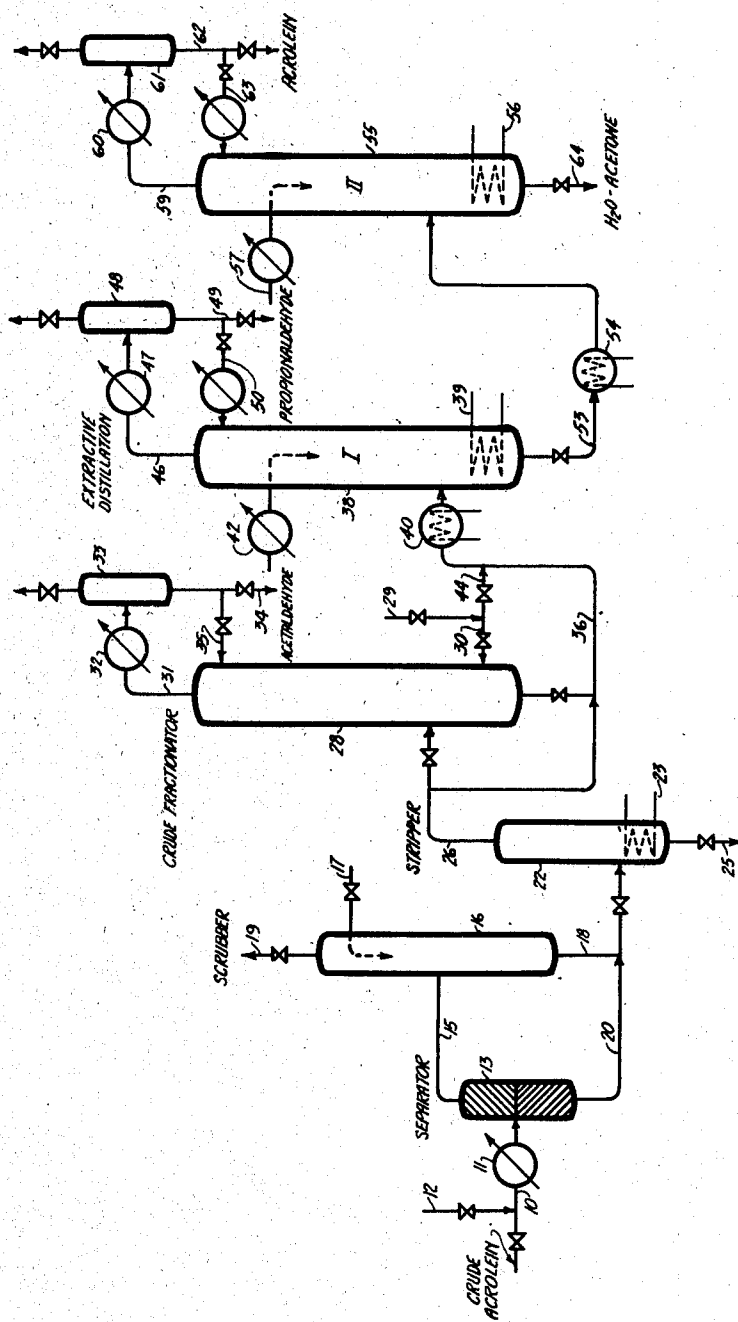


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REFINING AND CONCENTRATING CRUDE
UNSATURATED ALDEHYDES
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REFINING AND CONCENTRATING CRUDE
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This invention relates to the production of high purity unsaturated aliphatic aldehydes from hydrocarbon oxidation products comprising the unsaturated aldehydes in admixture with close boiling saturated carbonylic compounds inseparable therefrom by practical scale fractionating means. The invention relates more particularly to the separation of alpha-beta unsaturated aliphatic aldehydes in a state of high purity from mixtures comprising the unsaturated aldehydes in admixture with saturated aldehydes and/or ketones having the same number of carbon atoms as said unsaturated aldehydes. Still more particularly the invention relates to the production of acrolein in a state of high purity from mixtures comprising acrolein in admixture with propionaldehyde and/or acetone.

Production of the unsaturated aldehydes on a practical scale generally results in the obtaining of a crude product comprising the unsaturated aldehydes in admixture with substantial amounts of by-products unavoidably formed during the process. The ability to utilize the unsaturated aldehyde efficiently in many of its fields of application is often dependent upon the absence therein of any substantial amount of impurities. The large scale production of an unsaturated aldehyde of relatively high purity is, of necessity, limited to methods enabling the obtaining of a product comprising the unsaturated aldehyde in admixture with impurities which are readily separable therefrom by available practical scale separating means. Thus the production of acrolein from such starting materials as, for example, acetaldehyde and formaldehyde under carefully controlled conditions often enables the attainment of a product comprising the acrolein in admixture with impurities consisting essentially of acetaldehyde, formaldehyde and relatively high boiling organic materials. All of such impurities are readily separable from the acrolein on a practical scale by methods available heretofore comprising such steps as simple fractionation, water scrubbing, distillation and the like. Although acrolein of relatively high purity is often obtained by such methods these processes are generally handicapped by unavailability at sufficiently low cost of the starting materials. A particularly valuable source of the unsaturated aldehydes comprises the products obtained by the oxidation of the readily available hydrocarbons. It has recently been found that the readily available olefinic hydrocarbons can be

