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Paper B(Ch)

Chemistry

This paper comprises:

*	Patent application	2012/B(Ch)/EN/1-7
*	Communication (including Annex 1 with the originally filed claims)	2012/B(Ch)/EN/8-10
*	Document 1	2012/B(Ch)/EN/11-15
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*	Letter from the applicant	2012/B(Ch)/EN/18-19

Patent Application

Process and apparatus for making vinyl cyanide and acetonitrile

[001] The invention relates to processes and apparatus for making vinyl cyanide and acetonitrile.

[002] Vinyl cyanide is a well-known chemical intermediate. Vinyl cyanide is made by the reaction of propylene, ammonia and oxygen in the presence of an iron (III) catalyst such as iron (III) chloride, $FeCl_3$. The reaction is:

$$2CH_3CH{=}CH_2 + 2NH_3 + 3O_2 \rightarrow 2CH_2CHCN + 6H_2O$$

[003] It has now been found that if a copper (II) catalyst is used instead of an iron (III) catalyst the by-products of the reaction include significant amounts of acetonitrile.

[004] Acetonitrile has the chemical formula CH_3CN. Acetonitrile is also a well-known chemical intermediate. The price of acetonitrile can be very variable. It would be particularly useful to be able to produce varying amounts of acetonitrile as a by-product of another process so that, when prices are high, large amounts of acetonitrile can be produced but, in times of low prices, the plant would be occupied making other profitable materials.

[005] It has further been found that the yield of acetonitrile can be increased by adding carboxylic acid to the reactants before they contact the catalyst. The carboxylic acid is usually added as an aqueous solution. The concentration of the carboxylic acid is 1-30 carbon mol. % of the reactants. No effect is observed at concentrations below 1 carbon mol. % and no reaction occurs if more than 30 carbon mol. % of carboxylic acid is present. The higher the concentration of carboxylic acid the higher is the concentration of acetonitrile in the reaction product. The addition of more than 15 carbon mol. % of carboxylic acid, however, makes the reaction too slow to be economically viable. Carbon mol. % is the molar percentage of the carbon-containing compounds present. The carbon compounds that may be present include propylene, vinyl cyanide, acetonitrile, carbon dioxide and one or more carboxylic acids.

[006] According to the invention there is therefore provided a process for producing acetonitrile and vinyl cyanide comprising contacting a mixture containing propylene, ammonia and an oxygen-containing gas with a copper (II) catalyst at a temperature of from 200 to 350°C.

[007] According to the invention there is further provided an apparatus for producing acetonitrile and vinyl cyanide, the apparatus comprising:

i. a reactor for holding a reaction bed,
ii. means for heating the reaction bed in the reactor,
iii. at least one conduit for inputting reactants to the reactor,
iv. a conduit allowing materials to exit the reactor and enter
v. a spray tower for spraying water onto the materials exiting the reactor,
vi. a cooling tower for condensing the vinyl cyanide and acetonitrile exiting from the spray tower and
vii. a distillation tower for separating vinyl cyanide and acetonitrile from the condensate obtained in the cooling tower.

[008] The reactants are propylene (C_3H_6), ammonia and an oxygen-containing gas such as air, and optionally a carboxylic acid. It is not essential to use air. Oxygen-enriched air, pure oxygen or other oxygen-containing gases can be used. The presence of inert gases such as nitrogen from air does not reduce the yield. Inert gases make the process less thermally efficient since the inert gases must be heated. The carboxylic acid must be acetic acid or formic acid. The use of other carboxylic acids results in a reduced yield of acetonitrile and vinyl cyanide. It is essential that the product contains at least 80 carbon mol. % of acetonitrile and vinyl cyanide. Preferably the copper (II) catalyst comprises copper (II) chloride ($CuCl_2$) or copper (II) nitrate ($Cu(NO_3)_2$) but other salts can be used. The catalyst is in granule or powder form. The particle size is unimportant.

[009] Although not essential, the reactants are usually present at about stoichiometric levels. Commercially however, it is important to add the reactants at stoichiometric levels. This can be done, as is usual in industrial chemistry, using commercial systems such as EZE-KHEM ™ from Eze-Khem LLC.

[010] Figure 1 shows a schematic view of an apparatus according to the invention.

[011] Oxygen-containing gas such as air (A) is passed into the apparatus by conduit 1. A mixture (B) of propylene and ammonia enter the apparatus by conduit 2. To reduce the risk of explosion the oxygen-containing gas is usually kept separate from the propylene until the reactants enter the reactor.

