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(54) Titre : PURIFICATION DE 1,3-PROPANEDIOL PAR DISTILLATION
(54) Title: PURIFICATION OF 1,3-PROPANEDIOL BY DISTILLATION

(57) Abrégé/Abstract:
The present invention is a process for purification of 1,3-propanediol (PDO) by an inverted distillation sequence which comprises: (a) optionally removing water or other solvents from the crude 1,3-propanediol mixture; (b) distilling the crude 1,3-propanediol mixture under conditions which maximize the separation of components of the mixture which are heavier than 1,3-propanediol from the 1,3-propanediol and the components which are lighter than 1,3-propanediol; (c) drawing off a stream which contains at least most of the 1,3-propanediol and at least some of the components of the mixture which are lighter than 1,3-propanediol; and (d) distilling the stream of (c) to separate the 1,3-propanediol from components in the stream which are lighter than 1,3-propanediol and any residual components which are heavier than 1,3-propanediol.

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(54) Title: PURIFICATION OF 1,3-PROPANEDIOL BY DISTILLATION

(57) Abstract: The present invention is a process for purification of 1,3-propanediol (PDO) by an inverted distillation sequence which comprises: (a) optionally removing water or other solvents from the crude 1,3-propanediol mixture; (b) distilling the crude 1,3-propanediol mixture under conditions which maximize the separation of components of the mixture which are heavier than 1,3-propanediol from the 1,3-propanediol and the components which are lighter than 1,3-propanediol; (c) drawing off a stream which contains at least most of the 1,3-propanediol and at least some of the components of the mixture which are lighter than 1,3-propanediol; and (d) distilling the stream of (c) to separate the 1,3-propanediol from components in the stream which are lighter than 1,3-propanediol and any residual components which are heavier than 1,3-propanediol.

PURIFICATION OF 1,3-PROPANEDIOL BY DISTILLATION

Field of the Invention

This invention relates to the purification of 1,3-propanediol. More particularly, this invention relates to purification via distillation in a minimum of two steps, in which reactive heavy components are removed prior to one or more final distillation and purification steps, to allow efficient purification of PDO in the absence of reactive heavy components.

Background of the Invention

U.S. Patent 5,008,473 describes a process for the purification of 1,3-propanediol (PDO), especially when produced by hydration of acrolein with water, by extraction of the diol with cyclohexane. This process suffers from the disadvantages of only potentially removing turbidity from PDO and also not being specific to removal of components which may adversely affect color or purity of PDO and the property and performance of products made from PDO (such as polyesters).

U.S. Patent 5,527,973 describes a PDO purification process which comprises forming a solution of PDO in an acidic aqueous medium, adding a sufficient amount of base to the aqueous medium to form a basic solution having a pH greater than 7, heating the basic solution under conditions effective to distill a major portion of the water therefrom, and heating the basic solution under conditions effective to distill a major portion of the PDO therefrom to provide a PDO composition having a lower carbonyl content than the starting carbonyl-containing PDO composition. This process suffers from the disadvantages of requiring a number of acid-base cycles to obtain significant carbonyl and color body removal, thus generating significant byproduct salt,

and requiring a substantial capital investment or extending processing time requirements via repetitive batch cycle treatments.

World Patent Application WO 00/10953 also describes a process for the purification of PDO. The steps of this process comprise contacting PDO with an acid catalyst at a temperature above that required for impurities to react and below that required for extensive ether formation, and isolating purified PDO from impurities, reacted impurities, and the acid catalyst. This process suffers from the disadvantage of not removing specific ester or acid components which will lead to color bodies or color body precursors in final PDO product.

The normal method of purification of diols or other petrochemical products is a sequential distillation conducted in one or more columns, in which the lightest components (higher volatility) are removed first, followed by successive distillations to sequentially remove fractions ("cuts") of successively lower volatility (heavier) products and byproducts, as overhead or side-draw products including recovery of the desired product (in this case, PDO) as an overheaded or side draw product, and finally result in the production of a heavy components stream from the bottom of the final distillation step comprising components of low volatility. All components are thus separated and recovered in the order of their volatility. The distillation "steps" may be conducted batchwise in a single column, or semi-continuously in campaign mode using one or more continuous distillation columns with collection of bottoms for feed to a subsequent continuous distillation sequence, or in fully continuous manner in which multiple distillation columns are employed in series.

Quite surprisingly, this process cannot be used effectively with PDO because during distillation PDO and 3-

hydoxypropionic acid (3-HP acid - one of the impurities) react as water is removed forming a heavy di-hydroxy ester. The heavy ester has a volatility lower than PDO. However, as water is further removed from the product mixture, this component undergoes a dehydration reaction to form 3-hydroxypropyl acrylate, which is more volatile than PDO and thus travels up the column. For this reason, a pure PDO stream cannot be obtained from the distillation column because the light acrylate impurity is formed via reaction of heavy components in the column bottoms. This results in the "smearing" of this light acrylate component across the entire column, from bottom to top.