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converted efficiently to products consisting predominantly of unsaturated aldehydes such as, for example, the alpha-beta unsaturated aliphatic aldehydes, by catalytic oxidation in the presence of specific catalysts. Thus acrolein is obtained by the catalytic oxidation of propylene. The products obtained in such catalytic hydrocarbon oxidations, however, comprise besides the desired unsaturated aldehydes, saturated carbonylic compounds such as, saturated aldehydes and ketones inseparable therefrom on a practical scale by methods disclosed heretofore. The production of an alpha-beta unsaturated aliphatic aldehyde from the corresponding olefin, such as, for example, the production of acrolein from propylene results in the production of a product comprising the acrolein in admixture not only with readily separable impurities such as formaldehyde, acetaldehyde and high boiling material but also close boiling carbonylic compounds such as, for example, propionaldehyde and acetone, inseparable therefrom on a practical scale by separating means available heretofore. Inability to effect the efficient and yet substantially complete removal of close boiling carbonylic compounds from the unsaturated aldehydes has militated against any full realization of the substantial advantages inherent in the utilization of the readily available hydrocarbons as a source of these highly desirable and valuable compounds.

It is an object of the present invention to provide an improved process for the more efficient purification of the crude unsaturated aliphatic aldehydes obtained by the oxidation of hydrocarbons.

Another object of the invention is the provision of an improved process for the more efficient purification of crude alpha-beta unsaturated aliphatic aldehydes obtained by the oxidation of the corresponding olefinic hydrocarbon.

A more particular object of the invention is the provision of an improved process for the more efficient purification of the crude acrolein obtained by the catalytic oxidation of propylene.

A further object of the invention is the provision of an improved process for the more efficient separation of an aliphatic unsaturated aldehyde from admixture with saturated carbonylic compounds not readily separable therefrom by practical scale fractionating means.

Another object of the invention is the provision of an improved process for the more efficient separation of an alpha-beta unsaturated ali-

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phatic aldehyde from admixture with saturated carbonylic compounds having the same number of carbon atoms to the molecule.

Still another object of the invention is the provision of an improved process enabling the more efficient separation of an alpha-beta unsaturated aliphatic aldehyde from admixture with a saturated aliphatic aldehyde and/or ketone having the same number of carbon atoms to the molecule.

A particular object of the invention is the provision of an improved process enabling the more efficient separation of acrolein from mixtures comprising acrolein in admixture with propionaldehyde and/or acetone. Other objects and advantages of the invention will become apparent from the following detailed description thereof.

It has now been found that an unsaturated aldehyde, such as, for example, an alpha-beta unsaturated aliphatic aldehyde, is obtained in a high state of purity from the crude unsaturated aldehydes comprising it in admixture with saturated carbonylic impurities having boiling temperatures closely approximating that of the unsaturated aldehyde by a method of purification wherein the crude charge is subjected to two consecutive extractive distillations in the presence of a specific solvent. The process of the invention enables the efficient separation of the unsaturated aliphatic aldehyde from admixed saturated carbonylic impurities including saturated ketones and saturated aldehydes having the same number of carbon atoms to the molecule as the unsaturated aldehyde.

The process of the invention may be applied broadly to the separation of an unsaturated aldehyde from a mixture comprising it in admixture with saturated aldehydes and ketones having the same number of carbon atoms to the molecule as the unsaturated aldehyde regardless of the source of the mixture. Because of its ability to effect efficiently the substantially complete removal from an unsaturated aldehyde a plurality of close boiling saturated carbonylic impurities, such as saturated ketones and saturated aldehydes having the same number of carbon atoms to the molecule as the unsaturated aldehyde, the process of the invention is highly advantageous in the purification of the crude unsaturated aldehydes, such as the alpha-beta unsaturated aldehydes obtained by the oxidation of the corresponding hydrocarbons.

