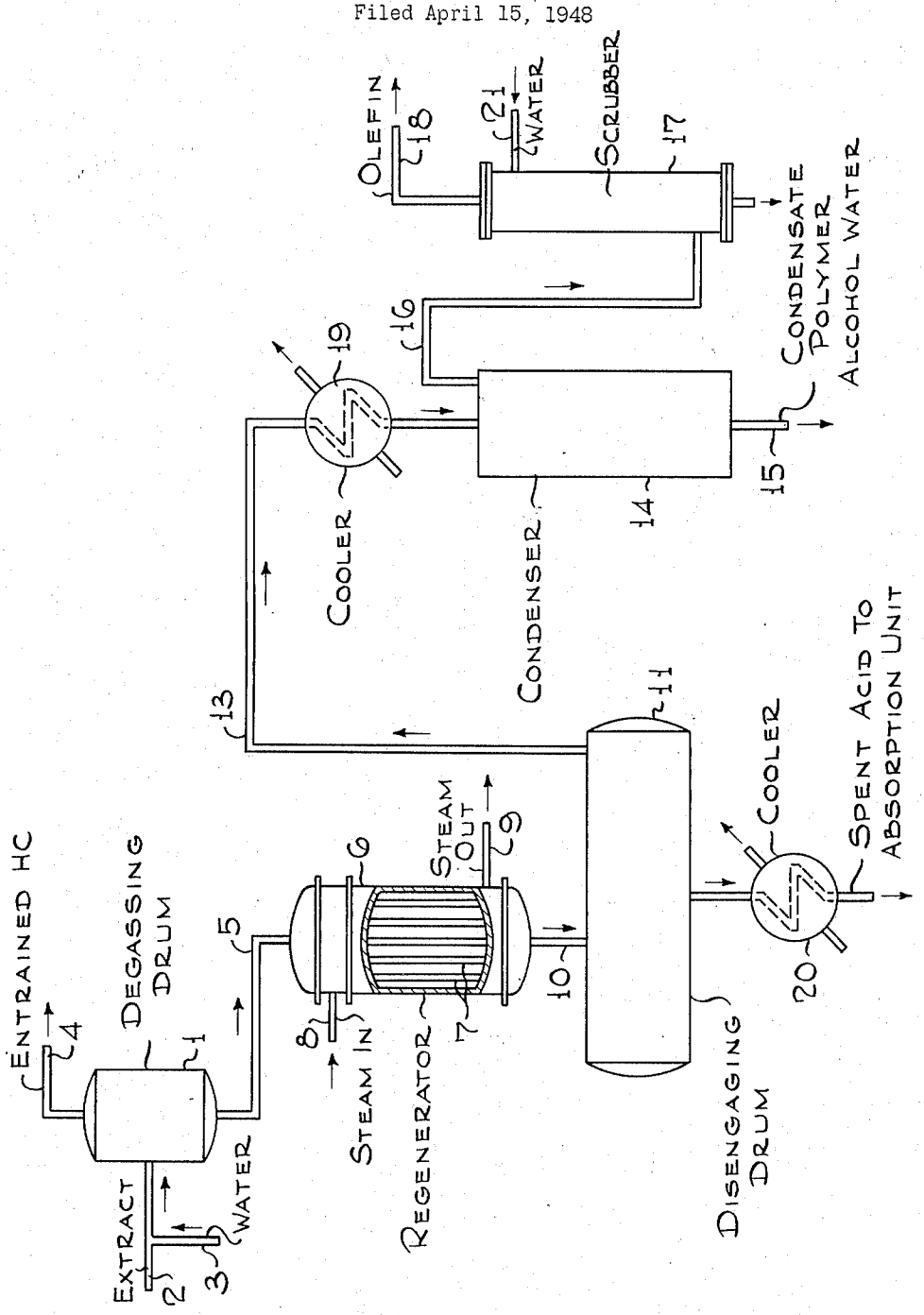
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REGENERATION OF OLEFINS FROM ACID SOLUTIONS

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REGENERATION OF OLEFINS FROM ACID SOLUTIONS

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This invention relates to a process for the recovery of olefin hydrocarbons from strong acid extracts of the corresponding alcohols or acid esters of the respective olefins. More particularly, the invention deals with the recovery of the lower molecular weight olefin hydrocarbons, e. g. of the C_2 to C_6 range such as ethylene, propylene, isobutylene, n-butenes, and the isomeric amylenes, etc., from acid extracts of their corresponding alcohols or acid esters. The desired olefin recovery is accomplished in this invention by passage of the acid extracts in long thin streams of definite length and cross-sectional area under specific conditions of temperature, flow rate, and acid strength to assure high yields of the desired olefin in high purity.

The prior art discloses that olefinic hydrocarbons can be prepared from the corresponding alcohols or acid esters by heating their acid solutions. The control over the reaction indicated by the prior art has been regulation of the temperature, acid strength and alcohol concentration. Some mention has been made of the concentration of esterified olefin present in the acid solutions. Disclosures of the prior art can be summarized by stating that the acid solutions are either (1) diluted, (2) maintained at a lower concentration by the presence of an excess of alcohol during distillation, (3) the distillation of the acid liquor is carried out in the presence of a salt, (4) acid liquor is heated to polymerize iso $C_4^=$. The following patents are representative of the prior art: Englehardt et al. 1,770,734; Deansley et al. 2,012,785; Snow 2,128,971; and Deansley 2,237,292.

