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MANUFACTURE OF MOTOR FUELS

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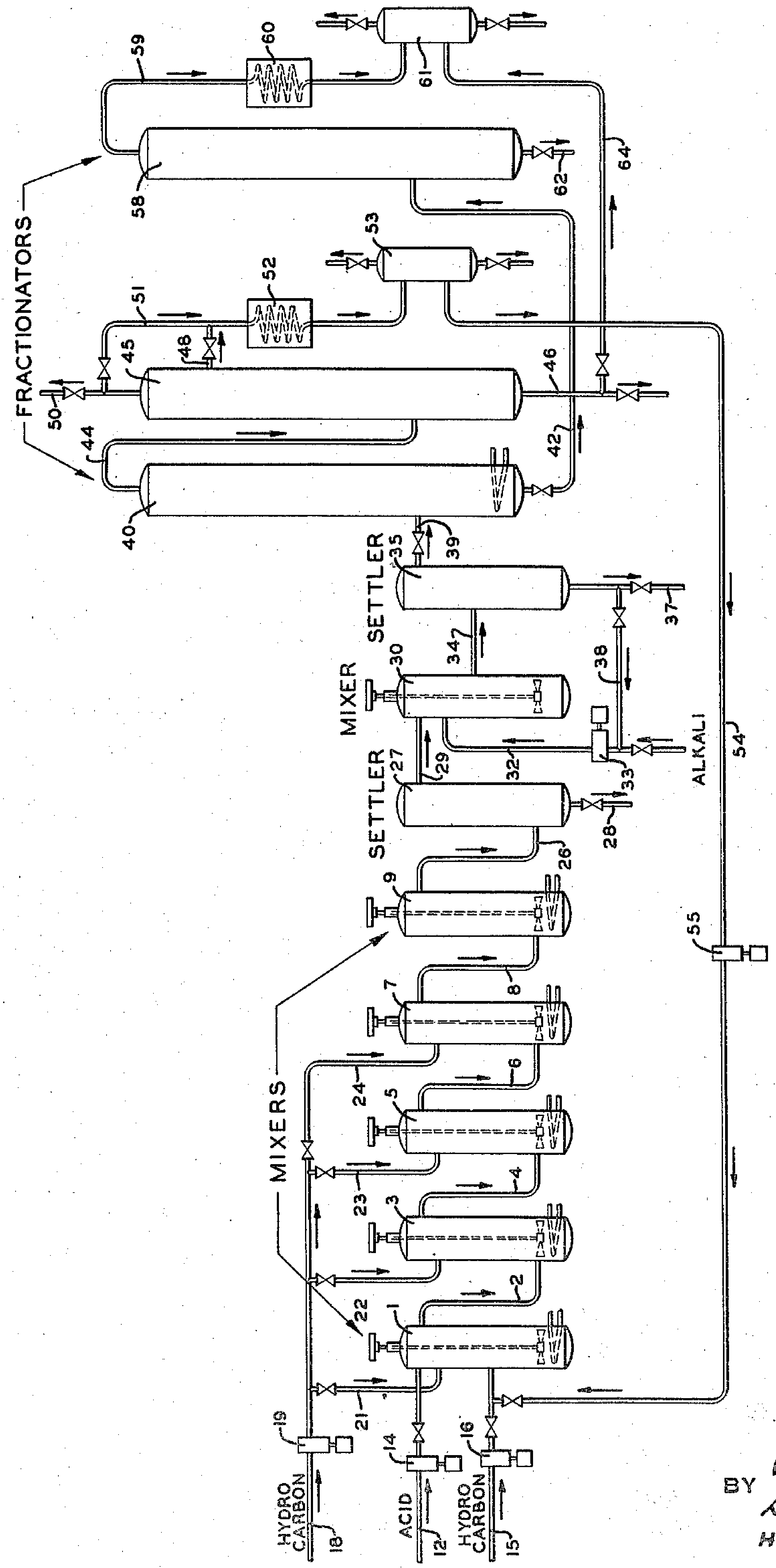

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MANUFACTURE OF MOTOR FUELS

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13 Claims. (Cl. 196—10)

This invention relates to the manufacture of motor fuels and has to do particularly with the production of high antiknock gasoline hydrocarbons by the alkylation of isoparaffins with olefins in the presence of an alkylation catalyst.

