(57) **Abstract:** A process for the oxidation of a $C_2$ to $C_4$ alkane to produce the corresponding alkene and carboxylic acid which process comprises separation of the alkene from a mixture of the alkene, the alkane and oxygen by absorption in a metallic salt solution, and recovery of an alkene-rich stream from the metallic salt solution. Integrated processes for the production of alkyl carboxylate and alkenyl carboxylate, which processes comprise oxidation of a $C_2$ to $C_4$ alkane to produce the corresponding alkene and carboxylic acid, separation of the alkene from a mixture of the alkene, the alkane and oxygen by absorption in a metallic salt solution, and recovery of an alkene-rich stream from the metallic salt solution for use in production of alkyl carboxylate or alkenyl carboxylate.

Claims:

1. A process for the oxidation of a $C_2$ to $C_4$ alkane to produce the corresponding alkene and carboxylic acid which process comprises the steps

(a) contacting in an oxidation reaction zone, an alkane, molecular oxygen-containing gas, optionally the corresponding alkene and optionally water, in the presence of at least one catalyst active for the oxidation of the alkane to the corresponding alkene and carboxylic acid, to produce a first product stream comprising alkene, carboxylic acid, alkane, oxygen and water;

(b) separating in a first separation means at least a portion of the first product stream into a gaseous stream comprising alkene, alkane and oxygen and a liquid stream comprising carboxylic acid;

(c) contacting said gaseous stream with a solution of a metallic salt capable of selectively chemically absorbing the alkene to produce a chemically absorbed alkene-rich liquid stream;

(d) recovering an alkene-rich stream from the metallic salt solution.

2. An integrated process for the production of an alkyl carboxylate which process comprises the steps :

(a) contacting in an oxidation reaction zone, an alkane, molecular oxygen-containing gas, optionally the corresponding alkene and optionally water, in the presence of at least one catalyst active for the oxidation of the alkane to the corresponding alkene and carboxylic acid, to produce a first non-flammable product stream comprising alkene, carboxylic acid, alkane, oxygen and water;

(b) separating in a first separation means at least a portion of the first product stream into a gaseous stream comprising alkene, alkane and oxygen and a liquid stream comprising carboxylic acid;

(c) contacting at least a portion of said gaseous stream with a solution of a metallic salt capable of selectively chemically absorbing the alkene to produce a chemically absorbed alkene-rich liquid stream;

(d) recovering an alkene-rich stream from the metallic salt solution and;

(e) contacting in a second reaction zone at least a portion of said alkene-rich stream from step (d), and a carboxylic acid, in the presence of at least one catalyst active for the production of alkyl carboxylate to produce said alkyl carboxylate,

3. An integrated process for the production of an alkenyl carboxylate which process comprises the steps:

(a) contacting in an oxidation reaction zone, an alkane, molecular oxygen-containing gas, optionally the corresponding alkene and optionally water, in the presence of at least one catalyst active for the oxidation of the alkane to the corresponding alkene and carboxylic acid, to produce a first non-flammable product stream comprising alkene, carboxylic acid, alkane, oxygen and water;

(b) separating in a first separation means at least a portion of the first product stream into a gaseous stream comprising alkene, alkane and oxygen and a liquid stream comprising carboxylic acid;

(c) contacting at least a portion of said gaseous stream with a solution of a metallic salt capable of selectively chemically absorbing the alkene to produce a chemically absorbed alkene-rich liquid stream;

(d) recovering an alkene-rich stream from the metallic salt solution and;

(e) contacting in a second reaction zone at least a portion of said alkene-rich stream obtained in step (d), a carboxylic acid and a molecular oxygen-containing gas, in the presence of at least one catalyst active for the production of alkenyl carboxylate to produce said alkenyl carboxylate.

4. The process according to claim 3, wherein, in step (e), said alkene-rich stream is fed to the second reaction zone as one or more streams, together with optional additional alkene.

5. The process according to claim 4, wherein the additional alkene may be fresh alkene and/or recycled alkene from the second reaction zone and/or a portion of the

kane/alkene stream from the oxidation reaction zone.

