

Claims:

1. A process for preparing an α,β -unsaturated C₃-C₆ carboxylic acid of greater than 98% by weight purity, which comprises the steps of:
 - a. oxidatively dehydrogenating a saturated C₃-C₆ carboxylic acid in a reactor to produce a first product stream comprising an α,β -unsaturated C₃-C₆ carboxylic acid and the saturated carboxylic acid wherein the weight ratio of the α,β -unsaturated to the saturated carboxylic acid is greater than about 0.2;
 - b. fractionally distilling the first product stream in a distillation unit to produce:
 - (1) an overhead stream wherein the weight ratio of the α,β -unsaturated to the saturated carboxylic acid is less than that in the first product stream and
 - (2) a bottoms stream wherein the weight ratio of the α,β -unsaturated to the saturated carboxylic acid is greater than that in the first product stream;
 - c. feeding the overhead stream into the reactor;
 - d. feeding the bottoms stream into a crystallization unit;
 - e. melt crystallizing the bottoms stream in the crystallization unit one or more times to produce
 - (1) a second product stream comprising greater than about 98% by weight, preferably greater than about 99.9% by weight, of the α,β -unsaturated carboxylic acid; and
 - (2) one or more mother liquor streams comprising greater than about 80% by weight of the α,β -unsaturated carboxylic acid; and
 - f. feeding the one or more mother liquor streams into the distillation unit.
2. A process as claimed in claim 1 wherein:
 - a. the weight ratio of the α,β -unsaturated to the saturated carboxylic acid in the overhead stream is less than about 0.5; and
 - b. the weight ratio of the α,β -unsaturated to the saturated carboxylic acid in the bottoms stream is greater than about 5.
3. A process as claimed in claim 2, wherein:
 - a. the weight ratio of the α,β -unsaturated to the saturated carboxylic acid in the overhead stream is less than about 0.1; and
 - b. the weight ratio of the α,β -unsaturated to the saturated carboxylic acid in the bottoms stream is greater than about 9.

~~4. A process as claimed in any preceding claim, wherein the step of melt crystallizing comprises:~~

- ~~i. crystallizing from about 50% by weight to about 70% by weight of the bottoms stream;~~
- ~~ii. separating the mother liquor stream;~~
- ~~iii. melting from about 5% by weight to about 50% by weight of the crystals to produce a second mother liquor stream;~~
- ~~iv. separating the second mother liquor stream from the remaining crystals;~~
- ~~v. optionally melting the remaining crystals and repeating steps i-iv, wherein melted remaining crystals are used in lieu of the bottoms stream, a number of times sufficient to obtain greater than 98% by weight of the α,β -unsaturated carboxylic acid in the remaining crystals.~~

5. A process as claimed in claim 4, wherein the mother liquor and the second mother liquor are combined prior to feeding to the fractional distillation column.

~~6. A process as claimed in any preceding claim, wherein the first product stream is dehydrated prior to fractional distillation.~~

1 X A process for preparing an α,β -unsaturated C₃ - C₆ carboxylic acid of greater than about 98% by weight purity, which comprises the steps of:

- a. oxidatively dehydrogenating a saturated C₃-C₆ carboxylic acid in a reactor to produce a first product stream comprising an α,β -unsaturated C₃-C₆ carboxylic acid and the saturated carboxylic acid wherein the weight ratio of α,β -unsaturated to saturated carboxylic acid is greater than about 15;
- b. feeding the first product stream into a crystallization unit;
- c. melt crystallizing the first product stream in the crystallization unit one or more times to produce;
 - (1) a second product stream comprising greater than about 98% by weight, preferably greater than 99.9% by weight, of the α,β -unsaturated carboxylic acid; and
 - (2) one or more mother liquor streams comprising greater than about 80% by weight of the α,β -unsaturated carboxylic acid;
- d. feeding the one or more mother liquor streams into a distillation unit;

- e. fractionally distilling the one or more mother liquor streams in the distillation unit ~~under conditions wherein the vapor pressure of the α,β -unsaturated C_5 - C_6 carboxylic acid is less than the vapor pressure of the saturated C_5 - C_6 carboxylic acid~~ to produce;
- (1) an overhead stream and
 - (2) a bottoms stream ;
- f. feeding the overhead stream into the reactor; and
- g. feeding the bottoms stream into the melt crystallizer.

