April 3, 1945. K. H. HACHMUTH 2,372,668

PROCESS FOR SELECTIVE ABSORPTION

Filed Oct. 5, 1942 2 Sheets-Sheet 1

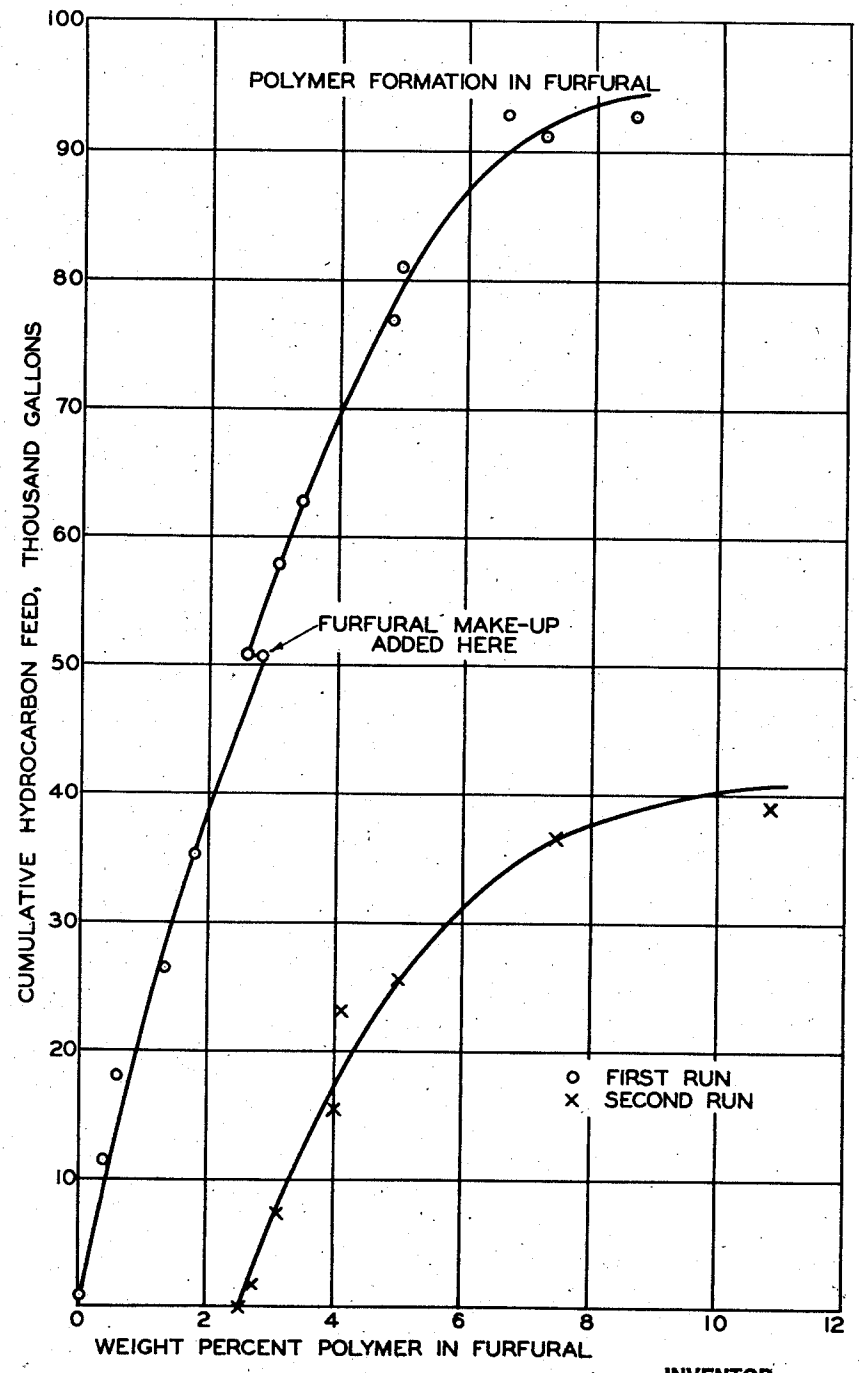


FIG. 1

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Filed Oct. 5, 1942 2 Sheets-Sheet 2

