the presence of added five carbon olefines and alkylating iso-paraffins in said alkylate hydrocarbons fraction with said five carbon olefines and separating the alkylate thus formed from said alkylating catalyst.

9. A process for alkylating iso-paraffinic hydrocarbons which comprises reacting butylene with molecular excess of isobutane in the presence of a liquid alkylating catalyst under alkylating conditions, separating the alkylation catalyst from the alkylate thus formed, commingling said alkylate with pentene and alkylation catalyst under alkylating conditions to alkylate iso-butane present in said alkylate with said added pentene and separating the alkylate thus formed from said alkylation catalyst.

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