[012] The reactants are passed into reactor 3 which contains a bed of the catalyst temperature of from 200 to 350°C. If the temperature is less than 200°C then too much propylene remains in the product. If the temperature is greater than 350°C then excessive oxidation occurs and too much carbon dioxide is formed instead of the intended products. The reaction products comprise vinyl cyanide, acetonitrile, carbon dioxide and acetic acid together with unreacted propylene.

[013] The reaction products exiting the catalyst bed are passed to a spray tower 4 by conduit 5 and contacted with a water spray (C). The water spray cools the reaction products. The acetic acid dissolves in the water and is removed for further use as described hereinafter or for disposal. The vinyl cyanide, acetonitrile and carbon dioxide pass to a cooling tower 6 where the vinyl cyanide and acetonitrile are condensed. The carbon dioxide is not condensed and is discharged along with inert gases and any unreacted propylene by conduit 7. Typically, these gases (F) are fed to a burner to heat the catalyst along with additional fuel if required. The condensed vinyl cyanide (D) and acetonitrile (E) are passed to a distillation tower 8 and separated by fractional distillation. The aqueous solution of acetic acid (G') obtained in the spray tower 4 can be recycled to the reaction bed by conduit 9. Alternatively acid (G) can be added to the reaction bed through conduit 10.

Examples

[014] Reactions were performed using a range of catalysts, temperatures and reactants. The results are shown in Table 1. In each case stoichiometric amounts of reactants as determined using EZE-KHEM ™ were used.

Table 1

Run Number	1	2	3	4	5	6	7	8	9	10	11
Catalyst	$FeCl_3$	$FeCl_3$	$CuCl_2$	$CuCl_2$	$CuCl_2$	$CuCl_2$	$CuCl_2$	$CuCl_2$	$CuCl_2$	$CuCl_2$	$Cu(NO_3)_2$
Temp. / °C	250	250	250	250	250	250	250	250	400	175	250
Added Formic Acid	0	0	0	5	0	0	0	0	0	0	0
Added Acetic Acid	0	5	0	0	5	10	0	0	0	0	0
Added Propionic Acid	0	0	0	0	0	0	0	5	0	0	0
Recycled Acetic Acid	0	0	0	0	0	0	2.5	0	0	0	0
Carbon dioxide in Product %	15	15	5	5	5	5	5	25	40	5	5
Vinyl Cyanide in Product %	80	75	90	87.5	87.5	85	88	66	50	40	90
Acetonitrile in Product %	0	0	1	2.5	2.5	5	2	1.5	0	0	1
Acetic Acid in Product %	0	5	2	2.5	2.5	2.5	2.5	2.5	10	0	2
Propylene in Product %	5	5	2	2.5	2.5	2.5	2.5	5	0	55	2

[015] The values shown are expressed as carbon mol. %. The composition of the product was measured in a sample of gas taken from conduit 5.

[016] The results in Table 1 show that at a temperature of from 200 to 350°C, whe using a copper (II) catalyst, acetonitrile is formed. No acetonitrile is formed when the prior art iron (III) catalyst is used. The addition of acetic acid or formic acid to the reactants increases the amount of acetonitrile produced. Furthermore, when formic or acetic acid is used a greater percentage of propylene feed is converted into vinyl cyanide and acetonitrile. The use of propionic acid, however, results in a high percentage of unwanted carbon dioxide being produced. The use of the acetic acid which is a by-product of the reaction is also shown to be possible.

Claims

1. A process for producing acetonitrile and vinyl cyanide comprising contacting a mixture containing propylene, ammonia and an oxygen-containing gas with a copper (II) catalyst at a temperature of from 200 to 350°C.
2. A process as claimed in claim 1 wherein the oxygen-containing gas is air.
3. A process as claimed in claim 1 or claim 2 wherein the copper (II) catalyst comprises copper (II) chloride or copper (II) nitrate.
4. Apparatus for producing acetonitrile and vinyl cyanide, the apparatus comprising:
    i. a reactor (3) for holding a reaction bed,
    ii. means for heating the reaction bed in the reactor (3),
    iii. at least one conduit (1, 2, 9, 10) for inputting reactants to the reactor (3),
    iv. a conduit (5) allowing materials to exit the reactor (3) and enter
    v. a spray tower (4) for spraying water onto the materials exiting the reactor (3),
    vi. a cooling tower (6) for condensing the vinyl cyanide and acetonitrile exiting from the spray tower (4) and
    vii. a distillation tower (8) for separating vinyl cyanide and acetonitrile from the condensate obtained in the cooling tower (6).