In accordance with the invention, low boiling isoparaffins are treated with olefins in the presence of a catalyst having the property of effecting the alkylation of the isoparaffins with the olefins, wherein the reaction takes place over a substantial temperature range. The invention is particularly applicable to the treatment of isoparaffins, such as isobutane or isopentane, with normally gaseous olefins or polymers thereof in the presence of a liquid catalyst, such as sulfuric acid, and preferably sulfuric acid of about 93 to 98% concentration, whereby branch chain saturated hydrocarbons of high antiknock value and within the gasoline boiling point range, are formed.

In the alkylation with such catalysts, there is often a deterioration or substantial decrease in concentration of the acid during the reaction, whereby its efficiency is substantially impaired. At low temperatures the deterioration is not so marked but the yield of gasoline, particularly aviation gasoline hydrocarbons, is decreased. At higher temperatures the deterioration of acid is greater but the yield of the desired hydrocarbons is increased. It is the normal practice to select an average constant temperature at which a satisfactory yield is obtained without excessive loss of catalyst.

It has been found that by carrying out the alkylation reaction over a graduated temperature range, it is possible to obtain more efficient use of the catalyst and a higher yield of hydrocarbons, of the desired boiling point range and antiknock value. The improved results are believed to be due largely to a more efficient use of the acid as it becomes spent, whereas in a constant temperature operation, the acid becomes less efficient as the deterioration or concentration thereof decreases. According to the method of the present invention, the efficiency of the used acid may be maintained by increasing the temperature which compensates for the loss of activity due to deterioration.

The invention is not restricted to any particular type of operation although it is well adapted to a continuous process, such as a concurrent flow, in which the catalyst and hydrocarbon are passed through a plurality of stages, throughout which a graduated range of temperature is maintained. It is also contemplated that the operation may be carried out in a counterflow system in which the temperature is increased in the direction of the flow of the catalyst.

The invention will be described in more detail in connection with the accompanying drawing which shows a diagrammatical sketch in elevation of apparatus suitable for carrying out a concurrent flow type of process.

Referring to the drawing, there is shown a series of mixers **1**, **3**, **5**, **7** and **9**, each equipped with stirring mechanisms and means for controlling the temperatures, such as heating coils. The mixers are connected in series by means of the lines **2**, **4**, **6** and **8**. While five mixers or stages of reaction are shown, it is to be understood that any number may be used. The acid catalyst is introduced into the first mixer through the line **12** by means of the pump **14**. The hydrocarbon, comprising isoparaffins to be alkylated, is introduced through the line **15** in which is located pump **16**. The olefin charging stock is drawn through the line **18** by the pump **19** and may be charged into any one or all of the mixers **1**, **3**, **5** and **7** through valve controlled manifold lines **21**, **22**, **23** and **24** respectively. The hydrocarbon and catalyst pass concurrently through the series of mixers wherein the desired alkylation is effected.

The reaction products pass from the last mixer **9** through the transfer line **26**, to a final settler **27** wherein the acid and hydrocarbons are allowed to separate into two layers. The acid layer in the bottom may be drawn off through the valve controlled line **28**. The upper hydrocarbon layer is passed through the line **29** to a mixer **30** wherein the hydrocarbons are contacted with an alkaline neutralizing agent, introduced through the line **32** by the pump **33**. The mixture of hydrocarbons and neutralizing agent is conducted through the line **34** to a settler **35** wherein the neutralizing agent is allowed to settle out and may be withdrawn from the bottom thereof through the valve controlled line **37** or recycled to the mixer through the line **38** which communicates with the alkali charging line **32**.

The neutralized hydrocarbons are passed through the line **39** to fractionator **40** wherein the hydrocarbons of higher boiling point than butanes are fractionated out and withdrawn as a liquid from the lower portion of the fractionator through the valve controlled line **42**. The vapor fraction, comprising the butane hydrocarbons and lighter, including normal and iso butane, is passed overhead from the fractionator **40** through the vapor line **44** to a secondary fractionator **45**. In the latter fractionator the normal butane is fractionated out and withdrawn from the lower portion of the fractionator through the line **46**. The remaining normally gaseous hydrocarbons may be fractionated in the upper portion of the fractionator **45** whereby an isobutane side stream may be removed through the line **48** and the lower boiling normally gaseous hydocarbons removed overhead through the valve controlled line **50**. When the hydrocarbons treated in the system comprise essentially C_4 hydrocarbons, there may be substantially no products of lower boiling point than isobutane, and in such instance, the isobutane may be removed overhead from the fractionator **45** through the vapor line **51**. The isobutane fraction removed as a side stream through the line **48** or overhead through the line **51**, as the case may be, is condensed in the condenser coil **52** and the condensate collected in the receiver **53**. The isobutane condensate may be withdrawn from the receiver **53** through the line **54** and forced by the pump **55** into the initial mixer of the system.

