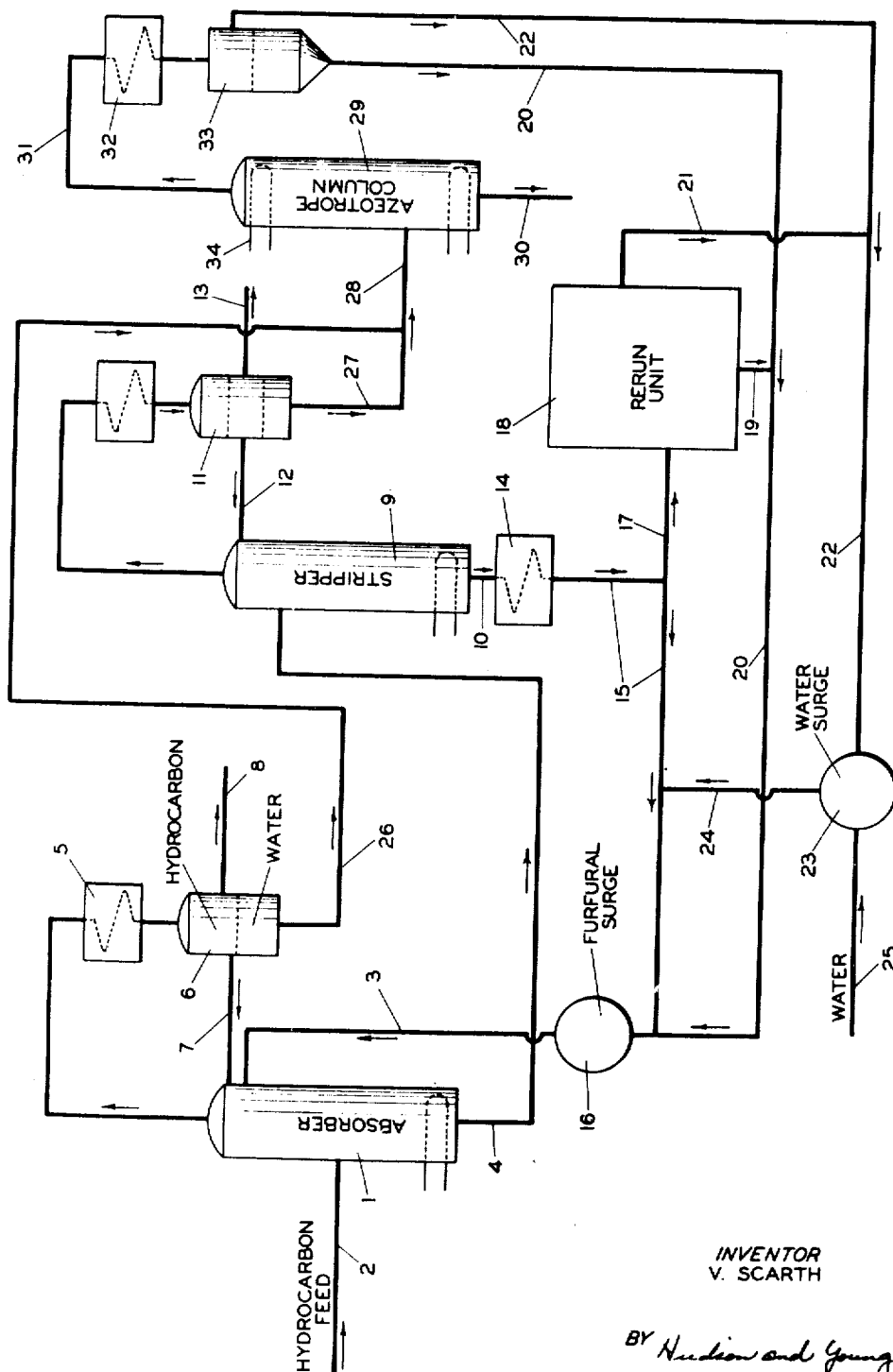


June 1, 1948.

