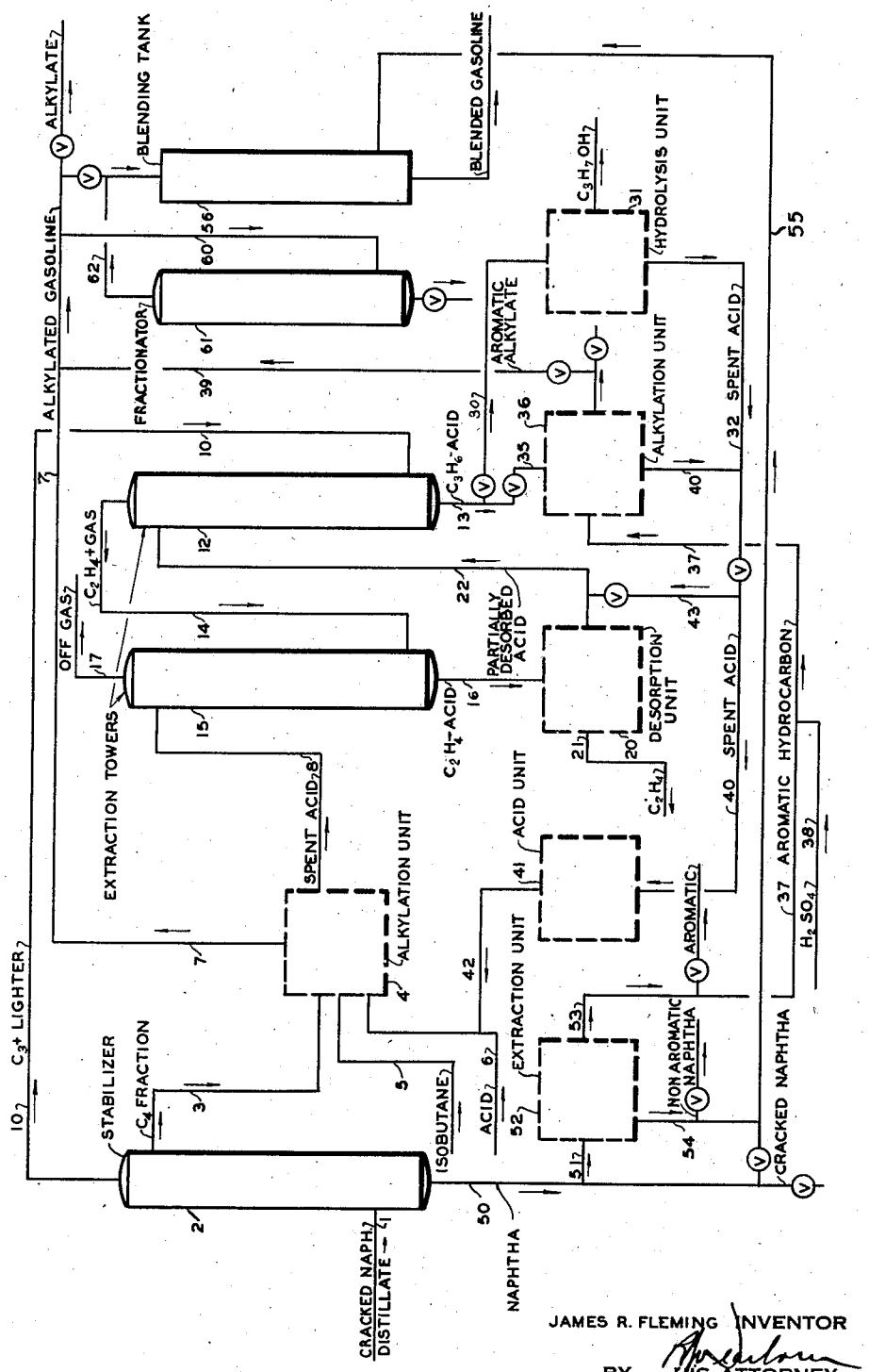
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TREATMENT OF HYDROCARBONS

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JAMES R. FLEMING INVENTOR

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TREATMENT OF HYDROCARBONS

James R. Fleming, Port Arthur, Tex., assignor to The Texas Company, New York, N. Y., a corporation of Delaware

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This invention relates to the treatment of hydrocarbons and particularly the separation of normally gaseous hydrocarbons from mixtures containing them with subsequent conversion into valuable products useful in the manufacture of gasoline and other products.

The invention contemplates a method of separating olefins from gaseous mixtures and separately treating the olefins to convert them into valuable products. It also contemplates a combination process for the manufacture of gasoline of high anti-knock value and having other desirable characteristics.