The present invention provides a distillation scheme for purification of PDO which overcomes the foregoing problem.

Summary of the Invention

The present invention is a process for purification of a crude PDO mixture in an inverted distillation sequence which comprises:

(a) optionally removing water or other solvents from the crude 1,3-propanediol mixture;

(b) distilling the crude 1,3-propanediol mixture under conditions which maximize the separation of components of the mixture which are heavier than 1,3-propanediol from the 1,3-proapanediol and the components which are lighter than 1,3-propanediol;

(c) drawing off a stream which contains at least most of the 1,3-propanediol and at least some of the components of the mixture which are lighter than 1,3-propanediol; and

(d) distilling the stream of (c) to separate the 1,3-propanediol from components in the stream which are lighter than 1,3-propanediol and any residual components which are heavier than 1,3-propanediol.

A small portion of the heavy components (components which are heavier and less volatile than PDO) may thus travel with the main PDO product stream to the downstream distillation column following the "bottoming step". The stream of (c) preferably contains a lower amount of components which are heavier than PDO than the mixture of (b) does, preferably no more than about 1% wt. In order to achieve a relatively color free PDO product, the PDO must be purified to the extent that less than about 10,000 ppm, preferably less than about 1,000 ppm, and most preferably less than about 100 ppm, of reactive heavy components that follow the PDO during separation of heavy ends from PDO in the "bottoming" step of the distillation sequence.

For a continuous process, it may be preferable that the heavy components (which can include reactive and non-reactive components) from the bottom of one or more subsequent distillation steps be recycled to the original "bottoming" distillation column. The reason for this is that the overall PDO recovery efficiency is best when there is only one final heavy component takeoff stream from the process.

The process of this invention can also be carried out by replacing one or more of the distillation columns with a flasher or evaporator which effects a single stage separation.

Brief Description of the Drawings

Figure 1 is a flow diagram of the process of this invention.

Figure 2 is a gas chromatographic analysis of the first pass distillation of Example 1.

Figure 3 is a gas chromatographic analysis of the second pass distillation of Example 2.

Detailed Description of the Invention

1,3-propanediol (PDO) is an intermediate in the production of polyesters for fibers and films. PDO may be made in a two-step process involving the catalyzed hydroformylation of ethylene oxide by reaction with synthesis gas, H_2/CO, to the intermediate 3-hydroxypropanal (HPA). The HPA is subsequently hydrogenated to form PDO. The initial hydroformylation process can be carried out at temperatures greater than 100°C and at high syngas pressures to achieve practical rates.

PDO can be made by other routes. For instance, there is a commercially used process which produces PDO by reaction of acrolein with water. Bio-based synthesis of PDO has been proposed, via direct fermentation of bio feedstocks, proceeding directly to PDO, or via production of 3-hydroxypropionic acid as an intermediate.

In the hydroformylation/hydrogenation process described above, crude PDO is readily produced via atmospheric distillation to remove water, trace solvent, and ethanol/propanol or other volatile coproducts. The PDO can, among many things, be used as a reactant in polyester polymerization. Further purification requires removal of color body precursors, including carbonyls, and monofunctional species which limit molecular weight in the polymerization of polytrimethylene terephthalate (PTT) from PDO. The degree of purification required was previously established via characterization of the finished polymer. This was difficult since many times the polymer was not made until months after the PDO was made.

Low carbonyl PDO (containing less than 1000 ppm "carbonyl" or carbonyl precursors) is difficult to produce from the hydroformylation process material described above. Alternate approaches to distillation, including absorption and/or treatment with an ion exchange resin, carbons,

zeolites, etc., liquid extraction, and extractive distillation, either do not reduce carbonyls to low levels, or require expensive separation equipment or purification materials. Rigorous hydrogenation to remove trace acetal or carbonyl color body precursors works well but requires a large capital investment in hydrogenation capability. The present invention was found to be economic and successful in producing polymer grade PDO.

The PDO purification scheme of the present invention solves the problems caused by "reactive distillation" in the first distillation column, resulting in the smearing of the acrylate impurity from top to bottom across the column. The formation of light 3-hydroxypropylacrylate from the heavy ester of 3-hydroxypropionic acid and PDO in the first distillation column necessitates the use of a second column to produce acrylate-free PDO, regardless of the number of theoretical stages employed.

