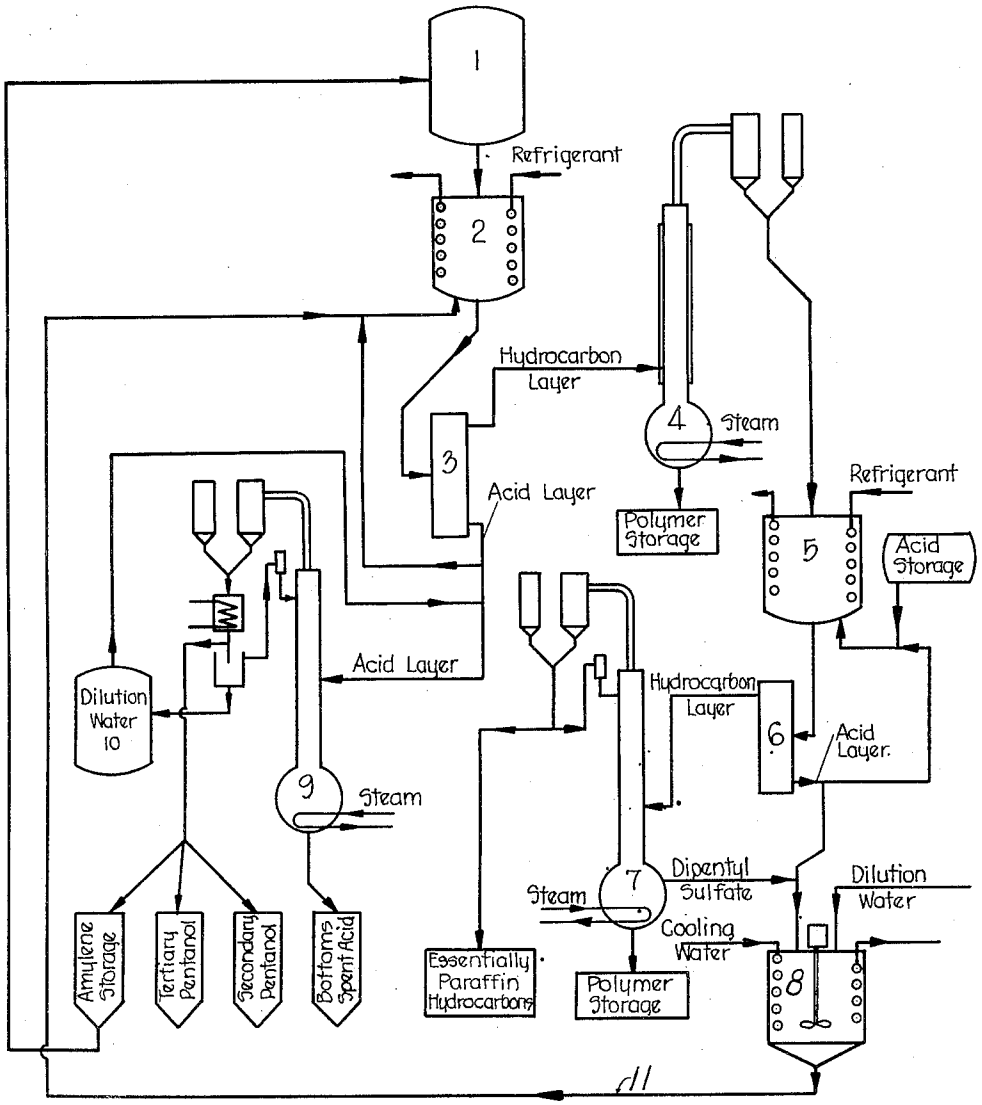
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PRODUCTION OF ALCOHOLS

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PRODUCTION OF ALCOHOLS

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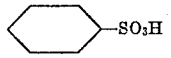
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23 Claims. (Cl. 260—156)

This invention relates to a process for the preparation of valuable olefine derivatives from olefinic mixtures and is more particularly concerned with a process whereby secondary and/or tertiary alcohols may be economically produced from olefinic mixtures with the minimum expenditure of reagents.