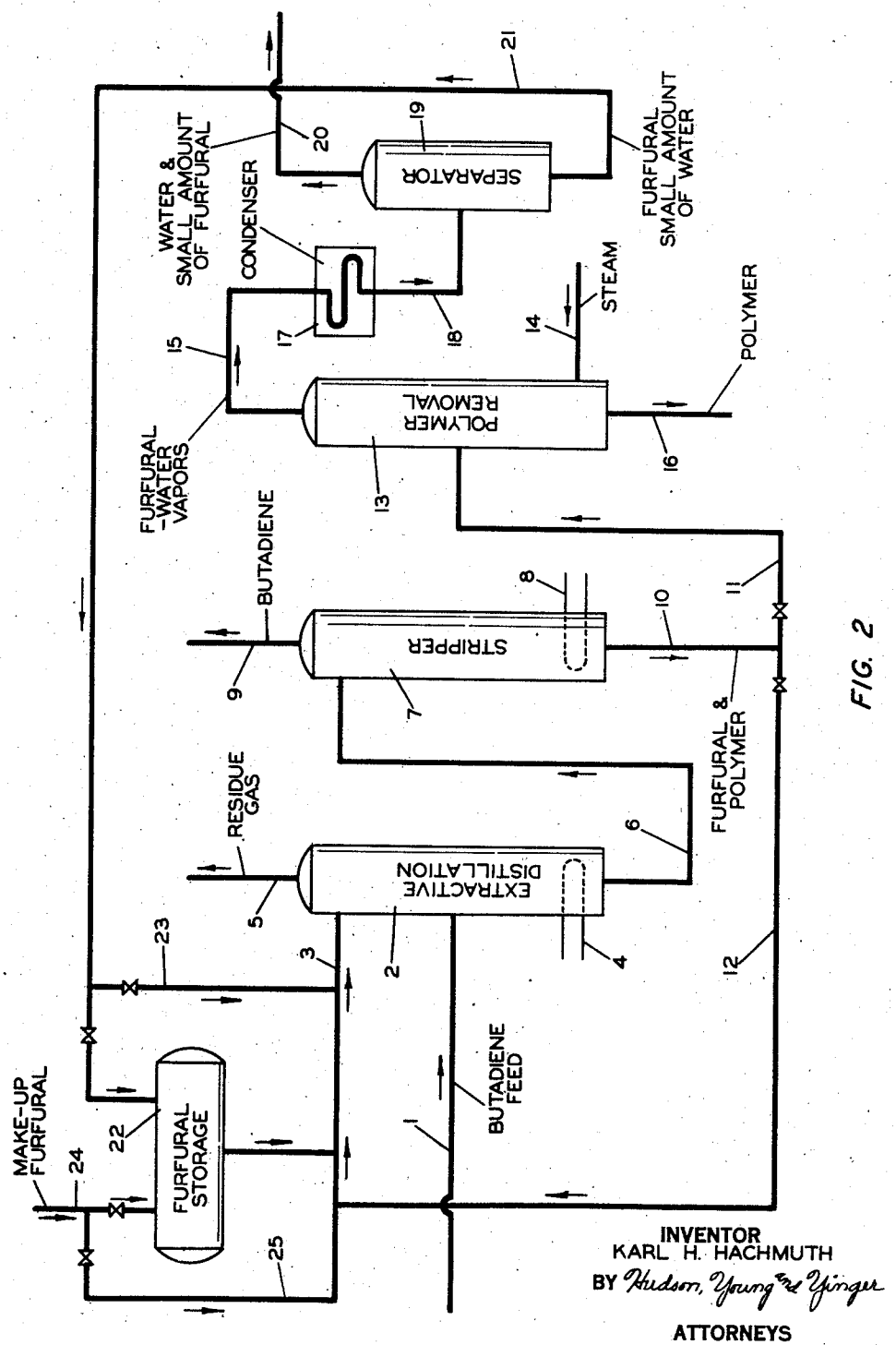


FIG. 2

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Patented Apr. 3, 1945 2,372,668

UNITED STATES PATENT OFFICE

2,372,668

PROCESS FOR SELECTIVE ABSORPTION

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Application October 5, 1942, Serial No. 460,874

9 Claims. (Cl. 260—677)

This invention relates to a process for the separation of olefins or diolefins from hydrocarbon mixtures containing the same by means of furfural as a selective solvent. Still more particularly it relates to an improved method for the utilization of furfural as an absorbent or selective solvent for the segregation of low-boiling aliphatic olefins or aliphatic conjugated diolefins, especially those containing four carbon atoms to the molecule, namely, normal butenes or butadiene.

This application is a continuation-in-part of my prior and copending application Serial No. 430,307, filed February 10, 1942.

Various hydrocarbon conversion processes, such as dehydrogenation of paraffins or olefins or mixtures thereof, high temperature-low pressure cracking of low-boiling paraffin hydrocarbons, heavy oils, etc., produce complex mixtures of hydrocarbons containing valuable olefins or diolefins or both. Such mixtures are valuable sources of these valuable olefins and diolefins when significant amounts of the materials can be economically separated in a suitably pure form. This is especially true of aliphatic conjugated diolefins, such as butadiene, which have important uses in the preparation of high molecular weight polymers, such as synthetic rubber.