The present invention can be used to purify PDO made by any of the above methods or any other method. If solvents other than water are used, these solvents are removed after reaction by any conventional means. If water is the solvent, then it is preferably removed in a drying apparatus, such as a distillation column, wherein the dried PDO is removed and becomes the feed stream for the purification process, specifically the "bottoming" distillation step of the present invention.

A conventional distillation may be broken down into any number of columns or batch steps, in which lightest or more highly volatile products are removed first, followed by removal of progressively lower volatility products or impurities. The process of this invention inverts the distillation sequence. The unconventional "bottoming" step of the present invention must be implemented in order to produce high purity PDO low in color body precursors.

This sequence is unconventional in that PDO is not removed sequentially according to its volatility. Rather, the product stream is "bottomed" (process conditions are selected to encourage the removal of a high percentage of the heavier components) to remove the heaviest components from the mixture before further distillation of the product (PDO) mixture to produce high purity PDO in a separate subsequent distillation step or distillation column.

"Bottoming" must be conducted in such a manner that a majority of 3-HP acid and esters of this acid of volatility lower than PDO are separated from a majority of the PDO product. The PDO stream thus produced may then be further distilled to high purity in the absence of reactions involving the acid and ester byproducts. The bottoming sequence should seek to remove heavy acid and acid-derived heavy impurities to less than about 1000 ppm, and preferably less than about 100 ppm, in the main PDO stream from the first distillation. Invariably, as a result of finite separation efficiencies in distillation, it will not be possible to separate all of the PDO from the heavy components containing acid and acid derivatives. Some PDO will therefore be "lost" to the heavy components stream. The total amount of heavy components plus residual PDO in the heavy components stream will depend on the selectivity of the reaction steps used to synthesize PDO. For an economic process the total amount of bottoms products will typically represent less than 20% by weight of the PDO product stream, and preferably less than 10%.

Figure 1 shows a general overview of the process. Crude PDO is fed as a mixture (stream 1) to column A. Some light components may be removed overhead as stream 2. Heavy components including reactive heavy components are removed as stream 4. PDO freed from reactive heavy components (stream 3) is fed to a second distillation step (column "B")

and separated from residual light (stream 5) and residual heavy (stream 7A) components, producing higher purity PDO product (stream 6). The heavy components from column "B" may optionally be fed back to column "A" (stream 7B) to improve recovery of PDO as described above.

Batch Process Distillation:

To implement the current invention in batch mode, crude PDO product is charged to a distillation column (column A). If desired, the crude PDO may be subjected to a preliminary light components removal step and/or water removal step. Distillation is conducted by applying heat to the bottom of the column to initiate boil up of the mixture. It is common practice to initially operate the column at atmospheric pressure or slightly above, for removal of the lightest (most volatile) components from the mixture, under conditions (pressure) where the vapors may be condensed to liquid upon removal from the top of the column, without requiring a refrigeration system to chill the vapor in order to liquefy.

Optionally, the initial distilled fractions may contain solvent and other light impurities or byproducts from the synthesis step. After removal of these light components as a separate fraction, the distillation is continued via continuing to apply heat to the column, and typically with application of vacuum to facilitate boil off of the progressively lower volatility components such as PDO. The overhead distillation fractions will contain substantial concentrations of PDO. These fractions are collected for subsequent distillation.

The "bottoming" distillation may be conducted at any temperature and pressure needed to distill PDO overhead from the heavy components stream. If the distillation is conducted at atmospheric pressure or slightly above (about 100 to about 130 kPa), the required temperature of the heavy

ends bottoms phase will be above about 200°C and as high as about 250°C. Additional degradation of PDO to byproduct impurities may occur under these conditions. It is therefore preferable to conduct a distillation under partial vacuum conditions in the column, with an absolute pressure of about 0.1 to about 30 kPa, and most typically about 1 to about 10 kPa, and a final bottoms temperature (for a batch process) of from about 140 to about 190°C, most typically about 150 to about 170°C. In general, lower absolute pressure (higher vacuum) leads to lower distillation bottoms temperature and reduced degradation or reaction of PDO product at the expense of higher vacuum equipment costs.

As the distillation proceeds, the PDO content of overhead fractions will diminish, leaving a bottoms fraction of heavy components. These components are discarded as the result of the "bottoming" step of the distillation sequence. Reactive components in the bottoms could otherwise prevent production of highly pure fractions of PDO (due to the above described formation of 3-hydroxypropyl acrylates).