6. The process according to any one of claims 3 to 5, wherein the concentration of alkene (optional additional alkene feed and alkene-rich stream feed) fed to the second reaction zone is at least 50 mol % of the total feed to the second reaction zone.

7. The process according to claim 6 wherein the concentration of alkene is least 60 mol% of the total feed to the second reaction zone.

8. The process according to claim 6 or claim 7 wherein the concentration of alkene is up to 85 mol% of the total feed to the second reaction zone.

9. The process according to any one of claims 3 to 8, wherein the molecular oxygen-containing gas used in the second reaction zone for the production of alkenyl carboxylate comprises unreacted molecular oxygen-containing gas from step (a) and/or additional molecular oxygen-containing gas.

10. The process according to claim 9, wherein the additional molecular oxygen-containing gas is oxygen.

11. The process according to any one of claims 3 to 10, wherein at least some of the molecular oxygen-containing gas is fed independently to the second reaction zone from the alkene and carboxylic acid reactants.

12. The process according to any one of claims 3 to 11, wherein the carboxylic acid introduced in to the second reaction zone comprises carboxylic acid produced from the oxidation reaction zone.

13. A process according to any one of the preceding claims, wherein the alkane is selected from the group consisting of $C_2$ to $C_4$ alkanes and mixtures thereof.

14. A process according to any one of the preceding claims, wherein the alkane is ethane, the corresponding alkene is ethylene and the corresponding carboxylic acid is acetic acid.

15. A process according to any one of the preceding claims, wherein the molecular oxygen-containing gas in step (a) is oxygen.

16. The process according to any one of the preceding claims, wherein the concentration of the molecular oxygen-containing gas (as fresh feed and/or recycle) is from greater than 0 to 20 mol % of the total feed, including recycles, to the oxidation reaction zone.

17. The process according to any one of the preceding claims, wherein the

concentration of alkene (as fresh feed and/or recycle component) is from 0 to 50 mol % of the total feed, including recycles, to the oxidation reaction zone.

18. The process according to claim 17, wherein the concentration of alkene is from 1 to 20 mol % of the total feed to the oxidation reaction zone.

19. The process according to any one of the preceding claims, wherein the concentration of water (as fresh feed and/or recycle component) is from 0 to 50 mol % of the total feed, including recycles, to the oxidation reaction zone.

20. The process according to claim 19, wherein the concentration of water is from 0 to 25 mol % of the total feed to the oxidation reaction zone.

21. The process according to any one of the preceding claims, wherein the alkene and water are co-fed into the oxidation reaction zone.

22. The process according to any one of the preceding claims, wherein the alkene and water are used in a ratio of 1 : 0.1-250 by weight.

23. A process according to any one of the preceding claims, wherein the concentration of oxygen present in the gaseous stream from the first separation means is at least 0.1 mol%.

24. A process according to claim 23, wherein the concentration of oxygen present in the gaseous stream from the first separation means is at least 0.2 mol%.

25. A process according to claim 24, wherein the concentration of oxygen present in the gaseous stream from the first separation means is 0.1 to 10 mol%.

26. A process according to any one of the preceding claims, wherein the first separation means is a membrane separation unit, condensing unit or a distillation unit.

27. A process according to claim 26, wherein the separation means employed is a condenser.

28. The process according to any one of the preceding claims, wherein the alkene is ethylene and the metal salt capable of selectively chemically absorbing the alkene comprises chromium, copper (I), manganese, nickel, iron, mercury, silver, gold, platinum, palladium, rhodium ,ruthenium, osmium, molybdenum, tungsten or rhenium.

29. The process according to claim 28, wherein the metallic salt comprises silver or copper (I).

30. The process according to claim 29, wherein the metallic salt is a silver salt.

31. The process according to claim 30, wherein the silver salt is silver nitrate or

ver fluoroborate.

32. The process according to claim 29, wherein the metallic salt is copper (I) acetate, copper (I) nitrate or copper (I) sulphate.

33. The process according to any one of the preceding claims, wherein the metal solution is aqueous or comprises an organic nitrogen-containing compound.

34. The process according to any one of the preceding claims, wherein the contacting of the gaseous stream from the first separation means with the metallic salt solution is carried out in an absorber column.