Efficient fractional distillation of such complex hydrocarbon mixtures ordinarily results in separation into portions consisting essentially of hydrocarbon atoms and exhibiting boiling ranges of say 10 to 30° F. Further precise fractionation may effect appreciable segregation of the individual components, but ultimate separation by this method is expensive and generally impractical because of the closeness of the boiling points and the formation of constant boiling hydrocarbon mixtures or azeotropes.

For example, the clean separation of butadiene from admixture with isobutylene or butene-1 or both by fractional distillation is practically impossible because of their extremely close boiling points. Again, the separation by fractional distillation of butadiene from normal butane is impossible because these two components form an azeotrope which contains approximately 80% butadiene and 20% normal butane and boils between butene-1 and butadiene so that it is practically inseparable from butene-1 and isobutylene.

The practice has now been developed in the art of separating butenes, especially normal butenes, and of butadiene from C_4 hydrocarbon streams containing the same by means of selective solvent extraction with furfural. In the preferred practice, what is now known as "extractive distillation" is employed, that is the extraction is combined with fractional distillation or rectification in a fractionating column, the furfural being supplied continuously to the top of the column and descending therein, and the hydrocarbon feed being vaporized upwardly countercurrently to the furfural, a reboiling arrangement being provided at the bottom of the column. The separation of butadiene in this manner is described in my copending applications, Serial No. 454,312, filed August 10, 1942, and Serial No. 438,844, filed April 13, 1942, and in the copending application of F. D. Mayfield, Serial No. 363,821, filed March 17, 1941. The separation of butenes and butadienes from their respective streams in this manner is described in the copending application of Arnold, Serial No. 450,725, filed July 13, 1942.

The temperature at the bottom of the extraction-rectification column is the boiling point of the liquid at that point under the operating pressure of the column. The operating pressure is sufficiently high to permit condensation of a portion of the overhead vapors for reflux. The liquid in the bottom of the absorption column is composed of furfural having dissolved therein the selectively absorbed hydrocarbons. The furfural dissolves diolefins in preference to the more saturated olefins or paraffins and dissolves olefins in preference to paraffins. The bottoms liquid is removed and introduced into another column near the top. In this second column the dissolved hydrocarbons are stripped out of the top while the lean furfural bottom-liquid is returned to the absorption column. Again, the temperature at the bottom of the stripping column is the boiling point of the liquid in the column at the operating pressure.

Thus the furfural used in a process of the type outlined above is continuously being subjected to repeated vaporization at relatively high temperatures, the highest occurring in the kettle of the stripping column where the kettle product is furfural practically free from absorbed hydrocarbons.

Furfural employed in the process described above in the presence of butadiene, butenes and related unsaturated hydrocarbons and under the influence of the heat and pressure employed deteriorates. This deterioration primarily involves the formation of heavy polymeric material caused by polymerization of furfural. The formation of the polymer is also accompanied by an increase in acidity of the furfural which is objec-

tionable. A minor part of the acids formed are volatile and the balance non-volatile. The mechanism of the polymerization of furfural under the foregoing conditions is not understood at present and the invention is not limited by any theory with respect thereto. The formation of polymer, gum, and other heavy or high-boiling materials may be due to polymerization or condensation of the furfural or of the diolefins and/or other unsaturates or to co-polymerization or condensation of the furfural with such diolefins or other unsaturates, or to other condensation or decomposition reactions occurring at the operating conditions. At any rate, the polymeric material does form in substantial amounts, with a number of disadvantages.

While the use of minor amounts of water dissolved in the furfural in accordance with my application Serial No. 438,844 above identified substantially reduces the polymer formation in addition to improving the selectivity of the solvent for the light unsaturated hydrocarbons, it does not by any means completely eliminate the polymerization. The process of the present invention is equally applicable whether anhydrous or water-containing furfural is used. In this specification, unless the context requires otherwise, the term "furfural" is to be taken as comprehending either anhydrous furfural or a solution of water in furfural.

Among the disadvantages of the polymer formation are the yield of desired hydrocarbon products is reduced, appreciable quantities of furfural are destroyed involving the continual expense of providing make-up furfural, and the efficiency of the furfural as a solvent is diminished due to the presence of dissolved and suspended heavy material. Furthermore, the equipment becomes clogged and corroded by the polymer and attendant acid, reducing the capacity and efficiency of the equipment and requiring frequent shutdowns for cleaning.