In accordance with the invention, normally gaseous hydrocarbons comprising olefins having from 2 to 4 carbon atoms per molecule are obtained from the products of hydrocarbon cracking and the olefinic constituents thereof are separately treated to convert them into valuable products. Thus, a C_4 fraction and a C_3 and lighter fraction are obtained. The C_4 fraction containing normal butylenes, isobutylene and paraffins is subjected to contact with concentrated sulphuric acid in the presence of a low boiling isoparaffin such as isobutane under alkylating conditions so that normally liquid alkylated hydrocarbons boiling within the range of gasoline are produced.

Sulphuric acid which has become spent as a catalyst for the alkylation reaction is then employed to effect selective absorption of ethylene from propylene in the C_3 and lighter fraction. The resulting ethylene acid mixture is subjected to elevated temperature so as to effect partial stripping of ethylene, thereby obtaining ethylene in substantially pure form and also producing a partially desorbed ethylene acid mixture.

The partially desorbed acid mixture is employed to extract propylene from the residual gases advantageously under conditions such that the residual ethylene contained in the acid mixture is displaced from the acid by propylene.

The resulting propylene acid mixture may be disposed of by subjecting it all or in part to elevated temperature so as to liberate propylene in substantially pure form. On the other hand, all or part of the propylene acid mixture may be subject to hydrolysis under conditions effective to convert the propylsulphate into alcohol.

Preferably the propylene rich acid is passed to an aromatic alkylation zone wherein the mixture is subjected to contact with a low boiling aromatic hydrocarbon such as benzene, toluene or xylene in the presence of some free acid so as to effect alkylation of the aromatic hydrocarbon with propylene. In this way cumene is prepared by alkylating benzene with the propylene while cymene is prepared by reacting toluene with the propylene.

Both cumene and cymene are desirable constituents of high grade aviation gasoline. These compounds are blended with gasoline so as to increase the rich mixture performance and thus permit obtaining more power from the fuel during take-off. These compounds may be mixed with the aforementioned alkylated gasoline obtained by alkylating C_4 olefins with isobutane and may be blended in the proportion of about 5 to 15% by volume.

In accordance with the invention, the aromatic hydrocarbon or hydrocarbons used in the aromatic alkylation may be derived from cracked naphtha or from hydro-formed naphtha.

The spent acid from the aromatic alkylation operation is advantageously passed to an acid concentrating zone or unit wherein the concentration is brought back to 94 to 100% H_2SO_4. The reconcentrated acid is then recycled to the first mentioned alkylation unit wherein C_4 olefins are reacted with isobutane. Some of the spent acid from the aromatic alkylation operation may be used for diluting the partially desorbed acid used for the selective extraction of propylene from the residual gases.

In order to describe the invention in more detail, reference will now be made to the accompanying drawing illustrating a diagram of flow suitable for the manufacture of gasoline.

As indicated in the drawing, a cracked naphtha distillate is conducted from a source not shown through a pipe 1. This distillate may be obtained by the catalytic cracking of gas oil for the production of gasoline. It will comprise normally gaseous hydrocarbons and normally liquid hydrocarbons boiling up to about 400° F.

The cracked naphtha is introduced to a stabilizer 2 wherein it is subjected to fractionation so as to segregate a C_3 and lighter fraction, a C_4 fraction and a stabilized naphtha. While a single tower is indicated it will be understood that two or more fractionating towers may be employed, the single tower indicated being merely diagrammatic.

The C_4 fraction is passed through a pipe 3 to an alkylation unit 4, shown in broken lines. This unit may comprise a plurality of apparatus including reaction vessels, separating vessels and fractionating equipment.

In the alkylation operation the C_4 fraction containing olefins is reacted with isobutane in the

presence of concentrated sulphuric acid. The isobutane is conducted from a source not shown through a pipe 5 while the acid is also conducted from a source not shown through a pipe 6.

The acid as already indicated has a concentration of about 94 to 100% H_2SO_4 on the basis of freedom from organic material.

The method of carrying out the alkylation reaction with concentrated sulphuric acid is now well known in the art and therefore need not be described in detail. The alkylated hydrocarbons may comprise some hydrocarbons boiling above the range of gasoline and therefore the alkylation unit may comprise provision for fractionating the alkylated gasoline hydrocarbons from the undesired higher boiling material.

At any rate the alkylated gasoline hydrocarbons are discharged from the unit through a pipe 7 while spent acid of about 90% H_2SO_4 (organic free) is discharged from the unit through a pipe 8.