The prior art does not disclose processes for recovery of olefins, particularly isobutylene, in high yields from acid extracts containing acid at or closely approaching absorbing strength for the olefin. Neither does it show a process for recovering olefin from an acid extract coincident with increasing the acid strength from somewhat below absorbing strength to absorbing strength. The teaching of the prior art that any suitable means of applying heat quickly to an acid extract will cause regeneration of olefin is only correct when olefin yields of less than 20% are considered as proper demonstation of the art. It will be demonstrated in the examples that to maintain yields of olefin above 50–60% it is necessary to use the process described by this invention as contrasted to any process to be devised by implications from the prior art.

The olefin regeneration process as described in this invention differs from the processes of the

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prior art in that: (1) extremely large yields of olefin, e. g. 80–90 weight percent and above, are obtained therefrom, (2) during the recovery process the acid strength is increased from somewhat below olefin-absorbing strength up to olefin-absorbing strength, thus requiring no restoration or reconcentration before being returned to the absorption system and (3) the purity of the regenerated olefin is extremely high, e. g. 96–99% in the case of isobutylene.

In application Serial No. 21,173 filed of even date herewith in the name of Matthew D. Mann, Jr. and Henry O. Mottern, there is described and claimed a process for the regeneration of olefins from acid extracts thereof by decomposition of the acid solution by flash vaporization under controlled heat transfer conditions whereby the extract is fed to the heat exchange zone in the form of streams of restricted length and cross-sectional area, such, for example, as would be obtained by passing the extract through the cylindrical tubes of a tube-in-shell type heat exchange.

The novelty of this invention resides in the olefin regeneration process wherein the acid extract or acid solution is fed to the decomposition zone in streams which are non-circular in cross-sectional area, e. g. a stream which is elliptical in cross-sectional area, whereby heat transfer into the vapor producing feed material under flash reaction conditions is enhanced. The improved yields of regenerated olefin achieved by employing streams whose cross-sectional area are non-circular, e. g. elliptical-shaped streams such as are obtained by passing the acid extract through a partially flattened tube, are not predictable from the Reynolds number since the velocity of flow increases about one hundred fold as the extract passes through the decomposition zone due to the formation of the gas phase.

It is an object, therefore, of this invention to provide an olefin recovery process in which high yields of recovered olefin are obtained.

It is another object of this invention to provide a process for olefin recovery from their acid solutions in which the acid is recovered from the regeneration in increased strength.

It is a further object of this invention to provide a process for olefin recovery in which the purity of the recovered olefin is extremely high.

These and other objects of the invention are accomplished by carrying out the regeneration according to the process which will now be set forth.

The practice of this invention will be described

for illustrative purposes only using isobutylene and its sulfuric acid extracts as the reference materials. The acid extracts are prepared by the methods disclosed in the art, namely, acid treatment of a butane-butene fraction from petroleum or other sources under controlled conditions of temperature and pressure using 60–70% H_2SO_4. After the acid extract is settled free of the unabsorbed hydrocarbon, it it decanted and is ready for use in the isobutylene recovery process.

The isobutylene recovery is carried out as follows: Isobutylene acid extract is diluted with water from absorbing strengths of 60–70% to 55–60% acid strength, calculated on a hydrocarbon free basis. The entrained and dissolved gases are allowed to disengage from the extract. The extract is then passed in long thin heated streams of restricted length and non-circular cross-sectional area into uniform contact with a heat exchange surface, preferably e. g. by passage through a partially-flattened tube contained in a tube-in-shell heat exchanger under carefully controlled flash vaporization conditions, hereinafter described, which causes the isobutylene to regenerate from the acid extract. The isobutylene gas and acid effluent from the exchanger tubes are carried rapidly into a disengaging vessel where the gas is taken overhead and the acid flows out the bottom through a cooler to a receiving vessel for recycling to the absorption unit. The isobutylene passes from the disengaging vessel to conventional scrubbing, compression and fractionating equipment for purification. The process is thus adapted to continuous operation.

The operation of the exchanger-generator is closely controlled as to acid extract flow rate, temperature, pressure, acid strength, extract saturation, etc., in order to minimize recovery of potential isobutylene as polymer or as alcohol.

Operating Conditions

The acid extract is fed to the exchanger tube at a rate which will maintain the entering liquid linear velocity at 0.4–2.0 ft./sec. for each stream entering the heat exchange surface. Velocities lower than 0.4 ft./sec. cause polymerization and velocities higher than 2.0 ft./sec. cause incomplete regeneration of the olefin. The preferred range of velocity is influenced partly by the saturation of the extract, viz. the mols olefin/mol acid. When the extract saturation is in the range of 0.2–.8 the preferred velocity is .4–.8 ft./sec. when the extract saturation is 0.8–1.0, the preferred velocity is .6–1.0 ft./sec. When the extract saturation is above 1.0 the preferred velocity is at 1.0–1.2 ft./sec.

The regeneration must be carried out at absolute pressures between 600–1000 mm. Hg. At pressures below 600 mm. too much of the olefin is recovered as the corresponding alcohol to give a good yield per pass and can only be converted to olefin by recycling to the process. At pressures over 850 mm. the yield of isobutylene is reduced through polymerization. Only at pressures close to atmospheric can the yield of olefin be held to a high figure, i. e., above 80 weight percent.

The temperature of the reaction is measured at the outlet to the exchanger tubes. This temperature is held at a point to indicate the boiling point of the acid at the desired strength. The temperature is a function of the pressure, rate of heat input and the partial pressure over the acid. The partial pressure is influenced by the quantity of olefin regenerated. For example, where temperatures of 150° C. may be required to recover the acid at 65% from extracts of 0.5 saturation, extracts at 1.0 saturation give sufficient gas to give 65% acid at 135° C. At the preferred rates of flow, the acid strength was held at 65%.