The principal object of this invention is to provide an improved process of separating olefins or diolefins from hydrocarbon mixtures containing the same by means of furfural. Another object is to provide an improved method of extracting butadiene by means of furfural. Another object is to provide an improved process for the "extractive distillation" of a butadiene-containing C_4 stream with furfural. Another object is to provide a process of the foregoing type for the segregation of butene. Another object is to provide a process for purifying used furfural prior to its re-use in a process of the foregoing type. Another object is to provide an improved process for purifying used furfural to free it from polymeric material, gum, etc., and re-using it in the extraction process. Another object is to effect the purification of the used furfural at a low temperature so that the formation of additional polymer during the purification is minimized or prevented. Numerous other objects will hereinafter appear.

In the accompanying drawings: Fig. 1 gives two curves showing the variation in polymer concentration with use in extraction of butadiene from a C_4 stream by means of furfural, and illustrates how the polymer formation is greatly accentuated after its concentration reaches the 5% figure. Fig. 2 is a schematic diagram of one arrangement of equipment found suitable for carrying out the process of the present invention.

I have discovered that greatly improved results may be obtained in the extractive distillation of low-boiling aliphatic olefins and diolefins from hydrocarbon streams by means of furfural as the solvent if the furfural be removed from the system either periodically or continuously, and treated to free it from polymer before its re-introduction to the system.

For example the stream of stripped polymer-containing furfural withdrawn from the stripping column may be, in part or in toto, passed to a polymer removal unit wherein polymer-free furfural is separated. This polymer-free furfural is recycled to the extraction-rectification column.

The removal of polymer may be accomplished in a number of ways, for example, by distillation of the furfural away from the polymer preferably with steam, for example by the method described in the copending application of Buell and Cooper, Serial No. 460,004, filed September 28, 1942, wherein the furfural is recovered from admixture with polymer by passing the mixture through a series of successive fractionating zones maintained at successively decreasing temperatures, steam being injected directly into the final zone only.

Instead of the preferred distillation of polymer-free furfural away from polymer, I may use other methods of separating furfural from polymer. Thus I may extract the furfural from the polymer-furfural solution or mixture by means of a liquid which preferentially dissolves the furfural and is a non-solvent for the polymer. Water is the preferred solvent for this purpose. For example, I may admix the polymer-furfural mixture with a relatively large amount of water to effect precipitation of the water-insoluble polymer dissolved in the furfural by dissolving the furfural in the water, following which I may separate the aqueous furfural solution from the polymer as by filtration, centrifuging, decanting, etc., and treat same to recover concentrated furfural for re-use in the extraction-distillation column. Thus the water-furfural phase may be distilled to remove overhead an azeotrope of furfural and water which may be condensed to from two layers, one layer of water containing furfural in solution and which may be recycled to the polymer precipitation step, and the other of furfural containing in solution a small amount of water and which may be recycled to the extraction column.

The solution of the furfural in water may be expedited by the use of a temperature sufficiently high to effect miscibility, so that a substantially smaller amount of water may be employed. Thus the polymer-furfural mixture may be admixed with the limited amount of water whereupon the mixture is heated to say 275° F. under a pressure of 40 pounds gauge to effect miscibility between the water and furfural and precipitation of the polymer which may then be settled out. The hot furfural-water phase is then separated and cooled to say 80° F. at which temperature water is no longer miscible with furfural so that two layers are formed, one of water containing limited amounts of furfural in solution and which may be recycled to the precipitation step, and the other of furfural containing a limited amount of water and which is ideally adapted for recycle to the extraction-distillation column.

Another method of polymer removal is to subject the furfural-polymer mixture to contact with an adsorptive medium such as charcoal, activated carbon, activated clay, silica gel, activated alumina, etc., whereby the high molecular weight

polymeric material is selectively adsorbed. Still other methods of polymer removal now known to the art or hereafter discovered may be utilized in carrying out the invention in its broad aspects, although I prefer to distill the furfural from the polymer under conditions preventing further polymerization of furfural. So far as I am aware, I am the first to suggest removal of the polymer from the furfural in any way as well as its separation by distillation of the furfural.