After removal and isolation of the heavy components fraction, the various overhead distillate fractions containing substantial PDO are recombined, or fed separately to a subsequent distillation step, where the process is repeated. Since the heaviest components containing reactive heavy components are no longer present in significant concentrations, the distillation may be conducted in the normal manner. An initial fraction of light or volatile impurities will be produced, possibly in part as a result of the degradation of heavy components during the proceeding distillation step. After removal of light components, distillation cuts or fractions of higher purity PDO may be obtained. A bottoms fraction concentrated in moderately heavy impurities may again be obtained. However, this bottoms fraction from the subsequent distillation step after

"bottoming" will have substantially reduced concentrations of reactive heavy components or color body precursors, typically less than 1000 ppm, and ideally less than 100 ppm, of carbonyl or color body precursors.

If the desired PDO product purity is not obtained due to limitations in separation efficiency afforded by the particular distillation column chosen, the PDO-rich distillate cuts may be recombined and subjected to yet another distillation. The need for conducting a third distillation may in part result from incomplete separation of all reactive heavy components in the initial "bottoming" separation, or this may simply be desirable to effectively induce more stages for separation of other components difficult to separate from PDO.

Continuous Process Description

Figure 1 describes a typical implementation of a continuous distillation process embodying this invention. Crude PDO may optionally be subjected to one or more purification and/or distillation and/or drying steps to remove water or a portion of the light components before entering "bottoming column" "A" as stream 1. Heavy components, which may include reactive components 3-HP acid and/or the dihydroxyester formed upon esterification of 3-HP acid via PDO, are removed from the reaction mixture in the "bottoming step" stream 4. Additional light components may be optionally separated from PDO as stream 2, with PDO removed as stream 3. Alternately, both light components and PDO may be removed as a single distillation tops stream. In either case, the PDO stream is fed to the subsequent distillation step in column B.

PDO-rich streams from column A are fed to column B for further purification. Residual heavy components may be present and can be removed via bottoms stream 7A. This stream will contain substantially less of the reactive heavy

components than are present in the bottom of column A (stream 4). The heavy components stream may optionally be recycled to column A, as shown for stream 7B, to improve the overall recovery of PDO.

Light components are separated (stream 5) from PDO (stream 6) in column B. Alternately, both streams may be produced as an overhead distillate and routed to another column for separation of PDO from the light components. A portion of the light components in stream 5 may result from degradation of heavy components in the bottom of column A. 3-hydroxypropylacrylate is one such species. This reaction hinders production of high purity PDO from column A (stream 3) regardless of the number of theoretical stages obtained (a measure of distillation column separation efficiency) in column A. Given less than an infinite number of theoretical stages in column A, a portion of the light components appearing in stream 5 will also result from incomplete separation of light components appearing in stream 2 of column A.

The key element of operation of the first distillation column is that conditions are chosen to remove the maximum amount, hopefully virtually all, of the reactive heavy components via bottoms stream 4. The amount of heavy components that must removed will depend on selectivity of the PDO reaction synthesis step. Typically, this stream will include essentially all heavy reaction byproducts, which for an economic process will typically comprise less than 20% of the PDO product stream, and preferably less than 10% of the PDO product stream. The first column cannot be boiled too hard or else reactive heavy components will go over into the second distillation column and the undesirable heavy reactive impurities will contaminate the PDO leaving that column, and react further in the second column. Generally, the goal is to achieve a reactive heavy

components content in the PDO leaving the first column of less than about 10,000 parts per million, preferably less than about 1000 parts per million, and most preferably less than about 100 parts per million.

Invariably, some PDO will be "lost" with the heavy components bottoms stream 4 as, due to finite separation efficiency in distillation, it will not be possible to separate all PDO into the PDO product stream while maintaining all reactive heavy components in the bottoms heavy components stream. Typically, the amount of PDO lost with the heavy components stream will be less than 50% of the mass flowrate of this stream (for an economic process). The bottoms stream may be subjected to other purification steps (extraction, further distillation, hydrogenation) to recover some of this PDO.

EXAMPLES

Example 1

A crude aqueous intermediate stream comprising 27.5% 1,3-propanediol (PDO), with light and heavy reaction byproducts, was obtained via continuous ethylene oxide hydroformylation in a 3-liter pilot plant with isolation via water extraction. The sample was analyzed and determined to contain 0.3 wt% weak acid (3-hydroxypropionic acid) which was partially neutralized to pH 5.7 via addition of sodium hydroxide. A portion of the water was subsequently removed by continuous flash distillation on the pilot unit.