Although the regeneration to high yield is operable in the range of 60–70% effluent acid strength the preferred range is 64–66%. The strength is sufficient for fast absorption rates and gives less polymerization in the exchanger generator. The dilution of the extract from the absorber is made to give 55–60% acid for regenerating isobutylene. The regeneration of ethylene, propylene or n-butylene is carried out at higher acid strengths and temperatures.

The length and diameter of the heated stream of extract must be limited to maintain a high yield of olefin. When a tubular heat exchanger is employed in the process, these factors can be controlled, of course, by the length and diameter of the exchanger tubes themselves. The length may preferably vary between 3 ft. and 10 ft. Tubes shorter than 3 ft. do not give enough surface and heat to insure complete regeneration or recovery of isobutylene. Tubes longer than 10 ft. cause development of pressures above 5 lbs. inducing excessive polymerization. The minor diameter of the stream (in the case of elliptical streams) or the central minor axis of the stream can vary between ¼'' and ¾'' in length, assuring a flow velocity for a given extract in the proper velocity range as indicated above.

The following discussion illustrates the effect of operating variables on the overall process yields etc. as determined by actual plant runs on the regeneration of isobutylene from sulfuric acid extracts.

Effect of Length and Diameter of Extract Stream

One of the major variables affecting the yield of isobutylene by the flash exchange-generator process is the diameter-length ratio of the extract stream, i. e. the diameter-length ratio of the exchanger tubes. A ½'' diameter tube was chosen as the largest size in the tantalum tubing which would not collapse under the external steam pressure. Copper was found to be equivalent in performance and was used in most of the experimental work. The tube length was varied at 3', 5' and 10' to explore the relationship between the volume of liquid feed and tube length. Lengthening the tube increased isobutylene yields at a given feed rate. Linear velocities below 0.3 ft./sec. show low yields of isobutylene for all tube lengths. At 0.4–0.8 ft./sec., regeneration yields approach a maximum for each tube length. This is shown in Table I following.

Table I

EFFECT OF FEED RATE ON TUBE LENGTH

[½'' O. D., 7/16'' I. D. copper tube. Extract saturation=0.5. Outlet temperature=150° C.]

Linear Velocity, ft./sec.	Tube Length		
	3'	5'	10'
	Weight Per Cent Iso C_4-(on Recovered Products)		
0.1	------	69.5	75.0
0.2	56.5	78.0	81.5
0.3	63.0	78.5	84.0
0.4	63.5	80.0	85.0
0.8	64.0	80.0	84.5

Maximum regeneration is approached for the ½'' tube at a length of 10 feet. Data set out in Table II below on the yield at a given velocity show that an increase in tube length beyond 10 feet would have little or no further effect on yield.

Table II

EFFECT OF TUBE LENGTH ON ISOBUTYLENE REGENERATION

[½'' O. D., 7/16'' I. D. copper tube. Feed rate=0.6 ft./sec. Extract saturation=0.5.]

Tube Length, Ft.	Weight Per Cent Iso $C_4^=$ Regenerated (on Recovered Products)
3	63.0
5	80.0
10	85.0

Polymer and alcohol formation are relatively constant over the range of practical feed rates—13.5% polymer and 1.5% alcohol. This is illustrated in Table III:

Table III

POLYMER AND ALCOHOL FORMATION

[½'' O. D., 7/16'' I. D. × 10 ft. Round Copper Tube. Extract saturation=0.5.]

Feed Rate, ft./sec.	Weight Per Cent Isobutylene to (on Recovered Products)	
	Polymer	t—BuOH
0.2	17.0	1.5
0.4	13.5	1.7
0.6	13.2	1.8
0.8	13.7	1.8

The small quantity of alcohol produced is contained in a water layer from the condensed overhead stream in the isobutylene recovery process. The entire water layer can be recycled to the initial dilution stage for reducing the effective acid strength of the extract to 60%. If a water balance is maintained only make-up water need be added to the dilution stage. Polymer composition is similar to that produced by current steam stripping regeneration technique. A typical analysis of the polymer produced from an extract containing 93 weight per cent isobutylene and 7 weight per cent normal butylene, 52.8% dimer, 22.7% trimer, and 24.5% codimer.

Tube diameters were varied between ¼'' and 1½'' for copper, Nichrome, and tantalum. The ½'' O. D. (7/16'' I. D.) tube was the largest diameter tubing used that gave no isobutylene in the spent acid. Too large a tube permits slugs of only partly heated extract to be blown through the tube before the olefin is adequately liberated. Since the ¼'' tubing seemed impractical for commercial use, the ½'' was chosen for study. The data on the effect of tube diameter of 3 ft. lengths are summarized in Table IV, following. It is apparent that the smaller the diameter, the greater is the regeneration of isobutylene.

Table IV

EFFECT OF TUBE DIAMETER

[Length=3 ft. Feed rate=0.4–0.6 ft./sec.]

Tube Inside Diameter	Weight Per Cent Iso $C_4^=$ to (on Recovered Products)			
	Regenerated Isobutylene	Polymer	t—BuOH	Iso $C_4^=$ in Spent Acid
¼'' copper	78.0	16.1	4.2	0
⅜'' steel	60.9	26.0	13.1	0
7/16'' copper	63.0	25.0	12.0	0
⅜'' Nichrome	55.3	8.0	3.0	32.5
1½'' tantalum thimble (heated internally)	35.5	27.5	2.7	33.3

EFFECT OF SHAPE OF EXTRACT STREAM DURING REGENERATION

Flash regeneration of isobutylene requires a high rate of heat input combined with a short contact time. The shape of the surface over which regeneration takes place has been found to affect the rate of heating and the uniformity of flow over that surface with consequent effect on regeneration. This relationship was demonstrated by altering the shape of the extract stream, i. e. for example, the shape of the exchanger tubes.