Referring again to the stabilizer 2, the C_3 and lighter fraction is removed through a pipe 10 which leads to the lower portion of a primary extraction tower 12. The C_3 and lighter hydrocarbons rise through the tower countercurrently to a stream of partially desorbed acid or diluted acid as will hereinafter be described. The extraction in the tower 12 is carried out under a temperature in the range of about 60 to 100° F. and under a pressure ranging from about 2 to 110 atmospheres. Propylene is absorbed in the acid and continuously discharged from the bottom of the tower through a pipe 13.

The residual gas containing ethylene and saturated paraffin hydrocarbons is continuously removed from the top of the tower through a pipe 14 which leads to the lower portion of a secondary extraction tower 15. In this extraction tower the gases rise countercurrently to a stream of spent alkylation acid, being introduced to the upper portion of the tower through the pipe 8. This extraction is carried out under a temperature ranging from about 50 to 175° F. and preferably from about 90 to 125° F. The pressure will range from about 1 to 100 atmospheres. Conditions are thus maintained so that ethylene is extracted by the spent acid. The resulting ethylene acid mixture is discharged from the bottom of the tower through a pipe 16 while the residual gases are discharged through the pipe 17.

The ethylene acid mixture will comprise ethylene in the form of ethyl disulphate and ethylene hydrogen sulphate. This mixture is passed to a desorption unit 20 wherein the acid mixture is subject to an elevated temperature in the range 350 to about 500° F. The heating is carried out so that the acid mixture is exposed to the elevated temperature for a short period of time insufficient to cause substantial decomposition.

The desorption is carried out so as to liberate about 50 to 60% of the ethylene in pure form which is discharged through pipe 21.

The ethylene so liberated is sufficiently pure to be useful for the manufacture of chemicals such as ethyl benzene.

The partially desorbed acid mixture retains a substantial amount of ethylene but the ethylene is sufficiently low in concentration so that it is present in the acid entirely in the form of ethyl hydrogen sulphate.

This partially desorbed acid is removed through a pipe 22 and conducted to the upper portion of the primary extraction tower 12 to provide the extracting medium therein.

Conditions are maintained in the extraction tower 12 so that the residual ethylene contained in the acid is displaced therefrom by the propylene contained in the feed gas entering the tower. The displaced ethylene passes overhead through the pipe 14. Thus, the propylene acid mixture drawn off from the tower through the pipe 13 is substantially free from ethylene.

The propylene acid mixture drawn off through the pipe 13 may be conducted in part through a branch pipe 30 leading to a hydrolysis unit 31, shown in broken lines, wherein the propylene sulphate is converted to alcohol. Spent acid is drawn off from the hydrolysis unit through a pipe 32.

On the other hand, the propylene acid mixture all or in part is conducted through a branch pipe 35 leading to an alkylation unit 36, shown in broken lines.

An aromatic hydrocarbon such as benzene, or a mixture of aromatics, is conducted through a pipe 37 to the alkylation unit. Free sulphuric acid of about 85% concentration may be introduced from a pipe 38 to the alkylation unit 36.

Conditions are maintained in the alkylation unit so that the benzene reacts with the propyl ester to produce alkylated aromatic hydrocarbons comprising mainly cumene. The alkylation reaction may be carried out at a temperature in the range of about 75 to 175° F. The amount of free sulphuric acid added through the pipe 38 may amount to about 1 to 2 parts by weight of the propylene acid mixture entering the alkylation unit.

As in the case of the aliphatic alkylation unit 4 the aromatic alkylation unit 36 may comprise a plurality of apparatus including provision for fractionating undesired high boiling material from the alkylate. The alkylated aromatics are removed through a pipe 39.

The spent acid from the alkylation unit 36 is drawn off through a pipe 40 and conducted all or in part to an acid concentrating unit 41 of conventional design and operation. The concentration of the acid is thus brought up to the range of about 94 to 100% which is effective as a catalyst for the aliphatic alkylation unit.

As indicated, some of the spent acid from the alkylation unit 36 may be by-passed through a branch pipe 43 which communicates with the pipe 22. The purpose of this is to adjust the concentration of the acid used in the extraction tower 12 whenver this may be necessary.

Thus, the concentration of sulphuric acid effective for the absorption of propylene is usually in the range of about 75 to 85% basis organic free. It is contemplated, however, that the ethylene hydrogen sulphate mixture passing through the pipe 22 will be adequate without further adjustment of the acid concentration to effect the selected extraction of propylene from the feed gases entering the tower 12.

The spent acid drawn off from the hydrolysis unit through the pipe 32 may also be passed via pipe 49 to the acid concentration unit 41.