In accordance with the process of the invention, a crude alpha-beta unsaturated aliphatic aldehyde containing close boiling saturated carbonylic impurities comprising saturated aldehydes and ketones having the same number of carbon atoms to the molecule as the unsaturated aldehyde, such as, for example, crude acrolein obtained by the catalytic oxidation of propylene and containing propionaldehyde and acetone, is subjected to extractive distillation at a pressure of about atmospheric pressure or a higher pressure in the presence of a sufficient amount of water to maintain a single liquid phase in a first extractive distillation zone. In the first extractive distillation zone liquid bottoms comprising water and substantially all of the acrolein together with carbonylic impurities having the same number of carbon atoms to the molecule as acrolein and consisting essentially of acetone, are separated from a vapor overhead comprising saturated carbonylic impurities having the same number of carbon atoms to the molecule as acrolein and consisting essentially of propional-

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dehyde. Bottoms from the first extractive distillation zone are passed into a second extractive distillation zone wherein they are subjected to a second extractive distillation in the presence of at least sufficient amount of water to maintain a single liquid phase in the second extractive distillation zone. In the second extractive distillation zone liquid bottoms comprising water and impurities having the same number of carbon atoms to the molecule as acrolein and consisting essentially of acetone are separated from a vapor overhead consisting essentially of acrolein free from any substantial amount of saturated carbonylic impurities inseparable therefrom by practical scale methods employed heretofore.

In order that the invention may be more readily understood it will be described in detail herein in its application to the production of acrolein of high purity from crude acrolein obtained by the catalytic oxidation of propylene. Reference will be had to the accompanying drawings wherein the single figure illustrates more or less diagrammatically one form of apparatus suitable for executing the process of the invention.

When the alpha-beta unsaturated aliphatic aldehyde-containing mixture to be purified in accordance with the invention consists essentially of a mixture such as the effluence from a reaction zone wherein the unsaturated aldehyde is produced by oxidation of the corresponding hydrocarbon, a fraction consisting essentially of the desired unsaturated aldehyde and admixed carbonylic compounds having the same number of carbon atoms to the molecule as the unsaturated aldehyde is separated from the mixture and passed into the first extractive distillation zone. Referring to the drawings, a crude acrolein-containing mixture consisting essentially of the effluence from the reaction zone wherein it was produced by the catalytic oxidation of propylene, and optionally emanating directly from such reaction zone, is passed through line 10 into a separating zone. When the charge emanates directly from the reaction zone and is at an elevated temperature it is preferably passed through suitable cooling means, such as, for example, a cooler 11. Optionally additional cooling means comprising the addition of a quenching medium, such as water to the stream by means of valved line 12, may be employed.

The propylene oxidation product will comprise besides the crude acrolein containing the acrolein in admixture with acetaldehyde, acetone, propionaldehyde and water, certain amounts of formaldehyde, high boiling organic materials, and substantial amounts of normally gaseous materials. The normally gaseous materials will comprise unconverted propylene, some other low boiling hydrocarbons, and varying amounts of gaseous products such as nitrogen, carbon dioxide, carbon monoxide and the like.

Within separator 13, a liquid layer comprising crude acrolein, close boiling carbonylic impurities, formaldehyde, water, and high boiling organic material is separated from a gaseous fraction comprising the normally gaseous materials as well as substantial amounts of acrolein containing close boiling carbonylic impurities. The gaseous phase is passed from separator 13 through line 15 into a scrubbing zone. The scrubbing zone may comprise a scrubbing column 16, optionally containing suitable packing material, baffle plates, or the like. Within column 16 the charge thereto is brought into counter-

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current contact with a suitable scrubbing medium such as, for example, water, selectively dissolving or absorbing the acrolein. Water is introduced into the upper part of column 16 by means of valved line 17. Normally gaseous material comprising propylene and fixed gases is eliminated from column 16 by means of valved line 19. Acrolein in admixture with close boiling saturated impurities such as propionaldehyde, and acetone as well as acetaldehyde and formaldehyde is taken from the lower part of column 16 together with the scrubbing water by means of valved line 18. A superatmospheric pressure, for example, in the range of from about 50 to about 500 pounds, and preferably from about 150 to about 250 pounds is maintained in column 16 to assure substantially complete absorption of the acrolein. The temperature within column 16 may range, for example, from about 10° C. to about 30° C. Higher or lower temperatures may however be employed.

The liquid phase separated within separator 13 is taken therefrom through line 20 and combined with the rich scrubbing liquid passing through line 18. From line 18 the combined stream is introduced into a stripping zone. The stripping zone may comprise a suitable stripping column 22 provided with suitable heating means such as, for example, a closed coil 23. Within stripping column 22 a vapor fraction consisting essentially of acrolein in admixture with saturated carbonylic impurities comprising acetaldehyde, propionaldehyde and acetone as well as water, is separated from a liquid fraction consisting essentially of water, formaldehyde and high boiling organic material.

The liquid fraction is taken from stripping column 22 by means of valved line 25 and eliminated from the system. The vapor fraction is taken overhead from stripping column 22 by means of valved line 26.