A ½'' tube, flattened to ¼'' minimum diameter, showed higher yields than a round tube of similar length. A comparison of 3' and 5' tube lengths in both round and flat tubes is shown in Table V.

Table V

EFFECT OF TUBE SHAPE ON REGENERATION

[Tube length=3' and 5'. Extract saturation=0.5. ½'' round tube vs. ½'' tube flattened to ¼'' minimum diameter.]

Linear Velocity, ft./sec.	Weight Per Cent Iso C_4 Reg. (on Recovered Products)			
	3' Round	3' Flat	5' Round	5' Flat
0.2	56.5	83.0	78.0	----
0.3	63.0	84.0	78.5	84.0
0.4	63.5	85.5	80.0	88.0
0.6	64.0	80.0	80.0	87.0

Feed rate appears critical for the flattened tubes for a given length.

The effect of flattening a ½'' x 5' tube on regeneration was equal to increasing the length of the cylindrical tube to 10 feet. Considerably higher yields were obtained for the flattened tube in a feed rate range of 0.3–0.6.

Table VI

EFFECT OF TUBE SHAPE ON REGENERATION

[½'' O. D. Cu Tube. Round vs. flattened to ¼'' minimum diameter.]

Linear Velocity, ft./sec.	Weight Per Cent Iso $C_4^=$ regenerated (on Recovered Products)	
	10' Round	5' Flat
0.2	81.5	73.0
0.3	84.5	83.0
0.4	85.0	88.0
0.6	85.0	87.0

Filler bars were tried in short length tubes larger than ¼''. In order to test this, ¼'', ⅜'' and 7/16'' filler bars were inserted within a ½'' x 3' tantalum tube. An annular space above

1/16" in a 3' tube showed favorable yields at 0.6 ft./sec. Table VII illustrates the effect of filler bars on regeneration at various feed rates. The data illustrate that the use of the filler bar provides good yields, particularly at the higher feed rates but, however, does not supply the same improved results as obtained by flattening the tube.

Table VII

EFFECT OF FILLER BARS ON REGENERATION

[½" I. D. tantalum round tube 3' long.]

Filler Bar O. D.	Annular Space	Weight Per Cent Iso $C_4^=$ Regenerated (on Recovered Products) at Linear Vel. (ft./sec.) of—		
		0.2	0.4	0.6
Inches	*Inches*			
¼	⅛	65.0	62.5	------
⅜	1/16	60.0	74.0	78.5
7/16	1/32	69.5	80.0	88.5

A different type of annular space was tested on a 1½" O. D. x 28" tantalum thimble inserted in a carbate lined spool piece leaving a ¼" in one case and ½" annular space in another case. In both cases low isobutylene yields were noted, probably due to poor distribution on the thimble. The following table illustrates the decrease in yield with increasing feed rates. Regeneration of the extract was incomplete in all cases.

Table VIII

EFFECT OF ANNULAR SPACE USING A TANTALUM THIMBLE

[Heated internally]

Linear Velocity, ft./sec.	Weight Per Cent Iso $C_4^=$ regenerated (on Recovered Products)	
	¼" Annular Space	½" Annular Space
0.2	55.7	31.4
0.4	41.4	35.2
0.6	35.3	24.1

Summarizing the data on the effect of tube shape or surface phenomena on regeneration in heat exchange equipment, it is shown that a flattened tube gives the highest isobutylene yield for a given length. The limiting capacity for an exchanger of a given surface area appears about the same with round or flat tubes. Table IX summarizes data on the effect of tube shape on regeneration.

Table IX

EFFECT OF TUBE SHAPE ON REGENERATION

Tube	Weight Per Cent Iso $C_4^=$ regenerated (on Recovered Products) at Linear Vel. (ft./sec.) of—		
	0.2	0.4	0.6
Round copper tube 7/16" I. D. x 36"	56.5	63.0	64.0
Flattened to ¼" (same as above)	83.0	83.5	78.5
½" I. D. x 36"+⅜" filler bar	57.0	74.0	78.5
1½" O. D. x 28" tantalum thimble (heated internally)	55.7	41.4	35.3

The extract streams being subjected to heat exchange should preferably flow in a descending stream. For example, when exchanger tubes are employed they should be placed in a vertical position to insure even distribution of extract through each tube. A pool of extract above the tube bundles would provide uniform distribution through orifices into each tube. Carbate is recommended as a material for the distribution plate and should be thick enough to thermally insulate the extract above the orifices. When the extract streams were allowed to flow in a lateral direction poor yields of regenerated olefin resulted. When the extract stream is subjected to heat exchange in an up-flow direction, extremely poor yields of regenerated olefin resulted. The poor yields in these instances are due, undoubtedly, to two factors, namely, the pressure required to promote proper flow of the extract stream, and secondly, the collection of acid which occurs under conditions of lateral flow and up-flow. The pressure employed is conducive to polymerization of the olefin, likewise, contact with acid at the temperature employed is conducive to polymerization which, of course, detracts from the yield of desired olefin.