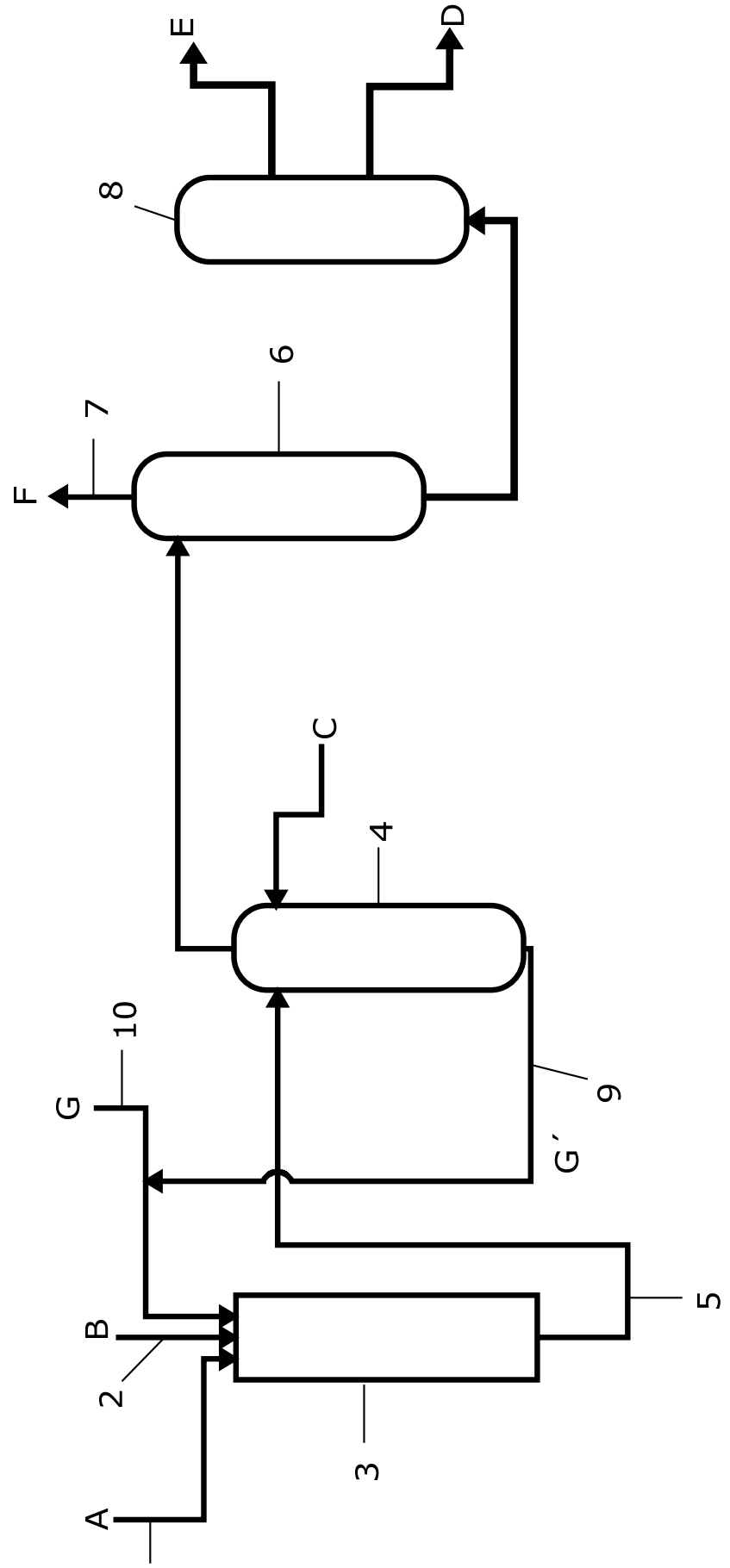

Fig. 1

Communication under Art. 94(3) EPC

1. The examination is based on the application documents as originally filed; a copy of the claims as originally filed is annexed to this communication (Annex 1).

2. Reference is made to the following documents; the numbering will be adhered to in the rest of the procedure:

D1: EP 2 222 222 (CONFEDERATE CHEM CORP) 1 June 2008.
D2 : J. CAT. CHEM., vol. 59, p225, LE PEU, AGATHA ET AL., "Copper (II) Catalysts Part 3" 3 July 2008.