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PURIFICATION AND RECOVERY OF FURFURAL IN
EXTRACTIVE DISTILLATION OF HYDROCARBONS
Filed Sept. 6, 1946

2,442,474



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2,442,474

PURIFICATION AND RECOVERY OF FURFURAL IN EXTRACTIVE DISTILLATION OF HYDROCARBONS

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Application September 6, 1946, Serial No. 695,224

5 Claims. (Cl. 202—39.5)

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This invention relates to improvements in the extractive distillation of unsaturated hydrocarbons with furfural as selective solvent. In one particular aspect it relates to methods for eliminating corrosive impurities which accumulate in water carried overhead from furfural absorber and furfural stripper units with concomitant recovery of furfural and water. This application is a continuation-in-part of my prior and copending application, Serial No. 569,244, filed December 21, 1944, now Patent 2,419,039, granted April 15, 1947.

It has become customary to recover unsaturated hydrocarbons, particularly butene and/or butadiene, from hydrocarbon streams containing the same in admixture with more saturated hydrocarbons by extractive distillation processes employing furfural as selective solvent. Processes of this type are described in the copending applications of Hachmuth 438,844, filed April 13, 1942, now Patent 2,434,796, granted January 20, 1948; Serial No. 454,312, filed August 10, 1942, now Patent 2,415,006, granted January 28, 1947; and Serial No. 481,305, filed March 31, 1943, now Patent 2,386,310, granted October 9, 1945. The first-mentioned application discloses and claims a selective solvent composed of furfural containing several per cent of water.

It will not be necessary to describe extractive distillation processes in detail since these are now well known in the art. Such processes are carried out by means of a fractional distillation column operated as an absorber, into the top of which a stream of moist furfural is continuously fed. A mixture of saturated and unsaturated hydrocarbons is introduced into a medial point in this absorber. The more saturated hydrocarbons pass off as an overhead product, while furfural containing water and rich in unsaturated hydrocarbons is withdrawn as a kettle product. This kettle product is passed to a stripper column where dissolved unsaturated hydrocarbons are driven off overhead, while furfural containing water is removed as a kettle product. Both absorber and stripper columns may be provided with means for refluxing with a portion of condensed overhead and both are provided with reboilers.

During absorbing and stripping operations polymer and other corrosive impurities are formed in the furfural and build up to an objectional extent. It becomes necessary to remove these impurities from the furfural. This is ordinarily done by passing a sidestream of furfural to a rerun unit where it is freed from such im-

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purities by a process involving steam distillation. Such processes are described in patents to Buell et al. 2,350,584 and to Hachmuth 2,350,609. Distillation of furfural in the presence of water results in an overhead product of steam and purified furfural vapors. Upon condensing the overhead vapors formed in such rerun distillation the condensate separates into two layers, a water layer and a layer of purified furfural. The water layer is saturated with furfural, and at 180° F. and atmospheric pressure will contain about 3 percent furfural.

The furfural content of this water layer has been recovered by utilizing this water as a source for steam used in steam distilling furfural in the rerun unit. However, in making steam by this method the tubes in the steam generator have been found difficult to keep clean because furfural dissolved in the water becomes polymerized and deposits on the tubes.

It has been commonly observed that even when furfural in such extractive distillation systems is rerun at a rate sufficient to rerun all the furfural in the system every two or three days the furfural in the main system, i. e. the extractive distillation system proper, becomes corrosive and attacks the equipment.

The causes of the development of corrosiveness in furfural are not understood at the present time. Some investigators believe that the corrosiveness results from the decomposition and polymerization of furfural under the particular conditions prevailing in absorber and stripper columns, with formation of organic acids and furfural polymers which are believed to be corrosive to carbon steel. It is thought that other factors are involved since corrosion is not always directly proportional to the acid content of furfural, especially at acid concentrations above 0.06 percent by weight, calculated as acetic acid. For example, while serious corrosion is not observed with acid concentrations below 0.04 percent, at acid concentrations between 0.04 and 0.66 percent serious corrosion may or may not occur depending on factors unknown at present; and at acid concentrations above 0.06 percent serious corrosion is usually encountered and is sometimes so excessive that the plant could be continued in operation for only a short time before being corroded so badly as to be unsafe. No completely satisfactory explanation of the causes of the development of corrosiveness in furfural has been made.