EFFECT OF EXTRACT SATURATION

The saturation of the extracts employed in the olefin regeneration process is preferably between 0.5 and 1.5. Experiments were carried out employing saturations in the above regions. Extracts of 1.0 saturation were found to give on regeneration, yields of 83% at 0.6 ft./sec. feed rate. On increasing the extract saturation to 1.5, it was found necessary to increase the feed velocity to to 1.1 ft./sec. to reach an 85% yield. The higher feed velocities were not necessary to secure good yields at the 0.5 saturation. At the higher extract saturation less steam pressure was necessary to maintain a spent acid strength of 65% H_2SO_4 indicating a greater steam efficiency for regeneration. Table X summarizes data on the effect of extract saturation at various feed velocities on isobutylene regeneration.

Table X

EFFECT OF EXTRACT SATURATION

[½" O. D., 7/16" I. D. x 10' copper tube.]

Extract Saturation	Weight Per Cent Isobutylene (on Rec. Prod.) at Linear Vel. of—			Steam Press., p. s. i. g.	Per Cent H_2SO_4 in Spent Acid
	0.4	0.6	1.1		
0.4–0.5	84.5	85.0	------	80–120	67.0
1.06	85.0	83.0	------	82–96	67.0
1.3–1.4	68.0	74.0	85.0	68–109	65.2

HEAT REQUIREMENTS

Heat requirements for regeneration and acid concentration were determined by measuring the total condensed steam from the heat exchanger. A blank run was made for each experiment for equipment heat loss. The results showed that 300–375 B. t. u. per lb. 60% acid extract would be required over the range of 0.5–1.5 saturation. This includes heat required to raise the acid from 15° C. to 150° C., to regenerate the isobutylene and to increase the acid strength from 60% to 65%.

ISOBUTYLENE PURITY

Isobutylene purity is in a range of 96–99%. An extract feed containing 91.5% isobutylene and 8.5% n-butene yields isobutylene of 98.9% purity (by HCl method). The normal olefins

are usually found as codimer in the polymer produced.

Reactor Pressure

Reactor pressure was maintained below 2.0 p. s. i. g. Previous laboratory work above this pressure showed that excessive polymerization occurred. Low pressure on the system was obtained by increasing the size of the outlet piping from the acid settler to reduce back-pressure.

Feed Extract Acid Strength

Feed extract acid strength of close to 60 weight percent H_2SO_4 (hydrocarbon free basis) was used in the regeneration of isobutylene. Previous laboratory studies indicated that 58–60 weight per cent feed acid (after dilution) gave higher yields and increased product purity.

Spent Acid Strength

Spent acid strength was held at 65% by controlling outlet temperatures. No isobutylene was present in the spent acid at optimum operating conditions. No further acid concentration of the spent acid is required for absorption. The spent acid is cooled and recycled directly. The strength of the spent acid was easily held during a wide range of operating conditions, i. e., feed rates 0.1–1.1 ft./sec., extract saturations of 0.5–1.5 and feed acid strength of 58–60%.

A very important part of the process for regenerating olefins by the technique described is that the acid can be recovered in condition for recycling directly to the absorption step. The acid as recovered contains only traces of separable carbonaceous and polymeric hydrocarbon material and these traces are removed by adequate settling facilities. Other processes requiring dilution and reconcentration steps often cause the inclusion of such materials in the acid of absorption strength and result in emulsion formation in the extraction step or foaming in the regeneration step. Acids recovered at recycling strength from the process described are clean enough to avoid such occurrences.

Outlet Temperatures

Outlet temperatures were adjusted to maintain a spent acid strength of 65% H_2SO_4. Extracts of 0.5 saturation were held at 150° C., 1.0 saturated at 145° C. and 1.5 extracts at 135° C. Temperatures were controlled by varying steam pressure on the shell side of the exchanger. The temperature employed must be such that polymerization and other secondary reactions are avoided. The latter undesirable effects are presented by properly correlating the temperature with the contact time.

Tube Metal

Tantalum metal is recommended for the exchanger tube construction. Tantalum was tested by passing 65% H_2SO_4 through a tube at a rate of 10 gallons/hour (0.6 ft./sec.) at 150° C. for 190 hours. No indication of corrosion or erosion was noted in this service. The experimental tube showed no signs of distortion under 125# external steam pressure.

The drawing represents a flow diagram showing an elevational view of typical plant apparatus employed in carrying out the invention.

Referring to the drawing the invention will be described with respect to the regeneration of isobutylene from acid extract although the invention is by no means limited to this particular olefin. Numeral 1 represents a degassing drum to which a 60–70% sulfuric acid extract is led via line 2. The extract consists of a solution of C_4 hydrocarbons obtained by sulfuric acid treatment of a butane-butene fraction from petroleum or other sources under controlled conditions of temperature and pressure employing 60–70 weight per cent sulfuric acid. This extract is diluted with water entering through line 3 until it reaches an acid strength of 55–60%. In the degassing drum entrained and less reactive, unabsorbed C_4 hydrocarbons are removed via line 4. The temperature employed in the degassing drum is a temperature below that at which polymerization of the isobutylene or copolymerization of isobutylene-butene occurs. The extract is pumped from degassing drum via line 5 to regenerator 6. In the drawing the regeneration zone is illustrated as a vertical tube-in-shell heat exchanger, the tubes of which have been partially flattened so as to be elliptical in cross-sectional area. Numeral 7 represents the exchanger tubes which may vary in length, preferably between 3 and 10 feet as previously described and ¼'' to ¾'' preferably ½'' in diameter. The extract is rapidly heated by passage through the tubes at a pressure below 2.0 p. s. i. g. and linear velocity of 0.4 to 1.2 ft./sec. The temperature during this passage is maintained at approximately the boiling point of the acid by circulation of steam or other fluid in indirect heat exchange with the extract by entrance through line 8 and exit through line 9. For the regeneration of isobutylene and other tertiary olefins such as tertiary amylene, a temperature in the range of 130–160° C., preferably 140–155° C., is employed. Straight-chain olefins of the C_2 to C_6 range require higher acid strengths for absorption. Consequently, to maintain an acid of absorbing strength at the outlet of the heating zone higher temperatures are required, e. g. 165° C. to 295° C., preferably 290° C. to 295° C. during ethylene regeneration, 165° C. to 278° C. during propylene regeneration, and 180° C. to 255° C. during n-C_4–C_6 olefin regeneration.