The separation of furfural from its polymer and other impurities which have accumulated therein has, in accordance with the present invention, been accomplished by distillation of the furfural from the solution of furfural in polymer, thereby leaving the polymer and other impurities as bottom product. The temperature of distillation for furfural removal from furfural-polymer solutions increases quite rapidly as the percentage of polymer, gum and other impurities increases. Since the formation of polymer, gum and coke in the solutions increases quite markedly with rise in temperature, it is desirable to carry out purification steps involving heating of furfural or furfural solutions at as low a temperature as possible. As pointed out hereinafter, I have still further found that the rate of polymer formation is greatly accelerated after a certain polymer concentration, usually about 5%, is attained and therefore I prefer to carry out the butene or butadiene extraction-rectification, the stripping, and the furfural purification steps at polymer concentrations below this point and as low as possible in order to avail this undesirable effect. Other disadvantages attend concentrations of polymer above the point referred to. For example, where the purification of furfural is carried out by distillation from a solution containing polymer initially somewhat in excess of 5%, under the usual conditions of operation, the heating of the solution is accompanied by further polymer formation and considerable coke formation. This polymer and/or coke deposits on the heating coils and acts as a heat insulator reducing the rate of and eventually preventing the distillation of the furfural. The polymer deposits may be converted to coke. Furthermore the local overheating due to the initial coke formation together with an apparently catalytic effect of the initial coke formed greatly accelerates the rate of carbonization of the furfural. Another disadvantage of this type of operation is the corrosive nature of the decomposition products of furfural which together with localized overheating results in excessive corrosion. This disadvantage coupled with the auto-catalytic action of the gum or polymer when the polymer concentration exceeds 5% makes operation at polymer concentrations above 5% exceedingly unfavorable.

I have found that if the furfural solution being purified contains initially less than 5% by weight of the polymer, the purification even by straight distillation of the furfural proceeds at a temperature not far above the boiling point of pure furfural and at this relatively low temperature the purification distillation proceeds without the deposition of coke on the equipment and without excessive polymer and gum formation. As a result the above-mentioned difficulties are not encountered and the purification distillation produces a gum-free furfural distillate and a viscous liquid or gummy solid residual bottoms essentially free of coke and with only a minimum loss of furfural in forming undesirable products.

Even greater advantages are attained when the furfural distillation is conducted in the preferred manner, namely, by means of steam. In such a furfural recovery process, the overhead consists of furfural and water and upon condensation yields two layers, one of furfural saturated with water and adapted for re-use in the extraction process and the other of water saturated with furfural. When using steam distillation to separate the furfural from polymer, the temperature is substantially below the boiling point of pure furfural, and may vary from 200 to 300° F. depending upon the pressure maintained and upon the temperature, pressure, and degree of superheat if any, of the steam introduced. As a result of this lower temperature and the presence of water, the rate of polymer and coke formation in the distillation unit is markedly reduced.

Fig. 1 of the accompanying drawings shows experimental data on the variation of polymer concentration in furfural with length of use during two separate and distinct furfural extraction runs in which a butadiene-containing C_4 stream is vaporized countercurrently to the furfural in the manner set forth in detail above. The polymer percentage in the furfural is plotted as abscissae against the cumulative hydrocarbon feed as ordinates. The break in the curve representing the first run is due to the addition of makeup furfural which has the effect of diluting the polymer and thereby delaying somewhat the ill effects of excessive polymer.

The following tabulation of calculations made from the curves of Fig. 1 shows the rate of polymer formation in relation to the percentage of polymer already in the furfural. The rate of polymer formation may be considered to be the rate of change of slope of the curve of polymer concentration plotted against time or length of use or cumulative feed treated.

Wt. per cent polymer in furfural	Rate of polymer formation, per cent formed per thousand gallon throughput	
	First run	Second run
0	0.040	
2	0.061	
4	0.097	0.090
6	0.20	0.19
8	0.44	0.38
10		1.0

From this tabulation, it will be seen that the rate of gum or polymer formation increases rapidly as the polymer content of the furfural increases above about 5% by weight. Thus, the maintenance of a relatively low polymer concentration by means of rerunning a suitable amount of the furfural minimizes furfural losses by polymerization.

Referring to Fig. 2 of the drawings, the butadiene-containing C_4 hydrocarbon feed enters the system and passes via line 1 to extraction-distillation column 2 which is supplied at its top with furfural introduced via line 3. The tower 2 is equipped with reboiling coil 4, and with means (not shown) for refluxing a suitable portion of the overhead vapors. The stripped butadiene-free vapors leave via line 5. The butadiene-rich furfural passes via line 6 to stripping column 7 where it is stripped of butadiene in known man-

ner, reboiling heat being applied near the base by means of coil 8. The butadiene leaves overhead via line 9. Again, means (not shown) for refluxing a suitable portion of the overhead is usually provided.

The stripped furfural leaves tower 7 via line 10. This furfural contains polymer in the same proportion relative to furfural as is present in columns 2 and 7. Part or all of this polymer-containing furfural, depending upon conditions and the wishes of the operator, is passed via line 11 to polymer removal steps presently to be described. Any balance is recycled to tower 2 via lines 12 and 3.

