produced in the methanol synthesis process.

In processes for the co-production of acetic acid and dimethyl ether, the presence of methyl formate in one or both of the methanol and methyl acetate feedstocks is undesirable as it results in the generation of formic acid which is difficult to separate from acetic acid by conventional fractional distillation techniques owing to the closeness of their boiling points. Instead more complex extractive distillation methods have been employed to achieve acetic acid product purities. Complex methods of this type for the separation of formic acid from acetic acid are described in, for example US 4,692,219 and US 5,227,029.

Thus, there remains a need for a process for the co-production of acetic acid and dimethyl ether from methanol and methyl acetate in which the purity of acetic acid is improved, and in particular a process in which acetic acid product has a reduced content of formic acid.

Accordingly, in one aspect, the present ~~invention~~ disclosure provides a process for the co-production of acetic acid and dimethyl ether which process comprises:

(a) purifying a mixture of dimethyl ether, methanol, water and methyl formate by:

(i) feeding the mixture of dimethyl ether, methanol, water and methyl formate to a distillation column;

(ii) distilling the feed mixture of dimethyl ether, methanol, water, formic acid and methyl formate to generate a heads stream depleted in methyl formate as compared to the feed mixture, a base stream depleted in methyl formate as compared to the feed mixture and comprising methanol and water and a sidedraw stream enriched in methyl formate as compared to the feed mixture;

(iii) withdrawing from the column the sidedraw stream enriched in methyl formate at a point above the feed point of the feed mixture to the column.

(b) feeding at least part of the base stream comprising methanol and water together with methyl acetate to a dehydration-hydrolysis reaction and dehydrating methanol and hydrolysing methyl acetate therein in the presence of at least one solid acid catalyst to produce a crude reaction product comprising acetic acid and dimethyl ether;

Claims:

1. A process for the co-production of acetic acid and dimethyl ether which process comprises:

(a) purifying a mixture of dimethyl ether, methanol, water and methyl formate by:

(i) feeding the mixture of dimethyl ether, methanol, water and methyl formate to a distillation column;

(ii) distilling the feed mixture of dimethyl ether, methanol, water, formic acid and methyl formate to generate a heads stream depleted in methyl formate as compared to the feed mixture, a base stream depleted in methyl formate as compared to the feed mixture and comprising methanol and water and a sidedraw stream enriched in methyl formate as compared to the feed mixture;

(iii) withdrawing from the column the sidedraw stream enriched in methyl formate at a point above the feed point of the feed mixture to the column.

(b) feeding at least part of the base stream comprising methanol and water together with methyl acetate to a dehydration-hydrolysis reaction and dehydrating methanol and hydrolysing methyl acetate therein in the presence of at least one solid acid catalyst to produce a crude reaction product comprising acetic acid and dimethyl ether;

(c) recovering acetic acid and dimethyl ether from the crude reaction product.

2. A process according to claim 1 in which process the feed mixture to the distillation column comprising dimethyl ether, methanol, water and methyl formate is obtained by

(I) dehydrating a methanol feed comprising predominantly methanol together with small amounts of methyl formate to form a dehydration product comprising dimethyl ether, water, methanol, formic acid and a reduced amount of methyl formate;

(II) separating formic acid from the dehydration product to form a mixture comprising dimethyl ether, methanol, water and methyl formate.

3. A process according to claim 1 or claim 2 wherein in step (a) the sidedraw stream enriched in methyl formate is withdrawn from the column as a liquid.

4. A process according to any one of claims 1 to 3 wherein in step (a) the sidedraw

stream enriched in methyl formate is withdrawn from the distillation column at or near the point of maximum concentration of methyl formate within the column.

5. A process according to any one of claims 1 to 4 wherein in step (a) the distillation column has at least 3 theoretical stages below the feed point of the feed mixture to the column.

6. A process according to any one of claims 1 to 5 wherein in step (a) the feed mixture has a methyl formate content of >0 to 0.5 mol%.

7. A process according to any one of claims 1 to 6 wherein in step (a) the distillation column is operated at a pressure of from 10 to 30 barg, a heads temperature of 40 to 90 °C and at a reflux ratio in the range 1 to 5.