Under these conditions the aqueous acid extract is decomposed to yield a gaseous mixture comprising isobutylene vapor, water vapor, alcohol and polymer vapor and liquid sulfuric acid. The gaseous mixture and acid effluent from the exchanger tubes are carried rapidly through line 10 into a disengaging drum 11. It is essential that the evolved olefin be removed from the hot acid as quickly as possible to prevent excessive polymerization of the olefin. In this drum the gas is separated from the acid and removed from drum 11 via line 13. The acid settles and is removed via line 12. This acid becomes concentrated during passage through the regenerator and is restored to 60–70% concentration in which condition it is ready for re-use in the absorption of the C_4-hydrocarbon stream. The gas emerging from line 13 passes to a partial condenser 14 in which hydrocarbon polymers, alcohol and water are condensed and removed from the system via line 15. Isobutylene is withdrawn through line 16 and countercurrently scrubbed in vessel 17 by dilute aqueous caustic for removal of traces of acid. The acid-free isobutylene is removed from vessel 17 via line 18. It is then water-scrubbed, condensed and stored.

It will be apparent that a system has been described for the rapid uniform heating of the extract with low contact time by passing it in finely-divided streams at high velocity in contact with heat exchange surfaces whereby the extract is decomposed and the isobutylene evolved there-

from. Although the flash evaporation process is preferably carried out employing the heat exchanger-generator described other means can be employed for providing a plurality of long unit paths of extract flow relatively thin in at least one transverse dimension so that all the extract liquid is kept within a certain specified distance at all times from the heat exchange surface.

Another successful method employs a system whereby the extract is sprayed via a shower spray, or series of sprays, countercurrent to a uniform blanket of steam maintained at a temperature hotter than the boiling point of the extract, i. e. above 150° C. for 65% H_2SO_4. Steam pressures of above about 54 pounds gauge are required. In this operation the olefin becomes disengaged from the decomposed extract and passes with the steam overhead from the settling acid. The gas is then separated, scrubbed and condensed as described above.

In the regeneration zone conditions throughout are to be closely controlled to attain best operation. Proper flow of the extract is necessary so that all parts of it receive substantially identical and immediate heat treatment. This is accomplished by proper association of the heating medium or heat transfer elements with the respective extract paths. Every part of the extract stream during its passage through the regeneration zone lies sufficiently close to the heating medium or heat transfer element to insure uniformity of temperature throughout the extract during its brief passage through the regeneration zone. The tube-in-shell heat exchanger equipment is preferred for the process of this invention because the design and arrangement of the tubes within the shell is such that the tubes seem to divide the body of extract entering the header thereof into a plurality of longitudinal streams whose greatest length is parallel to the direction of extract flow, thus offering maximum resistance to lateral flow. The dimensions of the longitudinal streams should preferably be 3 or more feet in length up to 10 feet and between ¼'' and ¾'', preferably ½'' in the smaller diameter. In this manner the distance of any extract particle from any heating medium or heat exchange surface will be kept at a required maximum during passage of the extract through the heating medium or heat exchange surface.

Isobutylene Regeneration

Experimental runs were carried out to demonstrate the improvement obtained by the use of flattened tubes for the regeneration of isobutylene from sulfuric acid solutions. In the runs listed the experiments were carried out under conditions falling within the following ranges:

1. Linear velocity of stream: 0.4 to 1.2 ft./sec.
2. Outlet temperatures: 130 to 160° C., usually 140–155° C.
3. Extract saturation: 0.4 to 1.4.
4. Regenerator pressure: 0.9 to 2.0 p. s. i. g.
5. Weight per cent H_2SO_4 in absorption stage: 63–65%.
6. Weight per cent H_2SO_4 in extract (hyd. free basis) after dilution 58.0–60.7%.
7. Weight per cent H_2SO_4 in spent acid (hyd. free basis) 65–68.0%.
8. Extract streams produced by passage through tubes as indicated.

Table XI is a summary of data showing the more advantageous results obtained employing a flattened stream of extract in the regeneration process. Such a stream is typified by a stream which is ellipsoidal in shape. In the runs tabulated in Table II such a stream was obtained by passing the extract through a ½'' diameter round copper tube which was flattened to a ¼'' minimum diameter. Using such a tube of 5'' length, equivalent or better results were achieved than those obtained with the ½'' diameter round tube of 10 ft. length. Even at 3 ft. length the flattened tube produced yields in all cases between 82.2% and 84.3%.