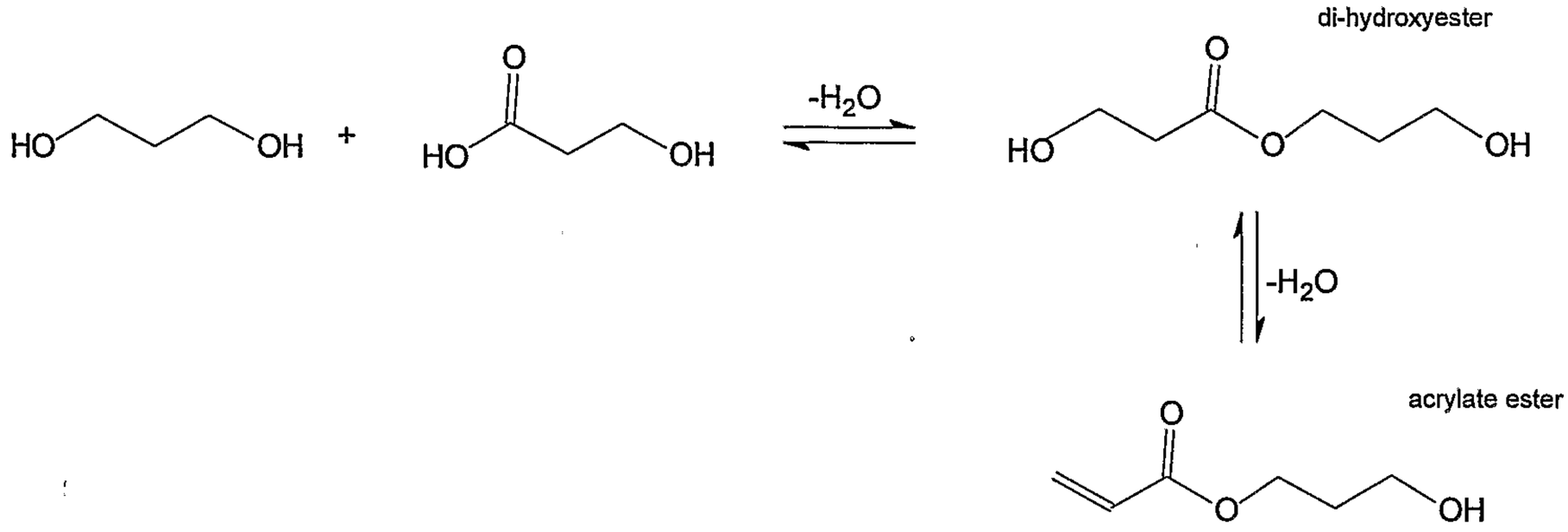
100.1 grams of this material was charged to a batch distillation assembly comprising a 1-inch diameter vacuum jacketed column packed with 27-inches of protruded metal distillation packing. An initial distillation was conducted at atmospheric pressure (760 mm Hg; 100 kPa) to remove the remainder of water and light ends, yielding 498 grams of product analyzed at 93 weight percent 1,3-PDO.

Vacuum was then applied to achieve 13 to 18 mm Hg pressure (1.7 to 2.4 kPa) and the distillation flask heated to 121 to 124°C to effect distillation and purification of PDO. The reflux ratio was adjusted to 10:1 return / take-off via a timed reflux splitter on the distillation head.

Distillation "cuts" (defined as fractions collected from the top of the distillation column) were isolated in 22 to 38 gram fractions and analyzed by gas chromatography (gc). Figure 2 shows the results which indicate recovery of 14.1 grams of cyclic acetal MW132 (2-hydroxyethyl-1,3-dioxane = condensation product of PDO with HPA), corresponding to an initial calculated concentration of 1.41 wt%, relative to a gc-measured value of 1.57 wt% (good agreement). This test revealed the MW 132 hydroxyacetal to be more volatile than PDO. Thus, acetal MW 132 was eliminated in early distillate cuts, producing PDO free of this impurity later in the distillation.

A new species not evident in the initial feed became dominant in later batch distillation cuts. Mass spectroscopy analysis indicated this to be 3-hydroxypropylacrylate. The mass balance of the amount of acrylate evident in distillation cuts indicated 0.8 wt% should have been present in the original feed to distillation. The gc trace showed no evidence for this species, however, with a resolution of less than 0.05 wt%. Despite increasing in successive batch distillation cuts (Figure 2), this species was also not evident at measurable concentrations in the distillation bottoms. This behavior indicates reactive formation of a volatile species during distillation. The acrylate probably formed from the known

3-hydroxypropionic acid present in the initial feed, following esterification with PDO and beta-hydroxy elimination:



Example 2: Redistillation of Overheaded Product

The residual heavy components were transferred out of the distillation flask followed by careful cleaning. "Cuts" or fractions of overheaded product were then reblended and charged back to the distillation pot, now free of heavy components. The distillation was conducted under the same conditions as before. However, both MW132 acetal and the acrylate impurity both diminished with successive overhead distillation cuts, such that a PDO fraction largely free of these impurities could now be obtained. This behavior is characteristic of a simple distillation to remove light impurities from a heavier PDO product, in the absence of reaction. The results are shown in Figure 3.