In the extractive distillation of unsaturated hydrocarbons with furfural containing dissolved

water as solvent, water is volatilized and is carried overhead in admixture with hydrocarbon vapor. This occurs in connection with both absorber and stripper columns. Small amounts of furfural vapors are also carried off overhead. Condensation of overhead vapors results in a condensate which separates into two liquid layers in reflux accumulators or other receiving vessels. The upper of these two layers is composed of hydrocarbons and the lower layer comprises water containing up to about 1 per cent of furfural. Corrosive impurities are also present in the water layer.

Conventional practice in the past has been to add this water layer to stripped furfural as make-up water in order to keep the water content of the furfural substantially constant, but this practice results in increasing the proportion of corrosive impurities in furfural in the extractive distillation system. In my co-pending application Serial No. 569,244, filed December 21, 1944, now Patent 2,419,039, granted April 15, 1947, I have disclosed and claimed processes for eliminating corrosive impurities from such water layers while recovering the furfural content thereof by employing the water layers as a source for steam introduced into furfural in rerun units, and by distillation of furfural and water from a kettle product containing corrosive impurities.

While the processes therein disclosed are effective, they are not so cheap and convenient as the process of the present invention under most commercial operating conditions.

It is an object of this invention to provide an improved process of carrying out extractive distillation of hydrocarbons with furfural containing water as selective solvent.

Another object is to provide an improved process for the recovery of normal butene and/or butadiene by extractive distillation of a mixed hydrocarbon stream containing the same with furfural containing water as selective solvent.

Another object is to provide a process of such type wherein corrosion of equipment used in the extractive distillation system is substantially reduced.

Another object is to provide a process of such type wherein corrosive impurities which accumulate in condensed overhead from absorber and stripper columns are eliminated with a minimum loss of furfural and with minimum distillation.

Another object is to provide a process of such type which is simple and economical to install and operate and which may be applied to existing furfural extractive distillation systems.

Other objects and advantages will become apparent to those skilled in the art from the following description.

The accompanying drawing portrays diagrammatically one arrangement of equipment for carrying out my invention.

While I have illustrated only one absorber and one stripper column with their accessory equipment it will be understood that any number may be employed. Commercial plants frequently are equipped with a plurality of each.

In accordance with my present invention water layers, formed by condensation and separation of overhead vapors from absorber and stripper columns, are separately withdrawn and are subjected to azeotropic distillation for the recovery of their furfural content. Corrosive impurities contained therein and excess water, not removed

as an azeotrope with furfural, are obtained as a kettle product and discarded.

In the operation of absorber and stripper columns great care is taken to prevent loss of furfural in overhead vapors. But in spite of all precautions a little furfural passes overhead together with water and hydrocarbon vapors. When these overhead vapors are condensed the condensate separates into a hydrocarbon layer and a water layer containing furfural in amounts up to about 1 per cent. Practically no inorganic matter is present in this water layer. Past practice has been to return this water layer as make-up water to furfural withdrawn from stripper columns in order to maintain the dissolved water content of the furfural substantially constant and in order to conserve furfural, which is expensive.

I have found that such water layers contain corrosive impurities. The nature of these corrosive impurities is not known nor is it known how they are formed or are carried overhead. It is believed that the corrosive materials probably form in absorber and stripper columns and are probably stripped from furfural therein and carried overhead. My invention is, however, not limited to any theory of formation of such corrosive materials. No matter how formed, corrosive materials are present in the water layer and are added to stripped furfural with the water when such water layers are used as make-up water, thus increasing the corrosiveness of the furfural.

I have found that this difficulty can be overcome while recovering substantially all furfural contained in the water layer by separately withdrawing the water layer and subjecting it to azeotropic distillation whereby a minimum boiling azeotrope of furfural and water passes overhead and the greater portion of the water containing the corrosive impurities is recovered as a kettle product and discarded.

I have discovered that the corrosive materials present exhibit very unusual volatility characteristics. In absorber and stripper columns where every precaution is taken to prevent any carry-over of furfural, such as maintaining the temperature of the top of the column relatively low and using reflux, there are nevertheless corrosive impurities present in the condensed overhead, and when the water layer from such condensate is again distilled under temperature conditions sufficiently high to insure carry-over of an azeotrope of furfural and water the corrosive impurities are left behind in the kettle product. Why this occurs I do not know. It is possible that some sort of chemical reaction such as polymerization or condensation involving the corrosive matter takes place. I do not wish to limit my invention to any theory or mechanism of chemical action since I do not know the explanation of this behavior.