The aromatic hydrocarbon or hydrocarbons used in the alkylation unit 36 may be derived from the stabilized naphtha by extraction with a suitable solvent.

For example, the stabilized naphtha removed from the stabilizer 2 through a pipe 50 may be passed in part through a branch pipe 51 to an extraction unit 52. In the extraction unit the naphtha may be extracted with a solvent consisting essentially of water at a temperature of about 450 to 550° F. and under an elevated pressure

sufficient to maintain liquid phase conditions. In this way the aromatic hydrocarbons are preferentially dissolved in the water and the water solution is removed and the dissolved aromatics removed therefrom. The removed aromatics are conducted through a pipe 53 which connects with the previously mentioned pipe 37. The extraction may be carried out so as to obtain the desired aromatic in concentrated form, or to obtain a mixture of aromatics of differing boiling point, such as a mixture of benzene and toluene. The resulting aromatic alkylate can then be fractionated later or otherwise utilized.

The non-aromatic portion of the naphtha is removed through a pipe 54 which may communicate with a pipe 55 leading to a blending tank 56.

The pipe 55 also communicates with the pipe 50 to permit passing stabilized naphtha to the tank 56.

Likewise, the pipe 7 communicates with the tank 56 to permit passing alkylated gasoline thereto.

The aromatic alkylate discharged through the pipe 39 may also pass to the blending tank 56. The several hydrocarbon components are thus blended to produce a high quality gasoline product.

As indicated in the drawing, provision may be made for fractionating the aliphatic alkylate and the aromatic alkylate outside their respective alkylation units. Thus, these two alkylated products may be discharged through a pipe 60 leading to a fractionator 61 wherein they are fractionated in the presence of each other to produce a distillate fraction which may be recycled through a pipe 62 to the blending tank 56.

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. A continuous method of selectively separating propylene and ethylene from a normally gaseous mixture of hydrocarbons which comprises passing a stream of said gaseous mixture through a primary extraction zone, subjecting it therein to contact with an extraction medium comprising partially desorbed sulphuric acid from a source later referred to, effecting said contact under conditions such that propylene is extracted by the acid from ethylene and non-olefinic hydrocarbons in said gaseous mixture, separately removing residual ethylene gas and propylene rich acid, passing said residual gas through a secondary extraction zone, subjecting it therein to contact with sulphuric acid of about 90 to 94% organic free acidity, effecting said contact in the secondary zone under conditions such that ethylene is extracted by the acid from the residual gas, separately discharging the residual gas and ethylene rich acid, subjecting the ethylene rich acid to elevated temperature whereby a major portion of the ethylene is liberated to produce partially desorbed acid, discharging the liberated ethylene and passing said partially desorbed acid to the primary extraction zone as the said extraction medium.

2. A continuous method of selectively separating propylene and ethylene from a normally gaseous mixture of hydrocarbons which comprises passing a stream of said gaseous mixture through a primary extraction zone, subjecting it therein to contact with an extraction medium comprising partially desorbed sulphuric acid from a source later referred to, effecting said contact under conditions such that propylene is extracted by the acid from ethylene and non-olefinic hydrocarbons in said gaseous mixture, separately removing residual ethylene gas and propylene rich acid, passing said residual gas through a secondary extraction zone, subjecting it therein to contact with sulphuric acid of about 90 to 94% organic free acidity, effecting said contact in the secondary zone under conditions such that ethylene is extracted by the acid from the residual gas, separately discharging the residual gas and ethylene rich acid, subjecting the ethylene rich acid to elevated temperature whereby a major portion of the ethylene is liberated to produce partially desorbed acid, discharging the liberated ethylene, passing partially desorbed acid to the primary extraction zone as the said extraction medium, treating said propylene rich acid to effect removal of propylene and produce spent acid, and passing at least a portion of said spent acid to said primary extraction zone.

3. A process for gasoline manufacture from C_4 and lighter hydrocarbons containing olefins which comprises forming a C_4 fraction and a C_3 and lighter fraction, subjecting said C_4 fraction to alkylation with a low boiling isoparaffin in the presence of concentrated sulphuric acid in an aliphatic alkylation zone, removing from said zone alkylated gasoline and spent alkylation acid, subjecting said C_3 and lighter fraction to contact in a primary extraction zone with an extraction medium comprising partially desorbed sulphuric acid, effecting said contact under conditions such that propylene is extracted by the acid from ethylene and non-olefinic hydrocarbons in said C_3 and lighter fraction, removing from the primary extraction zone residual ethylene gas and propylene rich acid, passing said residual gas through a secondary extraction zone, subjecting it therein to contact with said spent alkylation acid, effecting said contact under conditions such that ethylene is extracted by the acid from the residual gas, separately discharging residual gas and ethylene rich acid from the secondary extraction zone, subjecting the ethylene rich acid to elevated temperature whereby a major portion of the ethylene is liberated to produce partially desorbed acid, discharging liberated ethylene, recycling said partially desorbed acid to the primary extraction zone, liberating spent acid from the propylene rich acid mixture, reconcentrating said liberated acid and recycling the reconcentrated acid to the aliphatic alkylation zone.