Table XI

ISOBUTYLENE REGENERATION FROM ACID EXTRACT TUBULAR FLASH HEATER

Run No.	Weight Per Cent Conversions, Total $IsoC_4^=$ Recovered			Weight Per Cent Conversions, Total Olefin Recovered				Material Balances, Weight Per Cent on Charge			
	$IsoC_4^=$ Reg.	$IsoC_4^=$ to Polymer	$IsoC_4^=$ to t-BuOH	Total Olefin Reg.	Total Polymer	t-BuOH as Olefin	Sec. BuOH as Olefin	Total Olefin	$IsoC_4^=$	H_2SO_4	H_2O
½'' O. D., 7/16'' I. D. x 5' Round Copper Tube Heated Surface=0.563 sq. ft.											
58	77.7	21.0	1.3	73.6	23.8	1.3	1.3	100.1	100.1	99.1	94.5
65	77.9	20.1	2.0	73.6	23.1	1.9	1.4	98.4	98.1	99.7	94.8
64	79.7	17.7	2.6	76.5	20.0	2.5	1.0	101.5	101.6	102.5	96.7
½'' O. D., 7/16'' I. D. x 3' Round Copper Tube Heated Surface=0.340 sq. ft.											
35	67.7	28.2	4.1	62.3	31.5	3.8	2.4	95.6	95.6	95.5	91.3
29	63.6	22.5	13.9	63.6	22.5	13.9	----	96.8	96.8	100.0	97.2
31	63.5	26.3	10.2	63.1	26.7	10.2	0	99.0	99.0	100.0	102.0
½'' Round Copper Tube Flattened to ¼'' Minimum Diameter x 5' Heated Surface=0.563 sq. ft.											
63	88.7	8.9	2.4	86.7	10.6	2.4	0.3	105.0	105.0	95.0	96.2
67	84.9	12.5	2.6	82.3	14.0	2.5	1.2	101.3	101.2	102.8	104.0
62	90.2	7.0	2.8	88.4	8.4	2.8	0.4	102.8	102.7	99.7	98.1
½'' Round Copper Tube Flattened to ¼'' Minimum Diameter x 3' Heated Surface=0.340 sq. ft.											
51	82.3	15.1	2.6	80.3	15.5	2.5	1.7	100.0	100.0	100.3	97.4
50	84.3	11.4	4.3	81.9	12.2	4.1	1.8	100.0	100.0	101.6	95.4
56	84.1	13.3	2.6	78.2	17.6	2.4	1.8	99.9	99.9	97.9	100.5
57	82.2	14.8	3.0	76.3	20.3	2.8	0.6	100.9	100.6	99.6	101.5
52	82.3	14.0	3.7	78.9	15.5	3.5	2.1	100.0	100.0	100.1	97.7

TERTIARY AMYLENE REGENERATION

Two runs were carried out on the regeneration of tertiary amylene from acid extracts obtained by sulfuric acid absorption of a C_5-refinery hydrocarbon stream. In the preparation of the C_5-extract, sulfuric acid of about 70% strength was employed in the absorption operation. This acid, is of course, a little higher than that used in the preparation of the C_4-extract. The runs were carried out in the exchanger-generator apparatus as previously described employing a flattened tube of ½'' minimum diameter copper tubes of 10 ft. length. Operating conditions and results obtained are summarized in the following table:

Table XII

Run No.	1	2
Feed Extract Acid Strength (Diluted from 70% to 60%)	56.7	57.0
Extract Feed Rate, liters/minute	0.932	0.62
Extract Saturator	0.370	0.273
Regenerator Outlet Temp., °C	159	162
Spent Acid Strength	69.3	68.4
Hydrocarbon Content Spent Acid Product Analysis	trace-tar	trace-tar
Weight Per Cent:		
C_4-	5.0	11.4
t-C_5-	64.2	58.7
n-C_5-	12.4	7.9
sat.-C_5	4.4	7.5
C_6+(polymer)	8.7	12.0
alcohol	5.3	2.5
Per Cent Regen. based on Analysis of Product	91.3	88.0

Although the invention has been illustrated by the application of the process to the regeneration of isobutylene and tertiary amylene the invention is equally applicable to other mono-olefins, particularly those of C_2 to C_6 molecular weight. It should be borne in mind that each olefin has its own optimum acid regeneration strength. For example, when regenerating ethylene from its sulfuric acid extract it is recommended that the extract be diluted no lower than about 85% acid strength; propylene not below about 65% acid strength; n-butenes not more than 60% acid strength; tertiary amylene and isobutylene not below about 55%. These dilutions are recommended for practical yields of olefin, i. e., 70 weight per cent and above. When acid dilutions below these figures are employed olefin yield is sacrificed to alcohol production which would, of course, be recycled to the regenerator feed. Sometimes under these conditions ethers form, particularly if pressure develops in the regenerator. This, of course, promotes loss of olefin yields.

Phosphoric acid, benzenesulfonic acid or salts yielding such acids may be employed in place of the sulfuric acid. Mixtures of such acids may also be employed. In general polybasic mineral acids or polybasic mineral acid-acting substances may be employed for the preparation of the extract feed to the regenerator.

It will be apparent that the process of this invention is applicable to the evaporation of a vapor producing feed by submitting the feed in finely divided continuous streams of restricted length and cross-sectional area to constant and uniform heat exchange (direct or indirect) under controlled rates of flow, temperature etc. This is accomplished by providing preferably a plurality of long unit paths of flow of restricted cross-sectional area and relatively narrow in at least one transverse dimension through the path wherein the variation in length of paths travelled by different portions of the liquid flowing through the path is small. It will be seen, therefore, that the shape of the non-circular cross-sectional area of the stream passing through the regenerator is immaterial as long as any particle thereof is kept within the maximum distance tolerated from the heating surface or medium. The non-circular area may be square, rectangular, cross-rectangular, triangular, trapezoidal, polygonal, but preferably elliptical. However, according to the terms of the invention at least one diameter or central minor axis of the non-circular cross-sectional area must be ¼'' to ¾'' in length for an unobstructed stream (i. e. as previously explained the diameter may be increased if a filler bar is employed). Thus, the greatest distance of any particle from a heating surface or a heating medium will be ⅛'' to ⅜''. In this manner the proper amount of heat is applied to the liquid stream, uniformly, at the proper time and for the proper duration. This correlation of conditions is conducive to the high yields of regenerated olefin.