35. The process according to claim 34, wherein the metallic salt solution comprising the metal salt/alkene complex is removed from the base of the absorber column, and alkane and oxygen are removed as an overhead stream from the absorber column.

36. The process according to claim 35, wherein the alkane and oxygen containing gas stream is fed as one or more streams to the oxidation reaction zone together with additional alkane.

37. The process according to claim 36, wherein, prior to being fed to the oxidation reaction zone, the alkane and oxygen containing stream is separated into separate alkane and oxygen gas streams.

38. The process according to claim 36 or claim 37, wherein the additional alkane is fresh alkane and/or unreacted alkane from the oxidation reaction zone which has been recycled after the first separation means to the oxidation reaction zone.

39. The process according to any one of claims claim 36 to 38, wherein the alkane/oxygen stream and the additional alkane are introduced into the oxidation reaction zone together either as separate feed streams or as a single feed stream comprising both the alkane/oxygen and the additional alkane.

40. The process according to any one of the preceding claims, wherein the alkene-rich stream is recovered from the metallic salt solution complex by heat, reduced pressure or by a combination thereof.

41. The process according to claim 40, wherein the solution is subjected to a reduced pressure such that the complex decomposes to release the alkene.

42. The process according to any one of the preceding claims, wherein the alkene-rich stream comprises at least 50% alkene.

43. The process according to claim 42, wherein the alkene-rich stream comprises at

least 90% alkene.

44. The process according to any one of the preceding claims, wherein, the gaseous stream from the first separation means, prior to being contacted with the metallic salt solution, is treated to remove components selected from the group consisting of carbon dioxide and oxygenates.

45. An integrated process for the production of vinyl acetate which process comprises the steps:

(a) contacting in an oxidation reaction zone, ethane, molecular oxygen-containing gas, optionally ethylene and optionally water, in the presence of at least one catalyst active for the oxidation of ethane to ethylene and acetic acid, to produce a first non-flammable product stream comprising ethylene, acetic acid, ethane, oxygen and water;

(b) separating in a first separation means at least a portion of the first product stream into a gaseous stream comprising ethylene, ethane and oxygen and a liquid stream comprising acetic acid;

(c) contacting at least a portion of said gaseous stream with a solution of a metallic salt capable of selectively chemically absorbing ethylene to produce a chemically absorbed ethylene-rich liquid stream;

(d) recovering an ethylene-rich stream from the metallic salt solution and;

(e) contacting in a second reaction zone at least a portion of said ethylene-rich stream obtained in step (d), acetic acid and a molecular oxygen-containing gas, in the presence of at least one catalyst active for the production of vinyl acetate to produce vinyl acetate.