Suitable sources of hydrocarbons containing olefines are those which may be derived from carboniferous natural materials such as petroleum, coal, peat, oil shales, tars, petroleum products, and the like by straight distillation, destructive cracking, or dehydrogenation processes of any kind. Our process is more particularly concerned with the treatment of hydrocarbon fractions or mixtures which consist essentially of or predominate in hydrocarbons of the same number of carbon atoms to the molecule as a propane-propene, butane-butene, pentane-pentene, hexane-hexene, and the like, cut. Thus our process is applicable to any suitable hydrocarbon mixture regardless of its source and may be utilized with substantially pure mixtures of secondary base olefines, with tertiary base olefines, as well as with mineral oil fractions which also contain paraffin hydrocarbons.

We have discovered that tertiary base olefines (i. e. iso-olefines capable of yielding tertiary alcohols upon hydrolysis) can be selectively removed from olefinic mixtures by absorption in acid liquor. By "acid liquor" we mean a relatively strong mineral acid acting acid, such as H_2SO_4, H_3PO_4



its homologues, analogues, and the like, which has been previously employed in stronger concentration on a free acid basis in absorbing a secondary base olefine or olefines (i. e. iso and normal olefines capable of yielding secondary alcohols upon hydrolysis) of the same and/or different carbon content. The acid liquor usually comprises an aqueous solution of the neutral and/or acid esters with some free acid and may or may not contain small amounts of polymer, free alcohol and/or very low percentages of free hydrocarbons. In lieu of the thus commercially obtainable acid liquor one may employ relatively purer media such as may be prepared by dilution of acid and/or neutral esters with water. Such esters may be prepared, for example, by dissolving an alcohol (primary, secondary or tertiary) or an ester in an aqueous solution of a mineral acid acting acid such as referred to above. It is to be thus understood that our primary invention resides in the use of an acid liquor regardless of its source or manufacture for the selective absorption of tertiary base olefines.

More particularly our invention is concerned with the treatment of hydrocarbon mixtures containing secondary and tertiary base olefines wherein the secondary base olefine content is substantially reduced by absorption in a suitable medium such as a relatively strong acid, as H_2SO_4 and the like above mentioned, to yield an acid liquor which acid liquor is then diluted to a suitable degree prior to contacting with a similar hydrocarbon mixture which contains a relatively larger proportion of tertiary olefines whereby the tertiary olefine content thereof is substantially reduced and the resulting "fat acid" or acid liquor preferably subjected to a series of treatments whereby relatively pure secondary and tertiary alcohols are obtained. The hydrocarbon fraction which has been subjected to treatment with the diluted initial acid liquor is preferably then treated with fresh acid media to yield new acid liquor whereby the process can be operated in a continuous or intermittent manner.

For purposes of illustration only reference will be had to the following example of the application of our invention to the production of secondary and tertiary amyl alcohols. But it will be understood that by suitable modification of operating conditions, as will be obvious to those skilled in the art of synthetic alcohol preparation, secondary and/or tertiary butyl, secondary and/or tertiary hexyl and the like higher alcohols may be similarly prepared.

The preferred initial material is substantially stripped of hydrocarbons containing less than five carbon atoms to the molecule and suitably fractionated into a fraction containing pentane and secondary and tertiary amylenes. In certain instances it will be difficult to remove traces of higher or lower carbon compounds but their presence is not detrimental to our process. We prefer to practice our process with a substantially pure fraction of hydrocarbons of which each molecule contains the same number of carbon atoms. As paraffin hydrocarbons may be considered as inert compounds in our process, their presence in their corresponding carbon compound fraction is not accompanied by any detrimental effect.

In the substantially pure pentane-pentene mixture above referred to the following compounds may be present: normal pentane, the isopentanes; pentene 1, pentene 2, isopropyl ethylene, trimethyl

ethylene and unsymmetrical methyl ethyl ethylene and small amounts of methyl butadienes.

The example of the application of our invention to the production of secondary and tertiary amyl alcohols may be best explained by reference to the accompanying drawing which is a "flow-sheet" or diagrammatic representation of the steps of our process in one of its modifications applicable to the manufacture of these products.