Polymer removal is shown as effected by steam distillation in tower or still 13 to the base of which the steam is admitted via line 14. The unit 13 may comprise a series of evaporating units or zones as described in the Buell and Cooper application above-identified. Overhead via line 15 pass the pure furfural and water free from polymer. The polymer, together with small amounts of water and with or without small amounts of residual furfural leaves as bottoms via line 16.

Since at atmospheric temperature the polymer is dense and so viscous that it does not flow readily, it is desirable to retain a small amount of furfural in the polymer to keep it sufficiently fluid to permit easy removal from the still and to prevent local overheating and consequent coke formation on the heating elements of still 13.

The overhead vapors of pure furfural and water flow via line 15 to condenser 17 where they are condensed to liquid which flows via line 18 to separation unit 19 in which layer separation, as by gravity is effected. The upper layer of water leaves via line 20 while the lower layer of furfural leaves via line 21 and is recycled to furfural storage 22 or via line 23 to line 3. Makeup furfural may be introduced via line 24 directly to storage tank 22 or via line 25 to line 3.

Sufficient of the polymer is removed from the furfural in accordance with the present invention to maintain the polymer concentration in the furfural in the system, i. e., in at least the extraction and stripping units, any furfural storage tank and the associated piping and other equipment at a figure not exceeding that at which the ratio of polymer formation is greatly accelerated, or in other words, the point at which the rate of change of slope of the polymer concentration curve deviates from the linear in the direction of disproportionately increased polymer formation. In the practical applications of the invention, both in commercial plant operations and in experimental work, this upper limit of operation has been at the 5% polymer-in-furfural figure mentioned above. While it is conceivable that under exceptional circumstances a different figure might be encountered, the figure of 5% may be taken as the upper limit for satisfactory operation under most ordinary conditions.

A great many advantages flow from the practice of the invention. Chief among them are that loss of furfural is minimized by keeping down the polymer concentration in the system and that clogging and coking of equipment are prevented. Other advantages are the greater fluidity and lower boiling point of furfural containing less than 5% of polymer by weight, thus allowing more efficient and lower temperature absorption and stripping. Another advantage is that the furfural low in polymer has higher selectivity for the unsaturated hydrocarbons being extracted.

In a continuous operation in which the furfural-polymer mixture is continuously passed through the furfural still, a further and marked advantage is that the length of time during which the polymer is exposed to the distilling temperature is at a minimum.

A very important additional advantage of my invention is that most of the acids which are formed in the furfural in the extraction and stripping columns, apparently concomitantly with the loss of furfural by polymerization, and which appear in the representative lean furfural withdrawn from the stripper, are removed along with the polymer in the polymer removal step. Thus the acidity of the furfural in the system is kept as a suitable low level. In a typical rerunning step the acidity of the furfural, calculated as acetic acid, was reduced from 0.292% to 0.040%. Since the larger proportion of the acids is concentrated with the polymer in the polymer removal by distillation, the action of the acids in accelerating corrosion of equipment, polymer formation, and other undesirable effects is largely overcome by my invention.

It will be obvious from the foregoing that all or a portion of the furfural-polymer mixture may be removed either continuously or batchwise and the furfural distilled therefrom either batchwise or continuously, it being preferred to operate the entire system continuously. Usually I withdraw and re-run only a sufficient portion of the furfural to keep the polymer concentration in the extraction-rectification and stripping units from exceeding the critical figure discussed above.

The following non-limiting example illustrates one specific embodiment of the practice of my invention as applied to the separation of butadiene from a C_4 stream by means of furfural.

Example

Using the apparatus portrayed in Fig. 2, an essentially C_4 liquid feed consisting of

	Parts by weight
Propane	3
Butadiene	63
Butene-1	13
Isobutylene	5
Butene-2	13
Butane	3
Vinyl acetylene	Trace

was fed via line 1 to absorber 2 to which lean furfural was introduced via line 3.

Rich furfural containing all of the butadiene and some of the butene-2 (both high and low boiling) in the relative proportions by weight of 4 parts butadiene and 0.3 part butene-2 was withdrawn from the bottom of absorber 2 via line 6 to stripper 7. The absorber 2 was operated at a pressure of 65 pounds per square inch absolute, reflux ratio of 16.6 to 1, top temperature of 120° F. and bottom temperature of 240° F.

Stripper 7 was operated at 65 pounds per square inch absolute, reflux ratio of 1:1, top temperature of 103° F. and bottom temperature of 300° F. The overhead product consisting essentially of 93 parts butadiene and 7 parts of butene-2 along with traces of furfural was removed via line 9 and passed to a fractionation step (not shown) wherein 98.5% pure butadiene was separated.