The liquid product withdrawn from the bottom of fractionator **40** through the line **42** is passed to a fractionator or still **58** wherein the desired gasoline product is fractionally distilled and vapors thereof passed overhead through the vapor line **59** to a condenser **60**. The resulting condensate is collected in the receiver **61**. The hydrocarbons of higher boiling point than gasoline are withdrawn from the bottom of fractionator **58** through the line **62**. In some cases it may be desirable, in order to increase the volatility of the gasoline collected in receiver **61**, to combine therewith all or a portion of the butane fraction removed from the bottom of fractionator **45** by passing the butane to the receiver **61** through the line **64**.

The following results were obtained by alkylating isobutane with an olefinic charging stock comprising plant gas consisting mainly of unsaturated C_3 and C_4 hydrocarbon fractions from cracking stills:

Charge to stage:			
No. 1	Isobutane plant gas.	Isobutane plant gas.	Isobutane plant gas.
No. 2	Plant gas	Plant gas	Plant gas.
No. 3	Plant gas	Plant gas	Plant gas.
No. 4	Plant gas	Plant gas	Plant gas.
No. 5	Blank	Blank	Blank
Temp. ° F. stage:			
1	62	61	64
2	62	61	64
3	62	61	96
4	62	95	96
5	62	95	106
Percent conc. of sulfuric acid	98.3	98.3	98.3
Acid/olefin ratio	0.58	0.6	0.6
Isobutane/olefin ratio	3.17	3.24	3.24
Contact time, min	150	150	150
311 ° F. fraction:			
Percent yield by weight basis of olefin	119.7	127.9	137.5
Octane No. C. F. R. M	92.2	91.6	91.8
Bromine No	1	1	1
311° F.-400° F. fraction:			
Percent yield by weight basis of olefin	24.1	24.6	22.5
Bromine No	1.0	1	1.5
Material balance	95.7	97.1	96.6
Percent H_2SO_4 in the recovered acid	86.9	82.6	76.6

The concentration of acid employed may vary, but with the various concentrations of acid, the temperatures will be different. When using about 98% acid, it is contemplated that the temperature gradient may be from about 60° to 105° F. With weaker concentrations of acid, however, the temperature should be increased. Thus, with 94% acid the temperature range may be from about 75° to 120° F., and with 90% acid from about 85 to 130° F. Satisfactory results have been obtained with overall temperature gradients ranging from 40° to 60° F. Accordingly, when using a multiple stage unit containing five to ten stages, the temperature differential between the stages may be about 10° to 5°, and a fairly uniform temperature variation may exist from stage to stage.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. In the alkylation of low boiling isoparaffins with olefins to produce gasoline hydrocarbons wherein the hydrocarbons are contacted with strong sulfuric acid catalyst of alkylation strength while hydrocarbons and catalyst pass serially through a plurality of stages at reaction temperatures, the improvement which comprises maintaining the catalyst at a higher temperature in the later stages than in the early stages to increase the activity of the used catalyst in the later stages.

2. In the alkylation of low boiling isoparaffins with olefins to produce gasoline hydrocarbons wherein the hydrocarbons and fresh strong sulfuric acid catalyst of alkylation strength are passed through a multiple stage reaction zone from which spent acid and alkylation products are withdrawn, the improvement which comprises maintaining in that stage from which the spent acid is withdrawn, a higher temperature than in that stage to which the fresh acid is charged.

3. In the alkylation of low boiling isoparaffins with olefins in the presence of strong sulfuric acid of alkylation strength to produce gasoline hydrocarbons, the method comprising serially passing streams of hydrocarbon and acid through a multiple stage reaction zone wherein sufficient time and contact are provided to effect the reaction and increasing the temperature in the direction of flow of the acid through the successive stages to maintain a temperature differential between stages of about 5° to 10° F. whereby the efficiency of the acid is maintained substantially constant.