The amount of saturated carbonylic impurities contained in the crude acrolein taken overhead from stripping column 22 through valved line 26 will vary considerably often depending upon the specific condition employed in producing the crude acrolein. In general the amount of close boiling carbonylic impurities contained in the crude acrolein passed through valved line 26 will not substantially exceed about 10% by weight of the acrolein. It is to be understood, however, that the invention is in no wise limited to the purification of a crude acrolein containing close boiling carbonylic impurities in any specific amount. The water content of the crude acrolein overhead from stripping column 22 will be at least equivalent to that of the acrolein-water azeotrope at the pressure of operation, at atmospheric pressure this is 2.7% by weight of water based on acrolein. The saturated carbonylic impurities will generally consist essentially of acetaldehyde, propionaldehyde and acetone in varying amounts.

The following table is illustrative of the composition of crude acrolein obtained by water scrubbing and stripping of oxidation products of propylene as herein described:

	Percent by weight
Acrolein	80 to 90
Acetaldehyde	3 to 10
Propionaldehyde	0.5 to 3
Acetone	1.0 to 5
High boiling organic material	1.0 to 2.0
Water	2.4 to 6.0

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It is seen that in addition to acetaldehyde the crude acrolein contains propionaldehyde and acetone in contaminating amounts. These saturated compounds are not only lower boiling and higher boiling respectively, than acrolein but have boiling temperatures closely approximating that of acrolein and therefore preclude their separation by ordinary practical scale fractionating means. It is apparent that the production of substantially pure acrolein from such a mixture by methods available heretofore, if feasible at all, necessitates the use of such a plurality of steps and operations of such complexity as to render its large scale application highly impractical. The reduction of its water content below the relatively large amount contained in the acrolein-water azeotrope normally obtained in fractionation would occasion the resort to additional complex and costly operative steps.

A study of the distillation of crude acrolein mixture in the presence of polar solvents revealed that whereas the relative volatility (alpha) for the separation of acrolein from acetone is approximately 1.12 in the absence of a solvent the presence of most polar solvents results in a reduction of the relative volatility value below unity, that is acrolein is the more polar compound and is taken off with the bottoms of the column. It was found, however, that water, quite contrary to the behavior of other polar solvents, instead of decreasing the relative volatility value for the separation of acrolein from acetone increased it markedly, and that extractive distillation of crude acrolein in the presence of water resulted in the taking off overhead of a fraction containing acrolein that was poorer in acetone.

The relative volatility value for the separation of propionaldehyde from acrolein in the absence of a solvent was found to be about 1.12 and therefore is separable to at least a substantial degree by fractionation. In the presence of substantial amounts of water it was found that the relative volatility value was increased somewhat attaining a value of about 1.4 in the presence of about 90% by weight of water at atmospheric pressure. It was found, however, that if a pressure above atmospheric is employed in the extractive distillation in the presence of a substantial amount of water the alpha value is increased still further. Thus, in the presence of 95% by weight of water at a superatmospheric pressure resulting in a 73.6° C. distillation temperature the relative volatility for propionaldehyde over acrolein was found to be 1.75. In the pressure of 83% water at a distillation temperature of 74° C. the relative volatility was found to be 1.55.

In the process of the invention, the crude acrolein is therefore subjected to a first extractive distillation to effect the substantially complete separation of its propionaldehyde content therefrom, and the resulting bottoms are subjected to a second extractive distillation to separate acrolein from the admixed acetone. Since acetaldehyde present in the crude acrolein will go to the bottoms of the first extractive distillation and reduce efficiency of separation in the second extractive distillation step, it is preferably removed from the crude acrolein prior to the first extractive distillation step of the process.

Acetaldehyde, having a boiling temperature substantially below that of acrolein, and a relative volatility of about 3.5 in the absence of a solvent, may be separated to at least a substantial degree from the crude acrolein by fractionation. The crude acrolein containing acetalde-

hyde is passed from line 26 into a fractionating zone. The fractionating zone may comprise a suitable column such as, for example, fractionating column 28. Acetaldehyde-containing crude acrolein from an external source may be introduced into the system through valve lines 29 and 30. Such crude acrolein introduced through line 29 may constitute a part or all of the crude acrolein charge to the system. Within column 28 the crude acrolein is subjected to fractionation to effect the separation of a vapor fraction comprising acetaldehyde from a liquid fraction comprising acrolein in admixture with acetone and propionaldehyde.

The vapor fraction is passed overhead from fractionator 28 through line 31, provided with cooling means 32, into accumulator 33. Liquid condensate comprising acetaldehyde is taken from accumulator 33 through valved line 34 and eliminated from the system. A part of the liquid passed through valved line 34 is passed through valved line 35 as reflux to the top of fractionator 28. Such fractionation enables the elimination of at least a substantial part of the acetaldehyde from the charge to the extractive distillation zone. Although the removal of acetaldehyde is shown to be carried out by fractionation in the illustrative description of the invention, other methods enabling the separation of the acetaldehyde from the crude acrolein may be employed.