8. A process according to any one of claims 1 to 7 wherein in step (a) the methyl formate content of the base stream is 0.05 mol% or less.

9. A process according to any one of claims 1 to 8 wherein in step (b) methyl acetate is present as a component of the base stream from the distillation column and the base stream or part thereof, comprising methanol, water and methyl acetate is fed to the dehydration-hydrolysis reaction.

10. A process according to any one of claims 1 to 9 wherein in step (b) the crude reaction product comprising acetic acid and dimethyl ether has a formic acid content of 500 ppm or less.

11. A process according to any one of claims 1 to 10 wherein in step (c) dimethyl ether recovered from the crude reaction product comprises methyl formate and at least part of the recovered dimethyl ether is returned as a feed to the distillation column in step (a).

12. A process according to any one of claims 2 to 11 wherein the methanol feed to step (I) comprises 50 to 99 mol% and >0 to 1 mol% methyl formate.

13. A process according to any one of the preceding claims wherein the dehydration step (I) is carried out in the presence of at least one solid acid catalyst and wherein the at least one solid acid catalyst is a Brønsted acid catalyst selected from one or more of heteropolyacids and salts thereof and aluminosilicate zeolites.

14. A process according to any one of claims 2 to 13 wherein dehydration step (I) is conducted as a vapour phase process.

15. A process according to any one of claims 2 to 14 wherein the separation step (II) is carried out by distillation.

16. A process according to claim 15 wherein the distillation is carried out in a single distillation column which distillation column has at least 10 theoretical stages and is operated at a pressure of 5 to 30 barg and at a heads temperature of from 120 to 180 °C.

17. A process according to any one of the preceding claims which further comprises step (a^1) in which at least a portion of the sidedraw stream withdrawn from the distillation column in step (a) and comprising methyl formate, dimethyl ether and one or more of methanol and water is supplied as feed to a further distillation column and distilled therein to withdraw from the distillation column a sidedraw stream enriched in methyl formate as compared to the feed mixture, a heads stream comprising dimethyl ether and a base stream comprising one or more of methanol and water.

18. A process according to claim 17 wherein the sidedraw stream comprises the majority of methyl formate present in the feed to the column and is withdrawn as a vapour stream.

19. A process according to claim 17 or claim 18 wherein the distillation column in step (a^1) is operated at 0.1 to 1 barg lower pressure than the distillation column of step (a).

20. A process according to any one of the preceding claims wherein the process is operated as a continuous process.

Claims:

1. A process for the co-production of acetic acid and dimethyl ether which process comprises:

(a) purifying a mixture of dimethyl ether, methanol, water and methyl formate by:

(i) feeding the mixture of dimethyl ether, methanol, water and methyl formate to a distillation column;

(ii) distilling the feed mixture of dimethyl ether, methanol, water, formic acid and methyl formate to generate a heads stream depleted in methyl formate as compared to the feed mixture, a base stream depleted in methyl formate as compared to the feed mixture and comprising methanol and water and a sidedraw stream enriched in methyl formate as compared to the feed mixture;

(iii) withdrawing from the column the sidedraw stream enriched in methyl formate at a point above the feed point of the feed mixture to the column.

(b) feeding at least part of the base stream comprising methanol and water together with methyl acetate to a dehydration-hydrolysis reaction and dehydrating methanol and hydrolysing methyl acetate therein in the presence of at least one solid acid catalyst to produce a crude reaction product comprising acetic acid and dimethyl ether;

(c) recovering acetic acid and dimethyl ether from the crude reaction product.

2. A process according to claim 1 in which process the feed mixture to the distillation column comprising dimethyl ether, methanol, water and methyl formate is obtained by

(I) dehydrating a methanol feed comprising predominantly methanol together with small amounts of methyl formate to form a dehydration product comprising dimethyl ether, water, methanol, formic acid and a reduced amount of methyl formate;

(II) separating formic acid from the dehydration product to form a mixture comprising dimethyl ether, methanol, water and methyl formate.