- 2 ~~8~~ A process as claimed in claim ¹~~7~~, wherein the step of melt crystallizing comprises:
- i. crystallizing from about 50% by weight to about 70% by weight of the first product stream;
 - ii. separating the mother liquor stream;
 - iii. melting from about 5% by weight to about 50% by weight of the crystals to produce a second mother liquor stream;
 - iv. separating the second mother liquor streams from the remaining crystals;
 - v. feeding the mother liquor stream and the second mother liquor stream to the fractional distillation column;
 - vi. optionally melting the remaining crystals and repeating steps i-v, wherein the melted remaining crystals are used in lieu of the first product stream, a number of times sufficient to obtain greater than 98% by weight of the α,β -unsaturated carboxylic acid content in the remaining crystals.

- 3 ~~9~~ A process as claimed in claim ²~~8~~, wherein the mother liquor stream and the second mother liquor stream are combined prior to feeding to the fractional distillation column.

- 4 ~~10~~ A process as claimed in any ^{one} of claims ^{1 63}~~7 to 9~~, wherein the weight ratio of the α,β -unsaturated to the saturated carboxylic acid in the overhead stream is less than about 0.5, preferably less than about 0.1.

- 5 ~~11~~ A process as claimed in any ^{one the preceding} of claims ^{1 to 19}~~4 to 10~~, wherein the first product stream is dehydrated prior to melt crystallization.

~~12~~⁶ A process as claimed in any preceding claim, wherein the saturated carboxylic acid is selected from propionic, butanoic, and isobutyric acids, and is preferably isobutyric acid.

~~13~~² A process as claimed in any preceding claim, wherein means for holding material are incorporated in the lines connecting the distillation unit and the crystallization unit.

~~14. A process for preparing acrylic acid of greater than 98% by weight purity which comprises the steps of:~~

- a. oxidatively dehydrogenating propionic acid in a reactor to produce a first product stream comprising acrylic acid and propionic acid wherein the ratio of acrylic acid to propionic acid is greater than about 0.2;
- b. fractionally distilling the first product stream in a distillation unit under conditions wherein the vapor pressure of acrylic acid is greater than the vapor pressure of propionic acid to produce
 - (1) an overhead stream wherein the ratio of acrylic acid to propionic acid is greater than that in the first product stream and
 - (2) a bottoms stream wherein the ratio of acrylic acid to propionic acid is less than that in the first product stream;
- c. feeding the overhead stream into a crystallization unit;
- d. feeding the bottoms stream into the reactor;
- e. melt crystallizing the overhead stream in the crystallization unit one or more times to produce
 - (1) a second product stream comprising greater than about 98%, preferably greater than about 99.9%, by weight of acrylic acid; and
 - (2) one or more mother liquor streams comprising greater than about 80% by weight of acrylic acid; and
- f. feeding the one or more mother liquor streams into the distillation column.

15. The process of Claim 14, wherein the first product stream is dehydrated prior to fractional distillation.

16. A process as claimed in claim 14 or claim 15, wherein means for holding material are incorporated in the lines connecting the distillation unit and the crystallization unit.

~~17~~⁸ A process for preparing acrylic acid of greater than about 98% by weight purity, which comprises the steps of:

- a. oxidatively dehydrogenating propionic acid in a reactor to produce a first product stream comprising acrylic acid and propionic acid wherein the ratio of acrylic to propionic acid is greater than about 15;
- b. feeding the first product stream into a crystallization unit;
- c. melt crystallizing the first product stream in the crystallization unit one or more times to produce;
 - (1) a second product stream comprising greater than about 98%, preferably greater than about 99.9%, weight of acrylic acid, and
 - (2) one or more mother liquor streams comprising greater than about 80% by weight of the acrylic acid;
- d. feeding the one or more mother liquor streams into a distillation unit;
- e. fractionally distilling the one or more mother liquor streams in the distillation unit under conditions wherein the vapor pressure of acrylic acid is greater than the vapor pressure of propionic acid to produce
 - (1) an overhead stream and
 - (2) a bottoms stream;
- f. feeding the bottoms stream into the reactor; and
- g. feeding the overhead stream into the melt crystallizer

~~9~~⁸ A process as claimed in claim ~~17~~⁸, wherein the first product stream is dehydrated prior to melt crystallization.

~~10~~⁸ A process as claimed in claim ~~17~~⁸ or claim ~~18~~⁹, wherein means for holding material are incorporated in the lines connecting the distillation unit and the crystallization unit.

~~11~~²⁸ An α,β -unsaturated C₃-C₆ carboxylic acid whenever prepared by a process as claimed in any preceding claim.