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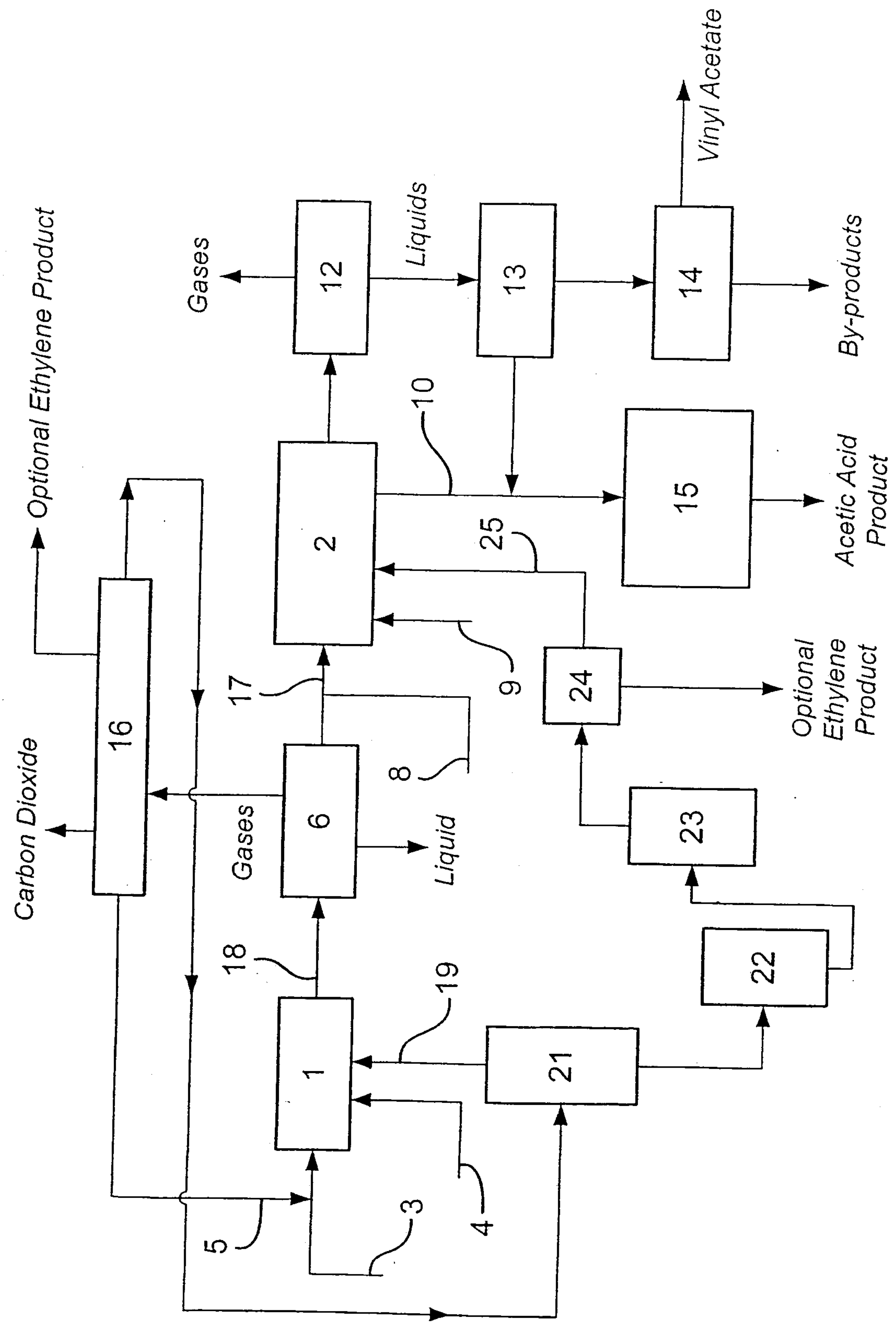
Optional Ethylene Product
Carbon Dioxide
16
Gases
6
Liquid
Gases
12
Liquids
13
14
Vinyl Acetate
By-products
2
15
Acetic Acid Product
24
Optional Ethylene Product
23
22
21
1
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The present invention relates to a process for the oxidation of a $C_2$ to $C_4$ alkane.

The present invention relates to the separation of alkenes from gas mixtures comprising said alkenes, alkanes and oxygen and, in particular, to the separation of ethylene from a mixture of ethylene, ethane and oxygen by absorption in a metallic salt solution.

The present invention also relates to the use of the separation process in (a) hydrocarbon oxidation processes such as the oxidation of a $C_2$ to $C_4$ alkane to produce the corresponding alkene and carboxylic acid and (b) in integrated processes in which the alkene and carboxylic acid produced from a hydrocarbon oxidation process are further used as reactants.

Ethylene and acetic acid may be produced by the catalytic oxidation of ethane. In a typical oxidation process to produce ethylene and acetic acid, ethane, oxygen and optionally ethylene and/or water are introduced into a reactor. The reactants are contacted with an oxidation catalyst such as a molybdenum/niobium/vanadium containing catalyst and react to produce an outlet stream comprising ethylene ( either as product or unreacted feed), acetic acid, unreacted ethane and unreacted oxygen. The outlet stream is removed from the reactor, condensed and separated into a gaseous stream and a liquid stream. The gaseous stream comprising ethane, ethylene and oxygen may be further purified to obtain ethylene therefrom. The liquid stream comprising acetic acid and water may be further purified.

It is known that the separation of ethylene from hydrocarbons such as ethane may be carried out by distillative processes such as cryogenic distillation and adsorption techniques such as pressure swing adsorption and reactive adsorption. In addition,