Lean furfural containing only a trace of C_4 hydrocarbons and a small amount of polymer together with water was removed from the bottom

of stripper 7 via line 10. This analyzed approximately as follows:

	Per cent by weight
Furfural	94.8
Polymer	1.4
Water	3.8

Eighty per cent of this lean furfural was recycled directly to the top of tower 2 via lines 12 and 3. The balance, 20%, was continuously passed via line 11 to polymer removal or furfural re-run 13 where it was steam distilled in three sections arranged in series, the steam being admitted to the last section only, and the liquid in each section being passed to the succeeding section while the vaporized furfural and water in each zone after the first is passed to the preceding zone. The furfural and water vapors leaving the first zone are free from polymer and are passed via line 15 to condenser 17 where they are condensed and thence via line 18 to separator 19 in which layer separation is accomplished. The lower layer is continuously recycled via lines 21 and lines 23 to line 3 for re-use in tower 2. Makeup furfural is added to line 3 as needed to compensate for system losses.

From the final zone in the furfural still 13 there is removed via line 16 a mixture of polymer, water and 3% of furfural by weight.

By proceeding in the manner of this example the polymer concentration in the extraction and stripping zones is maintained substantially at the figure of 1.4% by weight of the furfural-water-polymer mixture.

As used herein, the reference to per cent of polymer in furfural means the per cent by weight of the polymer based on the weight of furfural and polymer and any water present in the furfural.

While the above disclosure sets forth 5% as the upper limit of polymer concentration for ordinary operations, in actual plant operation I prefer to employ an upper limit of 2% or even lower.

I claim:

1. In a process for the separation of an unsaturated aliphatic hydrocarbon by the steps comprising extracting said hydrocarbon from a stream containing the same by means of furfural in an absorption zone, introducing the furfural rich in said hydrocarbon to a stripping zone and there stripping said hydrocarbon from said rich furfural, withdrawing lean furfural from said stripping zone and recycling it to said extracting step, and wherein elevated temperatures and pressures are employed in said extracting and stripping steps with the result that under the conditions prevailing therein furfural is converted to polymer, the improvement which comprises removing polymer from the furfural in the system to such an extent that the polymer concentration in said furfural in the system does no exceed that point at which increase in polymer concentration takes place in excess of linear.

2. In a process for the separation of an unsaturated aliphatic hydrocarbon by the steps comprising extracting said hydrocarbon from a stream containing the same by means of furfural in an absorption zone, introducing the furfural rich in said hydrocarbon to a stripping zone and there stripping said hydrocarbon from said rich furfural, withdrawing lean furfural from said stripping zone and recycling it to said extracting step, and wherein elevated temperatures and pressures are employed in said extracting and stripping steps with the result that under the conditions prevailing therein furfural is converted to polymer, the improvement which comprises removing polymer from the furfural in the system to such an extent that the polymer concentration in said furfural in the system does not exceed 5% by weight based on the weight of furfural, polymer and any water dissolved in the furfural.

3. In a process for the separation of an unsaturated aliphatic hydrocarbon by the steps comprising extracting said hydrocarbon from a stream containing the same by means of furfural in an absorption zone, introducing the furfural rich in said hydrocarbon to a stripping zone and there stripping said hydrocarbon from said rich furfural, withdrawing lean furfural from said stripping zone and recycling it to said extracting step, and wherein elevated temperatures and pressures are employed in said extracting and stripping steps with the result that under the conditions prevailing therein furfural is converted to polymer, the improvement which comprises effecting removal of said polymer by treating sufficient of said withdrawn lean furfural to remove sufficient polymer therefrom prior to said recycling to said extracting step to maintain the polymer concentration in furfural in said extracting and stripping steps at a level below that at which the rate of polymer formation deviates from linear in the direction of increased polymer formation, and recycling the resulting polymer-free furfural to said extracting step.

4. In a process for the separation of an unsaturated aliphatic hydrocarbon by the steps comprising extracting said hydrocarbon from a stream containing the same by means of furfural in an absorption zone, introducing the furfural rich in said hydrocarbon to a stripping zone and there stripping said hydrocarbon from said rich furfural, withdrawing lean furfural from said stripping zone and recycling it to said extracting step, and wherein elevated temperatures and pressures are employed in said extracting and stripping steps with the result that under the conditions prevailing therein furfural is converted to polymer, the improvement which comprises effecting removal of said polymer by treating sufficient of said withdrawn lean furfural to remove sufficient polymer therefrom prior to said recycling to maintain the concentration of polymer in furfural in said extracting and stripping steps at a figure not exceeding 5% by weight based on the weight of furfural, polymer and any water dissolved in the furfural, and recycling the resulting polymer-free furfural to said extracting step.