3. The present application does not claim priority. Its filing date is 4 July 2008.

4. Document D1 was published on 1 June 2008. Document D1 (see claims 1-4) describes a process for producing vinyl cyanide comprising contacting a mixture containing propylene, ammonia and an oxygen-containing gas with a copper (II) catalyst at a temperature of from 200 to 350°C. Document D1 also discloses the apparatus claimed in the application, the use of air as the oxygen-containing gas and copper (II) chloride and copper (II) nitrate as catalysts. Claims 1-4 therefore lack novelty over document D1 (Articles 52(1), 54(1) and (2) EPC).

5. Document D2 was published on 3 July 2008. Document D2 describes a process for producing acetonitrile and vinyl cyanide comprising contacting a mixture of propylene, ammonia and air with a copper (II) chloride catalyst at a temperature of 250°C. Claims 1-3 therefore lack novelty in view of document D2 (Articles 52(1), 54(1) and (2) EPC).

6. If the applicant wishes to maintain the application new claims should be filed w take the above objections into account. Care should be taken to ensure that the ne claims comply with the requirements of the EPC in respect of clarity, novelty, inventive step and, if necessary, unity (Articles 84, 54, 56 and 82 EPC). Care should also be taken that any amendments do not introduce subject-matter which extends beyond the content of the application as originally filed (Article 123(2) EPC).

7. In the letter of reply the difference between the new claim and the prior art disclosed in documents D1 and D2 should be indicated. The technical problem underlying the invention in view of the closest prior art and the solution to the problem should be readily derivable from the statement of the applicant (Rule 42(1) (c) EPC and EPO Guidelines, C-IV, 11.5).

8. In order to facilitate the examination as to whether the new claims contain subject-matter which extends beyond the content of the application as filed the applicant is requested to indicate precisely where in the application documents any amendments proposed find a basis (Article 123(2) and Rule 137(4) EPC).

Annex 1: Claims as originally filed

1. A process for producing acetonitrile and vinyl cyanide comprising contacting a mixture containing propylene, ammonia and an oxygen-containing gas with a copper (II) catalyst at a temperature of from 200 to 350°C.
2. A process as claimed in claim 1 wherein the oxygen-containing gas is air.
3. A process as claimed in claim 1 or claim 2 wherein the copper (II) catalyst comprises copper (II) chloride or copper (II) nitrate.
4. Apparatus for producing acetonitrile and vinyl cyanide, the apparatus comprising:
   i. a reactor (3) for holding a reaction bed,
   ii. means for heating the reaction bed in the reactor (3),
   iii. at least one conduit (1, 2, 9, 10) for inputting reactants to the reactor (3),
   iv. a conduit (5) allowing materials to exit the reactor (3) and enter
   v. a spray tower (4) for spraying water onto the materials exiting the reactor (3),
   vi. a cooling tower (6) for condensing the vinyl cyanide and acetonitrile exiting from the spray tower (4) and
   vii. a distillation tower (8) for separating vinyl cyanide and acetonitrile from the condensate obtained in the cooling tower (6).

Document 1 (EP 2 222 222)

Process and apparatus for making vinyl cyanide

[001] The invention relates to processes and apparatus for making vinyl cyanide.

[002] Vinyl cyanide is a well-known chemical intermediate. Vinyl cyanide is made by reaction of propylene, ammonia and oxygen in the presence of an iron (III) catalyst such as iron (III) chloride, $FeCl_3$. The reaction is:

$$2CH_3CH{=}CH_2 + 2NH_3 + 3O_2 \rightarrow 2CH_2CHCN + 6H_2O$$

[003] It has now been found, that if a copper (II) catalyst is used instead of an iron (III) catalyst, a higher yield of vinyl cyanide is obtained.

[004] According to the invention there is provided a process for producing vinyl cyanide comprising contacting a mixture containing propylene, ammonia and an oxygen-containing gas such as air with a copper (II) catalyst such as copper (II) chloride or copper (II) nitrate at a temperature in the range of from 200 to 350°C.

[005] According to the invention there is further provided an apparatus for producing vinyl cyanide, the apparatus comprising:

i. a reactor for holding a reaction bed,
ii. means for heating the reaction bed in the reactor,
iii. at least one conduit for inputting reactants to the reactor,
iv. a conduit allowing materials to exit the reactor and enter
v. a spray tower for spraying water onto the materials exiting the reactor,
vi. a cooling tower for condensing the vinyl cyanide exiting from the spray tower and
vii. a distillation tower for separating vinyl cyanide from the condensate obtained in the cooling tower.