The liquid fraction separated in fractionator 28 containing acrolein in admixture with propionaldehyde, acetone and water, and free of any substantial amounts of acetaldehyde is passed from a lower part of fractionator 28 through line 36 into a first extractive distillation zone. The first extractive distillation zone may comprise an extractive distillation column 38 provided with suitable heating means, such as, for example, a reboiler, or a closed heating coil 39. Line 36 is provided with suitable means enabling the introduction or removal of heat from the crude acrolein stream passing therethrough, such as, for example, an indirect heat exchanger 40. The charge may be introduced into the extractive distillation column 38 in the liquid, vapor or mixed phase. Within column 38 the crude acrolein is subjected to extractive distillation conditions in the presence of water introduced into the upper part of the column by means of valved line 42. Means for controlling the temperature of the water introduced into column 38 through valved line 42 such as, for example, an indirect heat exchanger is provided.

When the acrolein, comprising acrolein in admixture with one or more close boiling saturated carbonylic impurities such as, for example, acetone and propionaldehyde introduced into the system from any outside source by means of valved line 29, is free from any substantial amount of acetaldehyde, it is diverted through line 44 into line 40 leading into column 38.

Conditions within column 38 are controlled to maintain the pressure therein at substantially atmospheric pressure or a pressure above atmospheric. Thus the pressure within column 38 may be maintained in the range of, for example, from about atmospheric pressure to about 50 pounds absolute. While maintaining the desired pressure within the column other conditions are controlled to obtain an overhead comprising substantially all of the propionaldehyde originally present in the charge to the column. Under these conditions the temperatures within column 38 will generally be above about 60° C.

Essential to the attainment of the objects of the invention is the introduction into column 38 of sufficient water to maintain a single liquid phase throughout the column. The introduction of water into the column is controlled to maintain the water content of the total mixture therein at least equal to about 80% by weight.

Under the above-defined conditions, the crude acrolein is extractively distilled within column 38 with the separation of an overhead comprising close boiling carbonylic impurities consisting essentially of propionaldehyde, from liquid bottoms comprising water, acrolein and close boiling carbonylic impurities consisting essentially of acetone.

Overhead comprising the propionaldehyde is taken from column 38 through line 46 provided with cooler 47 and is passed into an accumulator 48. Propionaldehyde is drawn from accumulator 48 by means of valved line 49. A part of propionaldehyde is returned as reflux to the upper part of the column 38 by means of valved line 50.

Liquid bottoms consisting essentially of water, acrolein and acetone are passed from the lower part of column 38 through valved line 53 into a second extractive distillation zone. The second extractive distillation zone may comprise a column 55 equipped with suitable heating means such as, for example, a reboiler or a closed heating coil 56. Line 53 is provided with suitable means enabling the introduction or removal of heat from the stream passing therethrough such as, for example, an indirect heat exchanger 54. The charge may be introduced into the second extractive distillation zone in the liquid, vapor or mixed phase. Within column 55 the acrolein-containing charge is subjected to extractive distillation in the presence of water. Water required in addition to that contained in the charge to the column is introduced into the second distillation zone by means of valved line 57 equipped with suitable temperature controlling means such as, for example, an indirect heat exchanger. Within column 55 there is separated a vapor fraction consisting essentially of acrolein and a very small amount of water, from liquid bottoms comprising water and carbonylic impurities which are higher boiling than acrolein consisting essentially of acetone.

The pressure maintained within column 55 may be essentially that maintained within column 38. It is to be pointed out, however, that whereas a minimum pressure of substantially atmospheric is maintained within column 38 and the use of a superatmospheric pressure therein is preferred, a pressure of less than atmospheric may be employed in the column 55 comprised in the second distillation zone. In a preferred method of carrying out the process of the invention, the pressure within the column 38 is maintained in excess of atmospheric, and the pressure within column 55 is preferably maintained at atmospheric or subatmospheric pressures. Thus, a pressure in the range of from about 0.09 pounds absolute to about atmospheric pressure is preferably maintained within the column 55 comprised within the second extractive distillation zone of the process.

Sufficient water is at all times introduced into the second distillation zone to maintain a single liquid phase therein. Thus, the water content of the total mixture within the column 55 is maintained at about 80% by weight or higher.

Overhead, consisting essentially of acrolein, is taken from column 55 through valved line 59

provided with suitable cooling means, such as, for example, a cooler 60, and passed into an accumulator 61. Acrolein in a high state of purity, free from any substantial amount of carbonylic impurities, and containing only the small amount of water, equivalent to that of the acrolein-water azeotrope at the pressure of operation, is drawn from accumulator 61 by means of valved line 62 and eliminated from the system as a final product. A part of the acrolein drawn through line 62 is diverted through valved line 63 to the upper part of column 55 as reflux. Liquid bottoms from column 55 are drawn therefrom through valved line 64 and eliminated from the system. Bottoms thus withdrawn from column 64 may be passed to conventional separating means to separate carbonylics comprising acetone therefrom.