The above described pentane-pentene mixture having, for example, the following composition:

	Percent by weight
Pentanes	41
Secondary base olefines	37
Tertiary base olefines	22

is fed from a storage tank 1 to the tertiary reactor 2 where it is treated with dilute acid liquor, the preparation of which will be described later. By providing suitable agitation to insure intimate contact of the reagents for a period of about 10 to 20 minutes at a temperature of about 0° C. all but a few percent of the tertiary base olefines are absorbed and converted into tertiary amyl alcohol by autolysis, which alcohol is preferentially soluble in the acid layer. If the temperature is allowed to rise during this operation there is a tendency for the tertiary base olefines to polymerize which becomes very marked above 40° C. while at the same time the distribution of the tertiary alcohol between the acid and hydrocarbon becomes more unfavorable. The acid and hydrocarbon phases resulting are allowed to stratify in the separator 3 where they are then separated. The hydrocarbon layer having in a typical case, where the starting material was as shown above, the following approximate compositions:

	Percent by weight
Pentanes	49.5
Secondary base olefines	36
Tertiary base olefines	7
Polymers	7
Dipentyl sulfate	0.5

is preferably run to a still 4 where the polymer is removed as bottoms. The still 4 is preferably operated at a temperature above 100° C. to prevent loss of secondary amylenes which are soluble in the still bottoms and the amylene loss reduced in this way to less than 1% while the loss of dipentyl sulfate is negligible. This operation may, however, be entirely omitted and the hydrocarbon layer sent directly to the next treatment in the secondary reactor 5. In this case the polymer will gradually accumulate in the system until a maximum value of about 14% of the weight of hydrocarbon layer is reached as a result of the tendency of the incoming hydrocarbon to scrub out polymer from the acid liquor with which it is treated in the tertiary reactor 2. This accumulation of polymer in the system has been found to increase the acid consumption of our process in approximately the proportion of half a mol. of acid per mol. of polymerized olefine and we therefore refer to remove the polymer as described, or by other suitable means, prior to the introduction of the hydrocarbon phase into reactor 5.

In the tertiary reactor 2 the incoming hydrocarbon mixture besides having a tendency to remove any polymeric bodies present in the acid liquor also tends to remove any free hydrocarbon material, whether of paraffinic or olefinic character, which may be present in the acid liquor and any neutral esters present tend to distribute themselves, to some extent at least, in the hydrocarbon phase. At the same time the acid liquor tends to absorb some small percent of secondary olefines and the slight proportion of secondary alkyl esters present in the acid liquor is converted to the corresponding acid esters and/or alcohol as a result of the mild aqueous acid conditions existing in the tertiary reactor.

After polymer removal the hydrocarbon phase will have the following approximate composition:

	Percent by weight
Pentane	53.2
Secondary base amylenes	38.3
Tertiary base amylenes	8.5

This hydrocarbon mixture is treated in the secondary reactor 5 with H_2SO_4 of about 85 to 98% strength, preferably about 95% acid, in the ratio of about 0.9 to 1.3 mols of acid, most preferably about 1.0 mol., per mol. of secondary base olefine input, whereby the secondary base olefines are converted essentially into pentyl hydrogen sulfate together with some dipentylsulfate and secondary alcohol. The secondary reactor 5 like the tertiary reactor 2 is provided with suitable agitating means and with cooling coils through which a refrigerant may be circulated to maintain the desired temperature which in this case for the acid concentrations specified above is about 0 to 20° C., preferably about 5° C. It is of course obvious that the temperature used must be adjusted not only to the concentration of acid employed, but also to the character of the acid chosen and to the time of contact of the reagents as well as the character and concentration of the olefines involved. The upper limit for these factors is fixed by the degree of polymerization which results which will be influenced by the amount of tertiary olefines present, while the lower limit of acid concentration is set in our process at that at which efficient esterification of the secondary base olefines can be effected in a reasonable time. The time of contact in the secondary reactor 5 varies from one minute to several hours, depending on the acid strength.

After being allowed to settle and stratify in separator 6 the hydrocarbon layer having the following composition:

	Per cent by weight
Pentanes	60.4
Secondary base amylenes	1.9
Tertiary base amylenes	0.0
Dipentyl sulfate	5.0
Polymers	22.7

is removed from the acid layer and sent to still 7 where the pentanes and remaining olefines are separated from the polymers and dissolved dipentyl sulfate. The olefines thus obtained are in a very dilute condition and therefore not desirable for admixing with the initial material for recovery. One method of salvaging the olefine values of these materials is to scrub suitably or contact the olefines therein, either in the gaseous or liquid phase, with fresh absorption medium prior to the introduction of the latter into the secondary reactor 5. The dipentyl sulfate, partly converted to pentyl hydrogen sulfate, under distillation treatment in column 7, separates from the polymers as an acid layer in the bottom of the still 7 and is recovered and preferably added to the acid liquor going to the drowning tank 8, as shown, or may be sent to the hydrolyzing still 9 direct.