4. A process for gasoline manufacture from C_4 and lighter hydrocarbons containing olefins which comprises forming a C_4 fraction and a C_3 and lighter fraction, subjecting said C_4 fraction to alkylation with a low boiling isoparaffin in the presence of concentrated sulphuric acid in an aliphatic alkylation zone, removing from said zone alkylated gasoline and spent alkylation acid, subjecting said C_3 and lighter fraction to contact in a primary extraction zone with an extraction medium comprising partially desorbed sulphuric acid, effecting said contact under conditions such that propylene is extracted by the acid from ethylene and non-olefinic hydrocarbons in said C_3 and lighter fraction, removing from the primary extraction zone residual ethylene gas and propylene rich acid, passing said residual gas through a secondary extraction zone, subjecting it therein to contact with said spent alkylation acid, effecting said contact under conditions such that ethyl-

ene is extracted by the acid from the residual gas, separately discharging residual gas and ethylene rich acid from the secondary extraction zone, subjecting the ethylene rich acid to elevated temperature whereby a major portion of the ethylene is liberated to produce partially desorbed acid, discharging liberated ethylene, recycling said partially desorbed acid to the primary extraction zone, passing said propylene rich acid to an aromatic alkylation zone, subjecting it therein to contact with a low boiling aromatic hydrocarbon under conditions such that aromatic hydrocarbons react with propylene to form aromatic alkylate, removing from the aromatic alkylation zone aromatic alkylate and spent acid and blending at least a portion of said aromatic alkylate with said alkylated gasoline.

5. The process according to claim 4 in which the low boiling aromatic hydrocarbon is selected from the group consisting of benzene, toluene and xylene.

6. The process according to claim 4 in which spent acid removed from the aromatic alkylation zone is recycled in part to the primary extraction zone.

7. A continuous method of selectively separating propylene and ethylene from a normally gaseous mixture of hydrocarbons which comprises passing a stream of said gaseous mixture through a primary extraction zone, subjecting it therein to contact with an extraction medium comprising partially desorbed sulphuric acid from a source later referred to, effecting said contact under conditions such that propylene is extracted by the acid from ethylene and non-olefinic hydrocarbons in said gaseous mixture, separately removing residual ethylene gas and propylene rich acid, passing said residual gas through a secondary extraction zone, subjecting it therein to contact with sulphuric acid of about 90 to 94% organic free acidity, effecting said contact in the secondary zone under conditions such that ethylene is extracted by the acid from the residual gas, separately discharging the residual gas and ethylene rich acid, subjecting the ethylene rich acid to elevated temperature whereby a substantial portion of the ethylene is liberated to produce partially desorbed acid, discharging the liberated ethylene and passing partially desorbed acid to the primary extraction zone as the said extraction medium.

8. A continuous method of selectively separating propylene and ethylene from a normally gaseous mixture of hydrocarbons which comprises passing a stream of said gaseous mixture through a primary extraction zone, subjecting it therein to contact with an extraction medium comprising partially desorbed sulphuric acid from a source later referred to, effecting said contact under conditions such that propylene is extracted by the acid from ethylene and non-olefinic hydrocarbons in said gaseous mixture, separately removing residual ethylene gas and propylene rich acid, passing said residual gas through a secondary extraction zone, subjecting it therein to contact with sulphuric acid of about 90 to 94% organic free acidity, effecting said contact in the secondary zone under conditions such that ethylene is extracted by the acid from the residual gas, separately discharging the residual gas and ethylene rich acid, subjecting the ethylene rich acid to elevated temperature whereby a major portion of the ethylene is liberated to produce partially desorbed acid, discharging the liberated ethylene, passing partially desorbed acid to the primary extraction zone as the said extraction medium, treating said propylene rich acid to effect removal of propylene and produce spent acid, and adding at least a portion of said spent acid to said extraction medium such that the resulting acid mixture has an organic free acidity of about 75 to 85%.

JAMES R. FLEMING.