Treatment of crude acrolein, such as is obtained by the oxidation of hydrocarbons comprising propylene, in the process of the invention enables the separation of acrolein of a purity of 97% by weight. The acrolein thus obtained will generally comprise about 2.7% by weight of water. Removal of the water therefrom by further processing results in the obtaining of acrolein of a purity of 99.6% with a recovery of from about 95 to about 97% by weight of the acrolein originally present in the crude acrolein charge.

The efficiency with which acrolein is separated in a high state of purity from a crude acrolein obtained by the catalytic oxidation of propylene and comprising saturated carbonylic compounds having the same number of carbon atoms to the molecule as acrolein is illustrated by the following example.

Example I

A crude acrolein-containing mixture, obtained by the catalytic oxidation of propylene, is subjected to phase separation in a separator. The gaseous phase is scrubbed with water at a pressure of about 125 pounds gauge to recover crude-acrolein therefrom. The rich scrubbing water is combined with the liquid phase from the separator and subjected to distillation. Crude acrolein is separated as a vapor fraction from a liquid bottoms comprising water, formaldehyde and high boiling organic material. The crude acrolein thus obtained has the following composition:

	Weight per cent ¹
Acrolein	90.0
Acetaldehyde	6.0
Propionaldehyde	2.0
Acetone	2.0

¹ Water free basis (water content 3-6%).

The crude acrolein was freed of acetaldehyde by fractionation. The resulting crude acrolein-containing fractionator bottoms substantially free of acetaldehyde were subjected to a first extractive distillation in the presence of water under the following conditions:

Top column temperature °C.....	74° C.
Bottom column temperature °C.....	85° C.
Top column pressure.....	1436 mm.
Bottom column pressure.....	1586 mm.
Water content of column per cent by weight of total liquid on trays in column.....	83.0
Reflux ratio	59/1
Reflux/feed ratio	2.47

Composition of the crude-acrolein charge and the

products of the distillation are indicated in the following table:

	Crude acrolein feed to fractionation	Extractive Distillation		
		Feed Bottoms from Crude Fractionator	Overhead ¹	Bottoms ¹
	wt. %	wt. %		
Acrolein.....	90	95.7	47.0	97.8
Propionaldehyde.....	2.0	2.15	53.0	<0.2
Acetone.....	2.0	2.15	<0.1	2.24
Acetaldehyde.....	6.0	<0.2	<0.5	<0.2
Water.....	(3-6)	(3-6)	(3-5)	(92.7)

¹ Water-free basis.

The bottoms from the first extractive distillation now free of any substantial amount of propionaldehyde were subjected to a second extractive distillation in the presence of water under the following conditions:

Low pressure

Top column temperature °C.....	-9.7
Bottom column temperature °C.....	20
Kettle temperature °C.....	48
Top column pressure mm. Hg abs.....	50
Bottom column pressure mm. Hg abs.....	100
Water maintained in column in per cent by weight of total liquid on tray	83.0 above feed inlet 94.1 below feed inlet
Reflux to feed ratio (on water-free basis)	0.5

The composition of the overhead and bottoms of the column in per cent by weight are indicated in the following table:

	Overhead	Bottoms (Kettle)
Acrolein.....	99.6	9.0
Acetaldehyde.....	<0.1	-----
Propionaldehyde.....	<0.1	-----
Acetone.....	<0.1	91.0
Water.....	0.4	(99.87)

The process of the invention thus not only enables the large scale production of acrolein from crude acrolein, such as obtained for example by the catalytic oxidation of propylene, in a substantially higher state of purity than possible by practical scale methods used heretofore but makes possible its production with markedly improved efficiency.

Although the illustrative description of the invention has stressed the separation of acrolein from saturated carbonylic compounds the invention may be applied to the separation of unsaturated carbonylic impurities having boiling temperatures closely approximating that of the unsaturated aldehyde. The invention is applied with particular advantage to the separation of alpha-beta unsaturated aldehydes from the crude unsaturated aldehydes obtained by the oxidation of the corresponding hydrocarbons. Thus the invention may be applied to the separation of methacrolein from admixture with acetaldehyde, propionaldehyde, acetone, and isobutyraldehyde.

For the purpose of clarity, all parts of apparatus not essential to a complete description of the invention such as, for example, pumps, condensers, accumulators, etc., have been omitted from the drawing and the detailed description of the invention.