The acid layer from separator 6, containing

some free secondary amyl alcohol, pentyl hydrogen sulfate and dipentyl sulfate is conducted to the drowning unit 8, where it is diluted with sufficient water to reduce the acid content to about 65 to 80%, preferably about 68 to 72%, on a hydrocarbon free basis. The free acid content will then be of the order of about 25% to 30% of the total weight. The temperature is maintained at about 20 to 40° C., preferably about 30° C., for about 2 to 3 hours while the solution is agitated. Dilution and temperature control are necessary at this stage to prevent back decomposition to amylenes. By proper adjustment of the factors of acid concentration, temperature and time of contact approximately equivalent results are attainable under different sets of conditions. By operating in the preferred ranges above specified the dipentyl sulfate content of the solution can be reduced to less than 1% with a resulting increase in free secondary amyl alcohol and pentyl hydrogen sulfate. The solution is then ready to serve as the absorbing medium for the tertiary base olefines in the incoming pentane-amylene mixture as described and is pumped, preferably directly, to the tertiary reactor via line 11 as indicated. If desired, the dialkyl sulfate which tends to form a scum on tank 8 in the absence of agitation may be removed by skimming or other physical methods or may be contacted with a suitable solvent of the neutral ester such as a hydrocarbon solvent, for example pentane, prior to the introduction of the acid liquor in the tertiary reactor 2.

A part of the acid layer from separator 3 containing absorbed tertiary base olefines in the form of tertiary amyl alcohol together with free secondary amyl alcohol and also containing pentyl hydrogen sulfate may advantageously be returned to the tertiary reactor 2 for recirculation. It has been found that the completeness of absorption of the tertiary base olefines is roughly proportional to the amount of acid phase with which it is treated. The amount of acid phase which may be used is limited therefore in a reactor of a given size to that volume which permits substantially complete absorption of tertiary olefines under the rate of introduction of reagents therein. The acid layer from the secondary reactor 5, previously referred to, may likewise be advantageously recirculated through the secondary reactor. While the presence of large excesses of acid phase at the stage does not show such marked improvement in absorption efficiency as is the case in absorption of tertiary base olefine, nevertheless by employing an absorption medium comprising the acid derivatives of the secondary base olefines being absorbed advantages in completeness of absorption and economy in acid consumption are attained.

That portion of the acid layer from the tertiary reactor which is being withdrawn from circulation is preferably diluted with about twice to three times its volume of water from tank 10 and then suitably distilled for separation of its components whereby any free amylenes are recovered and returned to the incoming pentane-pentene storage tank 1; water is removed and since it contains some dissolved alcohols is collected for reuse at the diluting water tank 10; spent acid is separated as bottoms and pure fractions of tertiary amyl alcohol, boiling range 100–103° C. and secondary amyl alcohol, boiling range 116–119° C., are obtained as final products.

The separation of these products by distillation is indicated in the drawing as being carried out in one still 9 for the sake of simplicity and also because several satisfactory procedures are available for this operation. Straight distillation of the alcohols in dilute acid should not be resorted to, however, as large losses due to back decomposition into amylenes result. The diluted acid layer may be neutralized and then distilled successfully, but we have found that such treatment renders the subsequent recovery of secondary alcohols quite difficult, presumably as a result of the formation of mixed metallo-organo esters of sulfuric acid which are very difficult to hydrolyze. We prefer, therefore, to first dilute the acid layer, within the limits set by the tendency of strong acid solutions to set free amylenes at the temperature required for alcohol recovery and the economic limit for the distillation of dilute solutions, and then flash off the free alcohols in a stripping column with live steam. The secondary base sulfuric acid esters recovered as bottoms may then be separately hydrolyzed and the resulting alcohols recovered in a batch still or a stripping column. Due to the efficiency of polymer removal by the incoming hydrocarbon mixture in the tertiary reactor 2 these subsequent operations may be carried out in substantial freedom from these undesirable materials.

For the initiation of our process several alternative procedures are available. Referring to the preceding example for purposes of illustration, the acid liquor for the first cycle of absorption of tertiary base olefines may be prepared by solution of amyl alcohol, amyl chloride, or amyl acetate, for examples, in aqueous H_2SO_4 and this initial acid liquor later replaced by that prepared from the hydrocarbons remaining after such treatment in the usual manner of our invention. As alternatives the tertiary base olefines may first be removed by absorption in, or polymerization with, H_2SO_4 in the conventional manner and the acid liquor for use in our process then prepared from the resulting hydrocarbon mixture.