Referring to the accompanying drawing, a C_4 hydrocarbon feed containing an unsaturated hydrocarbon which it is desired to recover enters absorber 1 via line 2. Furfural containing water is continuously injected into the top of absorber 1 via line 3. The descending furfural absorbs unsaturated hydrocarbon and is withdrawn via line 4. The overhead from absorber 1 is condensed in condenser 5 and flows into accumulator 6 where it is allowed to separate into two layers, an upper layer comprising more saturated C_4 hydrocarbons and a lower water layer. A portion of the hydrocarbon layer is returned to column 1 via line

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7 as reflux, at a point above the point of furfural entry. The remainder of the hydrocarbon layer is withdrawn via line 8.

Furfural rich in unsaturated hydrocarbon is fed via line 4 to stripper 9 where the unsaturated hydrocarbon is driven off overhead in conventional manner. The overhead is condensed and flows into accumulator 11 where it separates into two layers. A portion of the upper unsaturated hydrocarbon layer is fed via line 12 to the top of column 9 as reflux and the remainder is withdrawn via line 13 to storage or use.

Stripped furfural is removed from stripper 9 as a kettle product and is passed through cooler 14 to lower its temperature to a point suitable for reintroduction into absorber 1, and is recycled to surge tank 16 whence it is fed into absorber 1.

A side stream of stripped furfural is passed via line 17 to rerun unit 18. Unit 18 may include any desired equipment for purifying furfural by steam distillation but I prefer to use the equipment shown in Fig. 2 of Buell et al. 2,350,584. In any case purified furfural and water containing furfural are the products obtained from the rerun unit. The purified furfural is passed via lines 19 and 20 to surge tank 16. Water containing furfural is led via lines 21 and 22 to surge tank 23 whence it is introduced via line 24 into stripped furfural in line 15. Additional water required is introduced via line 25 from a suitable source outside the system.

In accordance with the present invention, the water layers separating in accumulators 6 and 11 are withdrawn via lines 26 and 27, are merged and are introduced via line 28 to a medial point in a fractionating column 29 which may be conveniently provided with an internal reflux condenser 34. Column 29 is operated under conditions of heat and pressure required to take overhead a minimum boiling azeotrope of furfural and water. At atmospheric pressure this temperature will be about 208° F. The temperature will of course increase as the pressure increases but should not be allowed to go higher than about 3° F. below the boiling point of water at any higher pressure at which it may be desired to operate. Overhead vapors are led via line 31 to condenser 32 and the resulting condensate flows into accumulator 33.

Since the minimum boiling azeotrope will contain about 8 per cent or more of furfural, depending on whether the pressure used is atmospheric or above, and the feed contains about 1 per cent furfural it will not be necessary to distill more than about $\frac{1}{2}$ of the feed overhead in order to recover substantially all furfural contained therein. The greater portion of water contained in the feed is withdrawn as a kettle product via line 30 and is discarded. This kettle product contains substantially all corrosive impurities. The condensed overhead product is non-corrosive.

The condensed overhead is allowed to separate into layers in accumulator 33, an upper water layer saturated with furfural and a lower furfural layer. These layers are separately withdrawn via lines 22 and 20 respectively and are conducted to surge tanks 23 and 16 respectively.

It is obvious that if it be desired to recover substantially pure anhydrous furfural, rather than furfural containing water, this may be done by withdrawing the furfural layer from accumulator 33 and subjecting it to a second azeotropic distillation. This will result in the recovery of substantially anhydrous furfural as a kettle product,

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an azeotrope of furfural and water passing overhead.