WE CLAIM:

1. A process for the purification of a crude mixture of 1,3-propanediol which comprises:

(a) optionally removing water or other solvents from the crude 1,3-propanediol mixture;

(b) distilling the crude 1,3-propanediol mixture under conditions which maximize the separation of components of the mixture which are heavier than 1,3-propanediol from the 1,3-propanediol and the components which are lighter than 1,3-propanediol;

(c) drawing off a stream which contains at least most of the 1,3-propanediol and at least some of the components of the mixture which are lighter than 1,3-propanediol; and

(d) distilling the stream of (c) to separate the 1,3-propanediol from the components in the stream which are lighter than 1,3-propanediol and any residual components which are heavier than 1,3-propanediol.

2. The process of claim 1 wherein the distillation is conducted batchwise with removal of the heavy components prior to distillation of the stream of (c).

3. The process of claim 1 wherein the distillation is conducted in a semi-continuous mode wherein the stream of (c) is stored for a period of time prior to step (d).

4. The process of claim 1 wherein the distillation is conducted in continuous mode with at least two distillation columns wherein components which are lighter than 1,3-propanediol are removed from the second or later distillation column in a distillation tops stream.

5. The process of claim 4 wherein a distillaton bottoms stream from at least the second distillation column is recycled to the first distillation column.

6. The process of claim 4 wherein a distillation tops stream from the second or later distillation column is distilled to recover additional 1,3-propanediol.

7. The process of any one of claims 1 through 6 wherein the stream of (c) contains a lower amount of components which are heavier than 1,3-propanediol than are contained in the mixture of (b).

8. The process of any one of claims 1 through 7 wherein the stream of (c) contains no more than about 1 weight percent of components which are heavier than 1,3-propanediol.

9. The process of any one of claims 1 through 8 wherein the stream of (c) contains no more than about 1000 ppm of components which are heavier than 1,3-propanediol.

10. The process of any one of claims 1 through 9 wherein one or more of the distillation columns is replaced by a flasher or an evaporator.