Many modifications of our invention are possible. It may be carried out batchwise, intermittently or in continuous operation. It may be operated with hydrocarbons in either the gaseous or liquid phase and with or without the use of pressure. In lieu of drowning tank 8 one may employ a sufficient length of tubing of suitable diameter between separator 6 and reactor 2 to permit, after introduction of diluting water, conversion of neutral esters to the acid form, some simultaneous conversion of acid ester to alcohol also usually occurring. Alternatively the acid layer from separator 6 with added water may be introduced directly into reactor 2.

Furthermore the absorption of the tertiary base olefines may be carried out with an alkyl sulfate medium which is recycled after removal therefrom of the tertiary alcohol content as by crystallization or absorption, etc. The residual hydrocarbon mixture may then be diverted to other uses or separately treated by the above or other methods to yield secondary alcohols.

Among other modifications of our invention are included the preparation of tertiary amyl alcohol, for example, by the selective reaction of tertiary base amylenes with aqueous solutions of secondary hexyl, secondary propyl, primary heptyl, primary pentyl, primary butyl esters or other forms of acid derivatives in place of the secondary pentyl acid liquor used in the previously described example.

Although it has not been overly stressed, an-

other feature of our invention resides in the utilization of an acid liquor, prepared by the absorption of one or more secondary olefines containing the same number of carbon atoms in a suitable polybasic mineral acting acid, in the removal of corresponding secondary olefines from olefinic mixtures which may or may not contain paraffin hydrocarbons. For example, an aqueous acidic solution of isopropyl hydrogen sulfate may be used in removing propylene from a propane-propylene mixture or from one containing also ethylene and ethane and in the same manner the absorption product of secondary butylene and a relatively strong polybasic mineral acid may be used to remove secondary butylenes from their hydrocarbon fraction containing butanes and butenes but substantially devoid of tertiary butylene. Further the employment of secondary alkyl acid liquor on secondary olefines can be utilized in a system which is also concerned with the relative selective absorption of tertiary olefines, for example the acid liquor phase from separator 6 may be introduced with water into reactor 2 wherein the aqueous content of the acid liquor is taken up in part by the tertiary olefines in the incoming hydrocarbon mixture by autolysis. The effluent acid liquor from separator 3 may be suitably chilled or extracted so as to materially reduce the tertiary alcohol content thereof while the reconcentrated acid liquor, with or without added fresh acid, is returned to reactor 5.

Our process has many advantages over previous practice. It does not rely on a constant amount of continually degenerating acid for the removal of tertiary olefines but provides as an absorption medium acid liquor of substantially constant strength. This acid liquor is available for the preparation of tertiary alcohols at no extra expense as it represents the acid which is necessary for the absorption of secondary base olefines. As a result we have obtained in commercial practice yields of 1.13 mols to total alcohols per mol. of acid consumed as compared with 0.4 mol. of alcohol per mol. of acid which is the best yield claimed for previous processes.

Furthermore our process is not so markedly influenced by slight temperature fluctuations as is the case with other methods which use sulfuric acid as a tertiary base olefine absorbing medium as shown by the following figures obtained with a pentane-pentene mixture of approximately 43% pentane, 33% secondary base amylenes and 24% tertiary base amylenes.

	Percent of tertiary amylenes converted into tertiary amyl alcohol		
Temperature	0° C.	20° C.	40° C.
Absorbing medium:			
Sulfuric acid (70 to 75%)	60–70	5–10	
Pentyl hydrogen sulfate	70–80		40–50

As a result of the very efficient removal of tertiary base olefines possible by our process, notable improvements in the yield of secondary alcohols are possible and in factory practice 50 to 60% of the secondary olefine input is recovered as alcohol. The tertiary alcohol recovery at the same time is equal to 60 to 70% of the theoretical based on tertiary olefine input.

While we have in the foregoing described in some detail the preferred embodiment of our invention and some variants thereof, it will be understood that this is only for the purpose of making the invention more clear and that the invention is not to be regarded as limited to the details of operation described, nor is it dependent upon the soundness or accuracy of the theories which we have advanced as to the reasons for the advantageous results attained. On the other hand, the invention is to be regarded as limited only by the terms of the accompanying claims, in which it is our intention to claim all novelty inherent therein as broadly as is possible in view of the prior art.