By operating according to my invention corrosion in the extractive distillation is greatly reduced. Corrosive material is removed from water in condensed overhead from absorbers and strippers and is not returned to the main system. Far less heating and cooling are necessary than when the greater portion of water and furfural are distilled. It is much cheaper to pump fresh make-up water in amount required for use than to distill an equal amount. The process has the further advantage of being easily carried out in a simple and economical manner and that little additional equipment is required to adapt the process of the present invention to existing plants, which usually have some fractionating tower which could be used for azeotropic distillation, at least at intervals. It is obvious that the process of the present invention could be carried out intermittently as well as continuously if the water layers were withdrawn to storage and thereafter intermittently subjected to azeotropic distillation to recover their furfural content and to eliminate corrosive impurities.

Other advantages of the present invention will be apparent to those skilled in the art in the light of the disclosure.

Having described my invention and explained its operation, I claim:

1. In a process for the recovery of unsaturated hydrocarbon from admixture with more saturated hydrocarbon by extractive distillation with furfural containing dissolved water as selective solvent wherein small amounts of water and furfural are volatilized and pass overhead from absorbing and stripping steps, the total overhead product from each of said steps is condensed and is separated into two layers, namely, a hydrocarbon layer and a water containing dissolved furfural and corrosive impurities, that improvement which comprises withdrawing said water layers; introducing them into a distillation zone; therein distilling off an overhead product consisting of a minimum boiling azeotrope of furfural and water; withdrawing a kettle product comprising the greater portion of water introduced into said distillation zone and substantially all corrosive impurities contained therein; condensing said overhead product and separating it into a furfural rich layer and a water rich layer; returning said last-mentioned furfural rich layer to furfural in the extractive distillation system; and returning said last-mentioned water rich layer to the extractive distillation system as make-up water.

2. In a process for the recovery of unsaturated hydrocarbon from admixture with more saturated hydrocarbon by extractive distillation with furfural containing dissolved water as selective solvent wherein small amounts of water and furfural are volatilized and pass overhead from absorbing and stripping steps, the total overhead product from each of said steps is condensed and is separated into two layers, namely, a hydrocarbon layer and a water layer containing dissolved furfural and corrosive impurities, that improvement which comprises withdrawing said water layers; introducing them into a distillation zone; therein distilling off an overhead product consisting of a minimum boiling azeotrope of furfural and water; withdrawing a kettle product comprising the greater portion of water introduced into said distillation zone and substantially all corrosive impurities contained therein; and discarding said kettle product.

3. In a process for the recovery of unsaturated hydrocarbon from admixture with more saturated hydrocarbon by extractive distillation with furfural containing dissolved water as selective solvent wherein small amounts of water and furfural are volatilized and pass overhead from absorbing and stripping steps, the total overhead product from each of said steps is condensed and is separated into two layers, namely, a hydrocarbon layer and a water layer containing dissolved furfural and corrosive impurities, that improvement which comprises withdrawing said water layers; introducing them into a distillation zone; therein distilling off an overhead product consisting of a minimum boiling azeotrope of furfural and water; withdrawing a ket-

tle product comprising the greater portion of water introduced into said distillation zone and substantially all corrosive impurities contained therein; condensing said overhead product and separating it into a furfural rich layer and a water rich layer; introducing said last-mentioned furfural rich layer into a suitable furfural surge tank in the extractive distillation system; and introducing said water layer into a suitable water surge tank in said system.

4. The process of claim 1 wherein the unsaturated hydrocarbon is butene-1.

5. The process of claim 1 wherein the unsaturated hydrocarbon is butadiene-1,3.

VIRGIL SCARTH.

Certificate of Correction

Patent No. 2,442,474.

June 1, 1948.

VIRGIL SCARTH

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows: Column 2, line 43, for "0.66" read 0.06; column 6, line 40, after the word "water" insert *layer*; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 14th day of September, A. D. 1948.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.

3. In a process for the recovery of unsaturated hydrocarbon from admixture with more saturated hydrocarbon by extractive distillation with furfural containing dissolved water as selective solvent wherein small amounts of water and furfural are volatilized and pass overhead from absorbing and stripping steps, the total overhead product from each of said steps is condensed and is separated into two layers, namely, a hydrocarbon layer and a water layer containing dissolved furfural and corrosive impurities, that improvement which comprises withdrawing said water layers; introducing them into a distillation zone; therein distilling off an overhead product consisting of a minimum boiling azeotrope of furfural and water; withdrawing a ket-

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