FIG.1

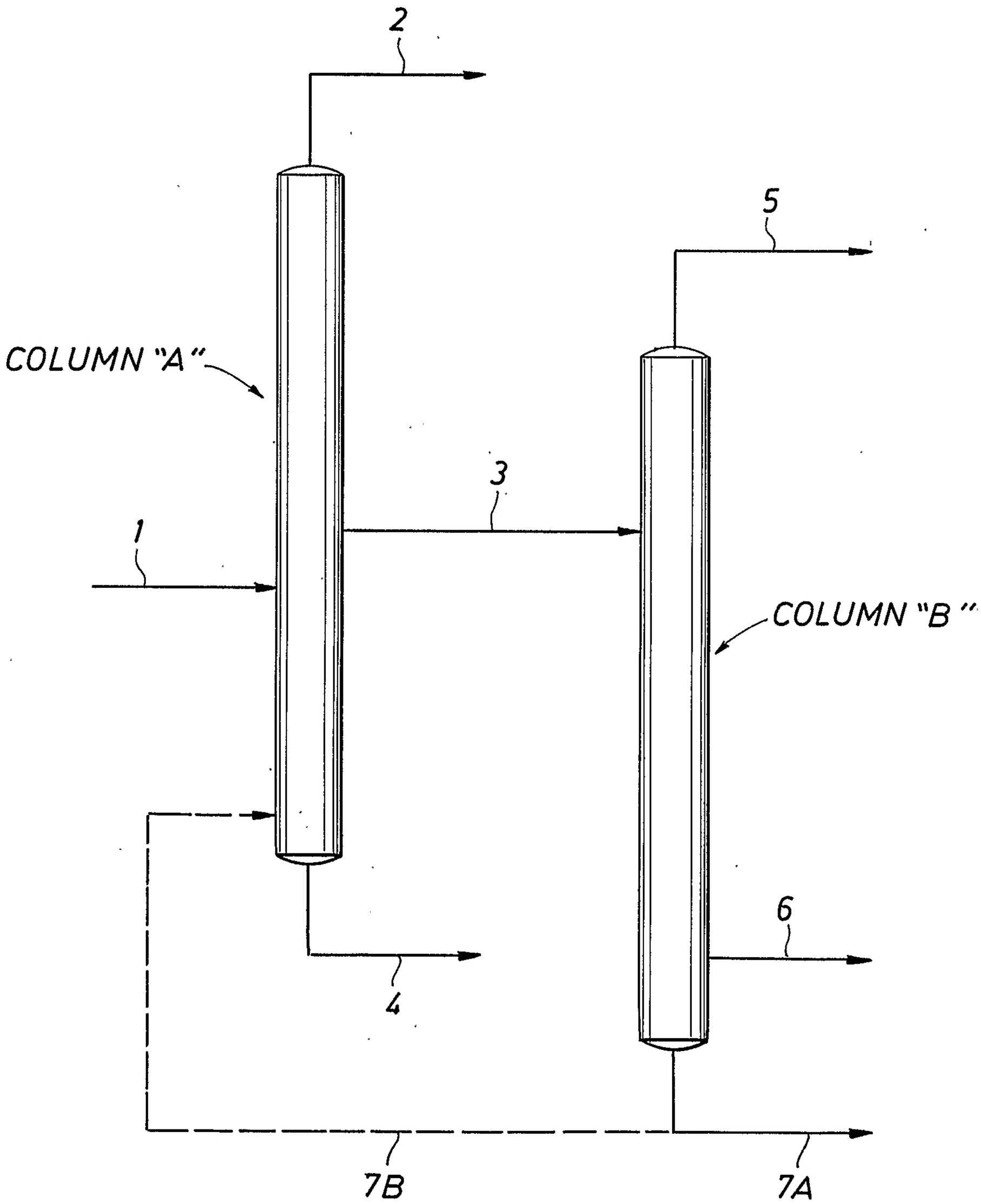


FIG. 2

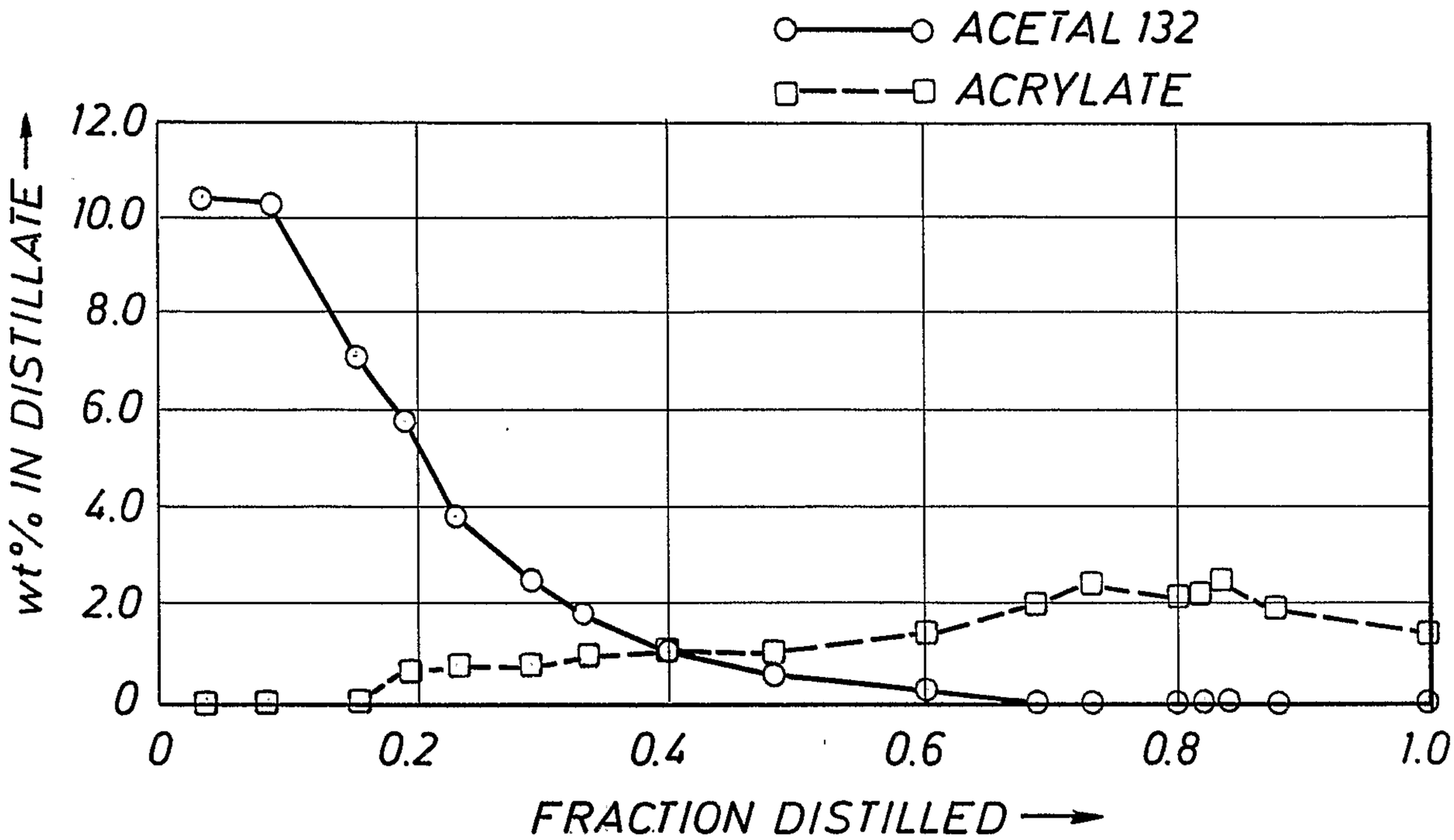
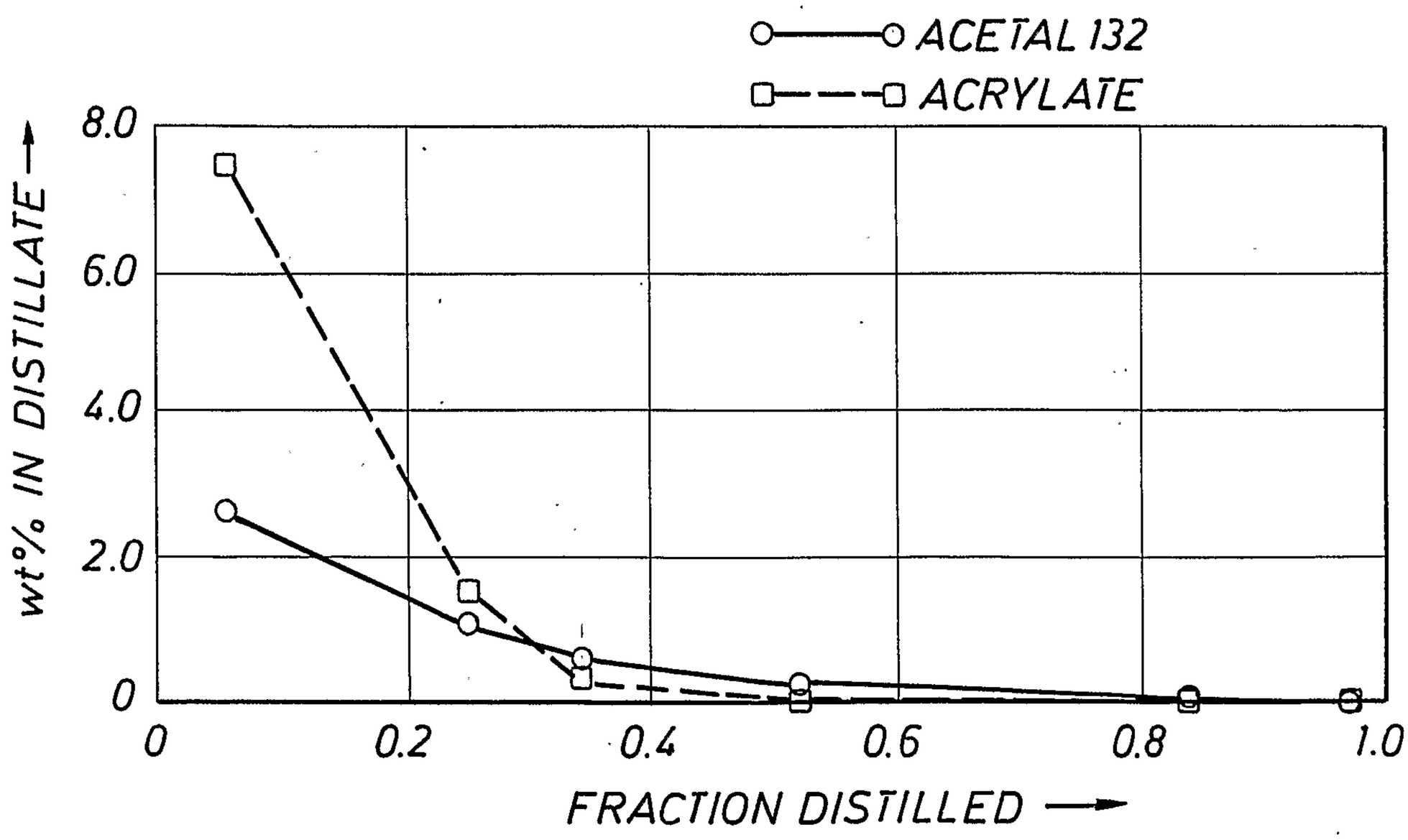

ACETAL 132
ACRYLATE
12.0
10.0
8.0
6.0
4.0
2.0
0
wt% IN DISTILLATE
0
0.2
0.4
0.6
0.8
1.0
FRACTION DISTILLED

FIG. 3


ACETAL 132
ACRYLATE
8.0
6.0
4.0
2.0
0
wt% IN DISTILLATE
0
0.2
0.4
0.6
0.8
1.0
FRACTION DISTILLED