3. A process according to claim 1 or claim 2 wherein in step (a) the sidedraw stream enriched in methyl formate is withdrawn from the column as a liquid.

4. A process according to any one of claims 1 to 3 wherein in step (a) the sidedraw

stream enriched in methyl formate is withdrawn from the distillation column at or near the point of maximum concentration of methyl formate within the column.

5. A process according to any one of claims 1 to 4 wherein in step (a) the distillation column has at least 3 theoretical stages below the feed point of the feed mixture to the column.

6. A process according to any one of claims 1 to 5 wherein in step (a) the feed mixture has a methyl formate content of >0 to 0.5 mol%.

7. A process according to any one of claims 1 to 6 wherein in step (a) the distillation column is operated at a pressure of from 10 to 30 barg, a heads temperature of 40 to 90 °C and at a reflux ratio in the range 1 to 5.

8. A process according to any one of claims 1 to 7 wherein in step (a) the methyl formate content of the base stream is 0.05 mol% or less.

9. A process according to any one of claims 1 to 8 wherein in step (b) methyl acetate is present as a component of the base stream from the distillation column and the base stream or part thereof, comprising methanol, water and methyl acetate is fed to the dehydration-hydrolysis reaction.

10. A process according to any one of claims 1 to 9 wherein in step (b) the at least one solid acid catalyst is at least one Brønsted acid catalyst selected from one or more of heteropolyacids and salts thereof and aluminosilicate zeolites.

11. A process according to any one of claims 1 to 10 wherein in step (b) the dehydration-hydrolysis is carried out as a vapour phase process.

12. A process according to any one of claims 1 to 11 wherein in step (b) the crude reaction product comprising acetic acid and dimethyl ether has a formic acid content of 500 ppm or less.

13. A process according to any one of claims 1 to 12 wherein in step (c) dimethyl ether recovered from the crude reaction product comprises methyl formate and at least part of the recovered dimethyl ether is returned as a feed to the distillation column in step (a).

14. A process according to any one of claims 2 to 13 wherein the methanol feed to step (I) comprises 50 to 99 mol% and >0 to 1 mol% methyl formate.

15. A process according to any one of the preceding claims wherein the dehydration step (I) is carried out in the presence of at least one solid acid catalyst and wherein the at least one solid acid catalyst is a Brønsted acid catalyst selected from one or more of

heteropolyacids and salts thereof and aluminosilicate zeolites.

16. A process according to claim 15 wherein the Brønsted acid catalyst is a zeolite which zeolite has a 2-dimensional or 3-dimensional channel system and possesses at least one channel which has a 10-membered ring.

17. A process according to claim 16 wherein the zeolite having a 2-dimensional or 3-dimensional channel system and possessing at least one channel which has a 10-membered ring is a zeolite selected from zeolites of framework type FER, MFI, HEU and NES.

18. A process according to any one of claims 2 to 17 wherein dehydration step (I) is conducted as a vapour phase process.

19. A process according to any one of claims 2 to 18 wherein the separation step (II) is carried out by distillation.

20. A process according to claim 19 wherein the distillation is carried out in a single distillation column which distillation column has at least 10 theoretical stages and is operated at a pressure of 5 to 30 barg and at a heads temperature of from 120 to 180 °C.

21. A process according to any one of the preceding claims which further comprises step (a^1) in which at least a portion of the sidedraw stream withdrawn from the distillation column in step (a) and comprising methyl formate, dimethyl ether and one or more of methanol and water is supplied as feed to a further distillation column and distilled therein to withdraw from the distillation column a sidedraw stream enriched in methyl formate as compared to the feed mixture, a heads stream comprising dimethyl ether and a base stream comprising one or more of methanol and water.

22. A process according to claim 22 wherein the sidedraw stream comprises the majority of methyl formate present in the feed to the column and is withdrawn as a vapour stream.

23. A process according to claim 21 or claim 22 wherein the distillation column in step (a^1) is operated at 0.1 to 1 barg lower pressure than the distillation column of step (a).

24. A process according to any one of the preceding claims wherein the process is operated as a continuous process.