Having described the invention in a manner so that it may be practiced by those skilled in the art, what is claimed is:

1. A process for the regeneration of a mono-olefin containing 2 to 6 carbon atoms per molecule from an acid extract thereof which comprises continuously passing the liquid extract downwardly at a linear velocity of 0.4 to 2.0 ft./sec. into one end of an externally heated non-cylindrical decomposition zone of 3 to 10 feet in length and ¼'' to ¾'' in central minor axis, maintaining the extract at a substantially uniform temperature between 130° C. and 295° C. during passage through the decomposition zone whereby the acid extract is decomposed to substantially a mixture comprising mono-olefin vapor, water vapor and liquid acid, continuously passing the total extract decomposition products from the other end of the decomposition zone into a disengaging zone and rapidly separating and removing said vapors from the liquid acid in the disengaging zone.

2. A process according to claim 1 in which the cross-sectional area of the stream is elliptical.

3. A process for the regeneration of a mono-olefin containing 2 to 6 carbon atoms per molecule from an acid extract thereof which comprises continuously passing the liquid extract downwardly at a linear velocity of 0.4 to 2.0 ft./sec. into one end of an externally heated elliptical decomposition zone of 3 to 10 feet in length and ¼'' to ¾'' in inner minor diameter, maintaining the extract at a substantially uniform temperature between 130° C. to 295° C. during passage through the decomposition zone whereby the extract is decomposed to substantially a mixture comprising mono-olefin vapor, water vapor and liquid acid, continuously passing the total extract decomposition products from the other end of the decomposition zone into a disengaging zone, rapidly separating and removing said vapors from the liquid acid in the disengaging zone, and recovering mono-olefin from said vapors.

4. A process according to claim 3 in which the extract is fed in a plurality of streams to a plurality of decomposition zones.

5. A process for the regeneration of a tertiary mono-olefin containing 4 to 6 carbon atoms per molecule from a sulfuric acid extract thereof which comprises continuously passing the liquid extract downwardly at a linear velocity of 0.4 to 2.0 ft./sec. into one end of an externally heated elliptical decomposition zone of 3 to 10 feet in length and ¼'' to ¾'' in inner minor diameter,

maintaining the extract at a substantially uniform temperature between 130° C. and 160° C. during passage through the decomposition zone whereby the extract is decomposed to substantially a mixture comprising tertiary mono-olefin vapor, water vapor and sulfuric acid, continuously passing the total extract decomposition products from the other end of the decomposition zone into a disengaging zone, rapidly separating and removing said vapors from the sulfuric acid in the disengaging zone, and recovering tertiary mono-olefin from said vapors.

6. A process for the regeneration of isobutylene from a sulfuric acid extract thereof containing 60–70 weight percent sulfuric acid which comprises diluting the extract with water until it contains 55–60 weight percent acid, continuously passing the diluted extract downwardly at a linear velocity of 0.4 to 1.2 ft./sec. into one end of an externally heated elliptical decomposition zone of 3 to 10 feet in length and ¼'' to ¾'' in inner minor diameter, maintaining the extract at a substantially uniform temperature between 140° C. and 155° C. during passage through the decomposition zone whereby the extract is decomposed to substantially a mixture comprising isobutylene vapor, water vapor and liquid sulfuric acid of 60–70 weight percent strength, continuously passing the total extract decomposition products from the other end of the decomposition zone into a disengaging zone, rapidly separating and removing said vapors from the liquid acid in the disengaging zone, and recovering isobutylene from said vapors.

7. A process for the regeneration of propylene from a sulfuric acid extract thereof containing 70–92 weight percent sulfuric acid which comprises diluting the extract with water until it contains 65–70 weight percent acid, continuously passing the diluted extract downwardly at a linear velocity of 0.4 to 1.2 ft./sec. into one end of an externally heated elliptical decomposition zone of 3 to 10 feet in length and ¼'' to ¾'' in inner minor diameter, maintaining the extract at a substantially uniform temperature between 165° C. and 278° C. during passage through the decomposition zone whereby the extract is decomposed to substantially a mixture comprising propylene vapor, water vapor and liquid sulfuric acid of 70–92 weight percent strength, continuously passing the total extract decomposition products from the other end of the decomposition zone into a disengaging zone, rapidly separating and removing said vapors from the liquid acid in the disengaging zone, and recovering propylene from said vapors.

8. A process for the regeneration of ethylene from a sulfuric acid extract thereof containing 93–98 weight percent sulfuric acid which comprises diluting the extract with water until it contains 85–90 weight percent acid, continuously passing the diluted extract downwardly at a linear velocity of 0.4 to 1.2 ft./sec. into one end of an externally heated elliptical decomposition zone of 3 to 10 feet in length and ¼'' to ¾'' in inner minor diameter, maintaining the extract at a substantially uniform temperature between 290° C. to 295° C. during passage through the decomposition zone whereby the extract is decomposed to substantially a mixture comprising ethylene vapor, water vapor and liquid sulfuric acid of 93–98 weight percent strength, continuously passing the total extract decomposition products from the other end of the decomposition zone into a disengaging zone, rapidly separating and removing said vapors from the liquid acid in the disengaging zone, and recovering ethylene from said vapors.

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