4. A process for the manufacture of gasoline hydrocarbons which comprises contacting low boiling isoparaffins and olefins with sulfuric acid of about 90 to 94% concentration in a multiple stage reaction zone and maintaining a progressively increasing temperature in the direction of flow of the acid between 75° and 130° F. whereby the loss in efficiency in the acid is substantially prevented.

5. In the manufacture of gasoline hydrocarbons by the alkylation of low boiling isoparaffins with olefins in the presence of sulfuric acid of about 90–98% concentration as an alkylation catalyst, wherein the catalyst decreases in concentration and loses its efficiency during the operation, the improvement which comprises progressively increasing the temperature to obtain a temperature gradient within the range of about 60°–130° F. during the operation to compensate for loss in efficiency of the catalyst as it becomes spent.

6. In a continuous process for the alkylation of low boiling isoparaffins with olefins in the presence of a sulfuric acid catalyst while contin-

uously bringing the catalyst and hydrocarbons together in a reaction zone, wherein the catalyst tends to deteriorate and cause loss in yield during the operation, the improvement which comprises raising the temperature within range of about 60°–130° F. as the catalyst deteriorates within the range of 90–98% to maintain the activity of the deteriorated catalyst and avoid loss in yield.

7. In a continuous process for the alkylation of hydrocarbons wherein low boiling isoparaffins and olefins are contacted with strong sulfuric acid of alkylation strength while the acid and hydrocarbons are passed serially through a multiple stage reaction zone under conditions of time and temperature sufficient to produce gasoline hydrocarbons, the method of increasing the efficiency of the acid which comprises maintaining the temperature of the acid at a succeeding stage of the stream higher than at a preceding stage of the stream in said zone.

8. In a continuous process for the alkylation of hydrocarbons, wherein low boiling isoparaffins and olefins are contacted with strong sulfuric acid of alkylation strength while the acid and hydrocarbons are continuously passed through an elongated reaction zone, under conditions of time and pressure sufficient to produce gasoline hydrocarbons and the acid deteriorates and loses efficiency during the reaction, the method of compensating for loss in efficiency of the acid by deterioration, which comprises maintaining the used acid leaving the reaction zone at a higher temperature than the feed acid by progressively increasing the temperature of the acid as it passes through said reaction zone.

9. In the alkylation of low boiling isoparaffins with olefins to produce gasoline hydrocarbons, wherein the hydrocarbons are contacted with strong sulfuric acid of alkylation strength in a sectional reaction zone, the improvement which comprises contacting hydrocarbons with fresh acid in one section of said zone and with partially spent acid in another section of said zone and maintaining a higher temperature in that section wherein the hydrocarbons contact the partially spent acid than in that section wherein the hydrocarbons contact the fresh acid to increase the efficiency of the partially spent acid.

10. In the alkylation of low boiling isoparaffins with olefins in the presence of strong sulfuric acid of alkylation strength to produce gasoline hydrocarbons, the steps of passing serially the acid and hydrocarbons through a plurality of reaction zones and maintaining a rising temperature gradient totaling about 40° to 60° F. in the acid in the direction of flow thereof through said zones.

11. A process for the alkylation of low boiling isoparaffins with olefins, which comprises serially passing a mixture of isoparaffins and strong sulfuric acid through a plurality of reaction zones, contacting the mixture in said zones with olefins while maintaining an excess of isoparaffins over the olefins, and progressively increasing the temperature of said mixture flowing through the consecutive zones to compensate for loss of the efficiency of the acid by deterioration.

12. A process for producing alkylated hydrocarbons by the interaction of isoparaffins and olefins, which comprises reacting the hydrocarbons to be alkylated with the olefins in contact with strong sulphuric acid and at optimum pressures and temperatures, and increasing the reaction temperature as the strength of the strong sulphuric acid decreases.

13. In the alkylation of low-boiling isoparaffins with olefins in the presence of strong sulfuric acid of alkylation strength to produce gasoline hydrocarbons, wherein the acid flows serially through at least two alkylation reaction zones where hydrocarbons are charged, the improvement which comprises maintaining a prior zone in the direction of flow of the acid at a lower temperature than a succeeding zone.

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