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The invention claimed is:

1. The process for separating acrolein in a high state of purity from a mixture comprising acrolein in admixture with propionaldehyde and acetone, which comprises extractively distilling said mixture in a first distillation zone at a minimum pressure of about atmospheric pressure in the presence of a sufficient amount of water to maintain substantially a single liquid phase in said distillation zone, separating a vapor fraction comprising propionaldehyde from liquid bottoms comprising acrolein and acetone substantially free of propionaldehyde in said first distillation zone, extractively distilling liquid bottoms separated in said first distillation zone in a second distillation zone at a maximum pressure of substantially atmospheric pressure in the presence of a sufficient amount of water to maintain substantially a single liquid phase in said second distillation zone, and separating a vapor fraction consisting essentially of acrolein free of any substantial amount of propionaldehyde and acetone from a liquid fraction comprising water and acetone in said second distillation zone.

2. The process for separating acrolein in a high state of purity from a mixture comprising acrolein in admixture with propionaldehyde and acetone, which comprises extractively distilling said mixture in a first distillation zone at a minimum pressure of about atmospheric pressure in the presence of a sufficient amount of water to maintain substantially a single liquid phase in said distillation zone, separating a vapor fraction comprising propionaldehyde from liquid bottoms comprising acrolein and acetone substantially free of propionaldehyde in said first distillation zone, extractively distilling liquid bottoms separated in said first distillation zone in a second distillation zone in the presence of a sufficient amount of water to maintain substantially a single liquid phase in said second distillation zone, and separating a vapor fraction consisting essentially of acrolein free of any substantial amount of propionaldehyde and acetone from a liquid fraction comprising water and acetone in said second distillation zone.

3. The process for separating acrolein in a high state of purity from a mixture comprising acrolein in admixture with propionaldehyde and acetone, which comprises extractively distilling said mixture in a first distillation zone at a pressure in the range of from about atmospheric to about 50 pounds absolute in the presence of a sufficient amount of water to maintain substantially a single liquid phase in said distillation zone, separating a vapor fraction comprising propionaldehyde from liquid bottoms comprising acrolein and acetone substantially free of propionaldehyde in said first distillation zone, extractively distilling liquid bottoms separated in said first distillation zone in a second distillation zone in the presence of a sufficient amount of water to maintain substantially a single liquid phase in said second distillation zone, and separating a vapor fraction consisting essentially of acrolein free from any substantial amount of propionaldehyde and acetone from a liquid fraction comprising water, and acetone in said second distillation zone.

4. The process for purifying crude acrolein-containing reaction products obtained by the oxidation of propylene, said reaction products comprising acrolein in admixture with normally gaseous hydrocarbons, formaldehyde, acetaldehyde, acetone, propionaldehyde and high boiling organic im-

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purities, which comprises separating a fraction consisting essentially of a crude acrolein comprising acrolein in admixture with propionaldehyde and acetone from said reaction products, extractively distilling said fraction in a first distillation zone at a minimum pressure of about atmospheric pressure in the presence of a sufficient amount of water to maintain substantially a single liquid phase in said distillation zone, separating a vapor fraction comprising propionaldehyde from liquid bottoms comprising acrolein and acetone substantially free of propionaldehyde in said first distillation zone, extractively distilling liquid bottoms separated in said first distillation zone in a second distillation zone at a maximum pressure of substantially atmospheric pressure in the presence of a sufficient amount of water to maintain substantially a single liquid phase in said second distillation zone, and separating a vapor fraction consisting essentially of acrolein free of any substantial amount of propionaldehyde and acetone from a liquid fraction comprising water and acetone in said second distillation zone.

5. The process for purifying crude acrolein-containing reaction products obtained by the oxidation of propylene, said reaction products comprising acrolein in admixture with normally gaseous hydrocarbons, formaldehyde, acetaldehyde, acetone, propionaldehyde and high boiling organic impurities, which comprises separating a fraction consisting essentially of a crude acrolein comprising acrolein in admixture with propionaldehyde and acetone from said reaction products, extractively distilling said fraction in a first distillation zone at a pressure in the range of from about atmospheric to about 50 pounds absolute in the presence of a sufficient amount of water to maintain substantially a single liquid phase in said distillation zone, separating a vapor fraction comprising propionaldehyde from liquid bottoms comprising acrolein and acetone substantially free of propionaldehyde in said first distillation zone, extractively distilling liquid bottoms separated in said first distillation zone in a second distillation zone in the presence of a sufficient amount of water to maintain substantially a single liquid phase in said second distillation zone, and separating a vapor fraction consisting essentially of acrolein free from any substantial amount of propionaldehyde and acetone from a liquid fraction comprising water, and acetone in said second distillation zone.