We claim as our invention:

1. A method of producing alcohol which comprises the substantially selective removal of tertiary base olefines from olefinic mixtures by absorption in aqueous acid liquor of a concentration and at a temperature whereby substantial polymerization of tertiary base olefines are avoided and insufficient to substantially absorb any secondary olefines present in said olefinic mixtures.

2. A method of producing alcohol which comprises preferentially absorbing a tertiary olefine in an aqueous solution of an alkyl ester of a polybasic mineral acid acting acid of a concentration and at a temperature whereby substantial polymerization of the tertiary base olefine is avoided and insufficient to substantially absorb any isomeric secondary olefine.

3. A method of producing alcohol which comprises absorbing a tertiary olefine in an aqueous medium comprising the polybasic mineral acid acting acid derivatives of olefines isomeric therewith of a concentration and at a temperature whereby substantial polymerization of the tertiary base olefine is avoided and insufficient to substantially absorb any isomeric secondary olefine.

4. A method of producing alcohol which comprises absorbing a tertiary base olefine in an aqueous solution of an alkyl ester of a polybasic mineral acid acting acid whose alkyl radical contains the same number of carbon atoms as said tertiary base olefine of a concentration and at a temperature whereby substantial polymerization of the tertiary base olefine is avoided and insufficient to substantially absorb any isomeric secondary olefine.

5. A method of producing alcohol which comprises preferentially absorbing a tertiary base olefine in an aqueous medium comprising an alkyl sulfuric acid ester of a concentration and at a temperature whereby substantial polymerization of the tertiary base olefine is avoided and insufficient to substantially absorb any isomeric secondary olefine.

6. A method of producing alcohol which comprises reacting a mixture of olefine and paraffin hydrocarbons containing tertiary base olefines with aqueous acid liquor at a temperature at which tertiary base olefines are preferentially absorbed without substantial polymerization, said acid liquor being of a concentration insufficient to substantially absorb any isomeric secondary olefine.

7. A method of producing alcohol which comprises treating an olefinic mixture containing essentially hydrocarbons of the same number of carbon atoms per molecule with acid liquor of a concentration and at a temperature whereby substantial polymerization of the tertiary base olefine content is avoided and insufficient to substantially absorb any isomeric secondary olefine.

8. A method of producing tertiary amyl alcohol which comprises absorbing tertiary amylenes in an aqueous medium comprising pentyl esters

of sulfuric acid of a concentration and at a temperature whereby substantial polymerization of the tertiary base olefine is avoided and insufficient to substantially absorb any isomeric secondary olefine.

9. A method of producing tertiary butyl alcohol which comprises absorbing isobutylene in an aqueous medium comprising butyl esters of sulfuric acid of a concentration and at a temperature whereby substantial polymerization of the tertiary base olefine is avoided and insufficient to substantially absorb any isomeric secondary olefine.

10. A method of producing alcohols which comprises reacting a substantially pure butane-butene mixture with acid liquor of a concentration and at a temperature effective for the preferential absorption of the tertiary olefine content while avoiding substantial polymerization thereof and insufficient to substantially absorb any isomeric secondary olefine.

11. A method of producing alcohols which comprises reacting a substantially pure pentane-amylene mixture with acid liquor of a concentration and at a temperature effective for the preferential absorption of the tertiary olefine content while avoiding substantial polymerization thereof and insufficient to substantially absorb any isomeric secondary olefine.

12. A method of producing alcohols which comprises reacting a tertiary base olefine with the absorption product of isomeric olefines in a relatively strong mineral acid acting acid after substantial dilution of said absorption product to a concentration whereby substantial polymerization of the tertiary base olefine is avoided and insufficient to substantially absorb any isomeric secondary olefine.

13. A method of producing alcohols which comprises removing a tertiary base olefine from an olefinic mixture containing paraffin hydrocarbons by absorption in acid liquor of a concentration and at a temperature whereby substantial polymerization of the tertiary base olefine is avoided and insufficient to substantially absorb any isomeric secondary olefine, separating the unabsorbed components and removing polymers from the latter.