5. In a process for the separation of an unsaturated aliphatic hydrocarbon by the steps comprising extracting said hydrocarbon from a stream containing the same by means of furfural in an absorption zone, introducing the furfural rich in said hydrocarbon to a stripping zone and there stripping said hydrocarbon from said rich furfural, withdrawing lean furfural from said stripping zone and recycling it to said extracting step, and wherein elevated temperatures and pressures are employed in said extracting and stripping steps with the result that under the conditions prevailing therein furfural is converted to polymer, the improvement which comprises effecting removal of said polymer by steam distilling a sufficient portion of said withdrawn lean furfural prior to recycling thereof to remove sufficient polymer to maintain the concentration of polymer in furfural in the extracting and strip-

ping steps at a figure not exceeding 5% by weight based on the weight of furfural, polymer and any water present in the furfural, and recycling the resulting polymer-free furfural to said extracting step.

6. In a process for the separation of an unsaturated aliphatic hydrocarbon by the steps comprising extracting said hydrocarbon from a stream containing the same by means of furfural in an absorption zone, introducing the furfural rich in said hydrocarbon to a stripping zone and there stripping said hydrocarbon from said rich furfural, withdrawing lean furfural from said stripping zone and recycling it to said extracting step, and wherein elevated temperatures and pressures are employed in said extracting and stripping steps with the result that under the conditions prevailing therein furfural is converted to polymer, the improvement which comprises effecting removal of said polymer by steam distilling a sufficient portion of said withdrawn lean furfural prior to recycling thereof to remove sufficient polymer to maintain the concentration of polymer in furfural in the extracting and stripping steps at a figure not exceeding 2% by weight based on the weight of furfural, polymer and any water present in the furfural, and recycling the resulting polymer-free furfural to said extracting step.

7. In a process for the separation of an unsaturated aliphatic hydrocarbon by the steps comprising extracting said hydrocarbon from a stream containing the same by means of furfural in an absorption zone, introducing the furfural rich in said hydrocarbon to a stripping zone and there stripping said hydrocarbon from said rich furfural, withdrawing lean furfural from said stripping zone and recycling it to said extracting step, and wherein elevated temperatures and pressures are employed in said extracting and stripping steps with the result that under the conditions prevailing therein furfural is converted to polymer, the improvement which comprises effecting removal of said polymer by steam distilling a sufficient portion of said withdrawn lean furfural prior to recycling thereof to remove sufficient polymer from the system to maintain the concentration of polymer in furfural in the extracting and stripping steps at a figure not exceeding 5% by weight based on the weight of furfural, polymer and any water present in the furfural, condensing the overhead from the steam distillation step, separating the condensed furfural phase from the condensed water phase, and recycling said furfural phase to said extracting step.

8. In a process for the separation of unsaturated aliphatic hydrocarbons from hydrocarbon mixtures containing the same wherein the hydrocarbon stream is introduced at an intermediate point to a combined extraction and rectification column, said column is maintained under superatmospheric pressure sufficiently high to allow condensation of overhead vapors, furfural is introduced adjacent the top of said column, heat is introduced into the bottom of said column to cause boiling of the bottom product under the pressure maintained therein, an overhead product comprising more saturated hydrocarbons is removed from the top of said column, a portion of said overhead is condensed and returned to said column as reflux therefor, a bottom product comprising said unsaturated hydrocarbons dissolved in said furfural is removed from the bottom of said column, said removed bottom product is introduced into a stripper column, said stripper column is maintained under superatmospheric pressure sufficiently high to allow condensation of overhead vapors, heat is introduced into the bottom of said stripper column to cause boiling of the bottom product therein under the pressure maintained therein, an overhead product comprising said unsaturated hydrocarbons is removed from the stripper column, a portion of said last-named overhead is condensed and returned to said stripper column as reflux therefor, and a bottom product comprising furfural and polymer is removed from the stripper column, the improvement which comprises steam distilling at least a portion of said removed stripper bottom product to remove overhead vapor comprising water and furfural free from polymer, condensing said vapor, separating the furfural phase of the condensate from the water phase, and recycling said furfural phase to the top of said combined column, the amount of polymer so removed in said steam distilling step being such as to maintain the concentration of polymer in furfural in said combined column and said stripper column at not exceeding 5% by weight based on the weight of furfural, polymer and any water dissolved in the furfural.

9. A process as set forth in claim 8 where the unsaturated hydrocarbon is butadiene and the hydrocarbon mixture is a C_4 stream containing the same.

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