6. The process for separating acrolein in a high state of purity from crude acrolein comprising acrolein in admixture with saturated carbonylic compounds having the same number of carbon atoms to the molecule as acrolein, said saturated carbonylic compounds including compounds which are higher boiling than acrolein and compounds which are lower boiling than acrolein, which comprises extractively distilling said crude acrolein in a first distillation zone at a minimum pressure of about atmospheric pressure in the presence of a sufficient amount of water to maintain substantially a single liquid phase in said distillation zone, separating a vapor fraction comprising said lower boiling saturated carbonylic compounds from liquid bottoms comprising acrolein and said higher boiling saturated carbonylic compounds substantially free of said lower boiling saturated carbonylic compounds in said first distillation zone, extractively distilling liquid bottoms separated in said first distillation zone in a second extractive distillation zone

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at a maximum pressure of about atmospheric pressure in the presence of a sufficient amount of water to maintain substantially a single liquid phase in said distillation zone, and separating a vapor fraction consisting essentially of acrolein free of any substantial amount of saturated carbonylic compounds from a liquid fraction comprising water and said higher boiling saturated carbonylic compounds in said second distillation zone.

7. The process for separating acrolein in a high state of purity from crude acrolein comprising acrolein in admixture with saturated carbonylic compounds having the same number of carbon atoms to the molecule as acrolein, said saturated carbonylic compounds including compounds which are higher boiling than acrolein and compounds which are lower boiling than acrolein, which comprises extractively distilling said crude acrolein in a first distillation zone at a minimum pressure of about atmospheric pressure in the presence of a sufficient amount of water to maintain substantially a single liquid phase in said distillation zone, separating a vapor fraction comprising said lower boiling saturated carbonylic compounds from liquid bottoms comprising acrolein and said higher boiling saturated carbonylic compounds substantially free of said lower boiling saturated carbonylic compounds in said first distillation zone, extractively distilling liquid bottoms separated in said first distillation zone in a second extractive distillation zone in the presence of a sufficient amount of water to maintain substantially a single liquid phase in said distillation zone, and separating a vapor fraction consisting essentially of acrolein free of any substantial amount of saturated carbonylic compounds from a liquid fraction comprising water and said higher boiling saturated carbonylic compounds in said second distillation zone.

8. The process for the separation of an alpha methylene aldehyde having from three to four carbon atoms to the molecule in a high state of purity from a mixture comprising said alpha-methylene aldehyde in admixture with saturated carbonylic compounds having the same number of carbon atoms to the molecule as said alpha-methylene aldehyde, said saturated carbonylic compounds including compounds which are higher boiling and compounds which are lower boiling than said alpha-methylene aldehyde, which comprises extractively distilling said mixture in a first distillation zone at a minimum pressure of about atmospheric pressure in the presence of a sufficient amount of water to maintain substantially a single liquid phase in said distillation zone, separating a fraction comprising at least a substantial part of said lower boiling saturated carbonylic compounds from liquid bottoms comprising said alpha-methylene aldehyde and at least a substantial part of said higher boiling saturated carbonylic compounds in said first distillation zone extractively distilling liquid bottoms separated in said first dis-

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tillation zone in a second distillation zone in the presence of a sufficient amount of water to maintain substantially a single liquid phase in said second distillation zone, and separating a vapor fraction consisting essentially of said alpha-methylene aldehyde free from any substantial amount of saturated carbonylic compounds from a liquid fraction comprising water and said higher boiling saturated carbonylic compounds in said second distillation zone.

9. The process for separating an alpha methylene aldehyde having from three to four carbon atoms to the molecule in a high state of purity from a crude alpha-beta unsaturated aldehyde obtained by the oxidation of the corresponding olefin, said crude unsaturated aldehyde containing said alpha-methylene aldehyde in admixture with saturated carbonylic compound-containing impurities boiling through a relatively wide temperature range, which comprises separating a fraction consisting essentially of alpha-methylene aldehyde in admixture with saturated carbonylic compounds having the same number of carbon atoms to the molecule as said alpha-methylene aldehyde and which saturated carbonylic compounds include compounds higher boiling and compounds lower boiling than said alpha-methylene aldehyde, extractively distilling said fraction in a first distillation zone at a minimum pressure of about atmospheric pressure in the presence of a sufficient amount of water to maintain substantially a single liquid phase in said distillation zone, separating a vapor fraction comprising at least a substantial part of said lower boiling saturated carbonylic compounds from liquid bottoms comprising said alpha-methylene aldehyde and at least a substantial part of said higher boiling saturated carbonylic compounds in said first distillation zone, extractively distilling liquid bottoms separated in said first distillation zone in a second extractive distillation zone in the presence of a sufficient amount of water to maintain substantially a single liquid phase in said distillation zone, and separating a vapor fraction consisting essentially of said alpha-methylene aldehyde free of any substantial amount of saturated carbonylic compounds from a liquid fraction comprising water and said higher boiling saturated carbonylic compounds in said second distillation zone.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,179,991	Bright et al.	Nov. 14, 1939
2,198,651	Bludworth	Apr. 30, 1940
2,238,016	Downey	Apr. 8, 1941
2,261,704	Wagner	Nov. 4, 1941
2,283,911	Brant et al.	May 26, 1942
2,290,636	Deanesly	July 21, 1942
2,321,748	Hopkins	June 15, 1943