14. A method of producing alcohols in accordance with claim 13 in which the polymer removal is effected by distillation.

15. A method of producing alcohols which comprises treating an olefinic mixture, the tertiary base olefine content of which has been substantially reduced, with a polybasic mineral acid acting acid, contacting an olefinic mixture containing tertiary olefines with the product obtained in the presence of water so that its concentration is sufficient whereby substantial polymerization of the tertiary base olefine is avoided and insufficient to substantially absorb any isomeric secondary olefine and submitting the last mentioned olefinic mixture whose tertiary olefine content has been substantially reduced to the first mentioned acid treatment.

16. A method of producing alcohols which comprises treating a liquid olefinic mixture, from which a substantial part of the more reactive olefines have been removed, with a polybasic mineral acid acting acid, diluting the product so obtained with water, scrubbing an olefinic mixture of relatively higher reactive olefine content with said diluted product of a concentration and at a temperature whereby substantial polymerization of the higher reactive olefine content is avoided and insufficient to substantially absorb any isomeric less reactive olefine and submitting the scrubbed mixture to the first mentioned acid treatment.

17. A method of producing alcohols which comprises reacting a liquid paraffin-olefine mixture with an acid liquor of a concentration and at a temperature whereby substantial polymerization of the tertiary olefine content is avoided and insufficient to substantially absorb any isomeric secondary olefine, separating the products so obtained into a hydrocarbon phase and an acid phase, treating the hydrocarbon phase with a polybasic mineral acting acid and returning at least a part of the acid phase to the first mentioned paraffin-olefine mixture treatment.

18. A method of producing an alcohol which comprises preferentially removing a tertiary base olefine from a hydrocarbon mixture with aqueous acid liquor of a concentration and at a temperature whereby substantial polymerization of the tertiary base olefine is avoided and insufficient to substantially absorb any isomeric secondary olefine and reacting the resulting hydrocarbon mixture with an absorption medium for the secondary base olefine content thereof.

19. A method of producing alcohols which comprises preferentially removing a tertiary base olefine from a hydrocarbon mixture, reacting the resulting hydrocarbon mixture with an absorption medium for the secondary base olefine content thereof and reacting the resulting absorption media with fresh hydrocarbon mixture containing a tertiary base olefine in the presence of water said absorption media then possessing a concentration whereat substantial polymerization of the tertiary base olefine is avoided and insufficient to substantially absorb any isomeric secondary olefine.

20. In a process of producing alcohols the steps which comprise reacting a hydrocarbon mixture in the liquid phase consisting essentially of paraffin and secondary base olefine compounds and containing tertiary olefine of the same carbon content with an acid liquor obtained by the absorption of a secondary base olefine of the same carbon content in a relatively strong polybasic mineral acting acid said acid liquor possessing a concentration whereat substantial polymerization of the tertiary base olefine is avoided and insufficient to substantially absorb any isomeric secondary olefine and stratifying the resulting mixture into two liquid phases comprising an acid phase and a hydrocarbon phase.

21. A method of producing a mixture of amyl alcohols which comprises reacting tertiary amylene containing hydrocarbons in the liquid phase in the presence of water with an absorption product of a secondary amylene in sulfuric acid, said absorption product having a free acid content of about 25% to about 30% by weight.

22. A method of producing a mixture of isomeric alcohols which comprises contacting a tertiary base olefine containing hydrocarbon mixture with a water diluted absorption product of an isomeric secondary base olefine in a relatively strong polybasic mineral acid-acting acid solution said absorption product possessing a concentration whereat substantial polymerization of the tertiary base olefine is avoided and insufficient to substantially absorb any isomeric secondary olefine, separating unabsorbed hydrocarbons from the resulting mixture and reacting the resulting absorption product containing absorbed isomeric tertiary and secondary olefines with

fresh tertiary-base olefine-containing hydrocarbons.

23. A method of producing a mixture of amyl alcohols which comprises contacting a liquid pentane-amylene mixture containing tertiary and secondary amylenes with an absorption product of tertiary and secondary amylenes in an aqueous sulfuric acid solution, substantially absorbing the remaining tertiary amylene content of said mixture in diluted acid liquor in the presence of water said acid liquor possessing a concentration whereat substantial polymerization of the tertiary amylene is avoided and insufficient to substantially absorb any secondary amylene, separating the unabsorbed hydrocarbons from the resulting mixture and reacting thereupon with sulphuric acid to remove secondary amylene therefrom and form the said acid liquor.

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