[006] The catalyst comprises a copper (II) salt. Preferred copper (II) salts include copper (II) chloride and copper (II) nitrate both of which are commercially available.

[007] The reactants are propylene (C_3H_6), ammonia and an oxygen-containing gas, such as air. It is not essential to use air. Oxygen-enriched air, pure oxygen or other oxygen-containing gases can be used. The presence of inert gases such as nitrogen from air does not reduce the yield. Inert gases make the process less thermally efficient since the inert gases must be heated.

[008] Although not essential, the reactants are usually present at about stoichiometric levels. Commercially however, it is important to add the reactants at stoichiometric levels. This can be done as is usual in industrial chemistry using commercial systems such as EZE-KHEM ™ from Eze-Khem LLC.

[009] Figure 1 shows a schematic view of an apparatus according to the invention.

[010] Oxygen-containing gas such as air is passed into the apparatus by conduit 1. A mixture of propylene and ammonia enter the apparatus by conduit 2. To reduce the risk of explosion the oxygen-containing gas is kept apart from the propylene until the reactants enter the reactor. In order to further reduce the explosion risk a further conduit may be present to supply an inert gas to the reactor.

[011] The reactants are passed into reactor 3, which contains a bed of the catalyst at a temperature of from 200 to 350°C. If the temperature is less than 200°C then too much propylene remains in the product. If the temperature is greater than 350°C then excessive oxidation occurs and too much carbon dioxide is formed instead of the intended products. The reaction products comprise vinyl cyanide, carbon dioxide, acetic acid and other materials including an as yet unidentified low molecular weight species.

[012] The reaction products, together with unreacted propylene exiting the catalyst are passed to a spray tower 4 by conduit 5 and contacted with a water spray. The water spray cools the reaction products. The acetic acid dissolves in the water and is removed for disposal. The vinyl cyanide, carbon dioxide and other materials pass to a cooling tower 6 which condenses the vinyl cyanide and some by-products. The carbon dioxide is not condensed and is discharged along with inert gases and any unreacted propylene by conduit 7. Typically these gases are fed to a burner to heat the catalyst along with additional fuel if required. The condensed vinyl cyanide is passed to a distillation tower 8 and purified by fractional distillation.

Examples

[013] Reactions were performed using a range of catalysts, temperatures and reactants. The amounts of ammonia and oxygen (in air) used were stoichiometric. The results are shown in Table 1.

Table 1

Run Number	1	2	3	4	5
Catalyst	$FeCl_3$	$CuCl_2$	$CuCl_2$	$CuCl_2$	$Cu(NO_3)_2$
Temp. / °C	250	250	400	175	250
Carbon Dioxide in Product %	15	5	40	5	5
Vinyl Cyanide in product %	80	90	50	40	90
Unidentified by-product in Product %	0	1	0	0	1
Acetic Acid in Product %	0	2	10	0	2
Propylene in Product %	5	2	0	55	2

[014] The composition of the product (measured on a sample taken from conduit 5) is expressed as carbon mol. % (the mol. % of all the carbon-containing compounds present).

[015] It will be clearly seen from Table 1 that by using a copper (II) catalyst at about 250ºC the yield of vinyl cyanide is greater than when the prior art iron (III) catalyst is used.

Claims

1. A process for producing vinyl cyanide comprising contacting a mixture containing propylene, ammonia and an oxygen-containing gas with a copper (II) catalyst at a temperature in the range of 200 to 350°C.
2. A process as claimed in claim 1 wherein the oxygen-containing gas is air.
3. A process as claimed in claim 1 or claim 2 wherein the copper (II) catalyst comprises copper (II) chloride or copper (II) nitrate.
4. Apparatus for producing vinyl cyanide, the apparatus comprising:
    i. a reactor (3) for holding a reaction bed,
    ii. means for heating the reaction bed in the reactor (3),
    iii. at least one conduit (1, 2) for inputting reactants to the reactor (3),
    iv. a conduit (5) allowing materials to exit the reactor (3) and enter
    v. a spray tower (4) for spraying water onto the materials exiting the reactor (3),
    vi. a cooling tower (6) for condensing the vinyl cyanide exiting from the spray tower (4) and
    vii. a distillation tower (8) for separating vinyl cyanide from the condensate obtained in the cooling tower (6).

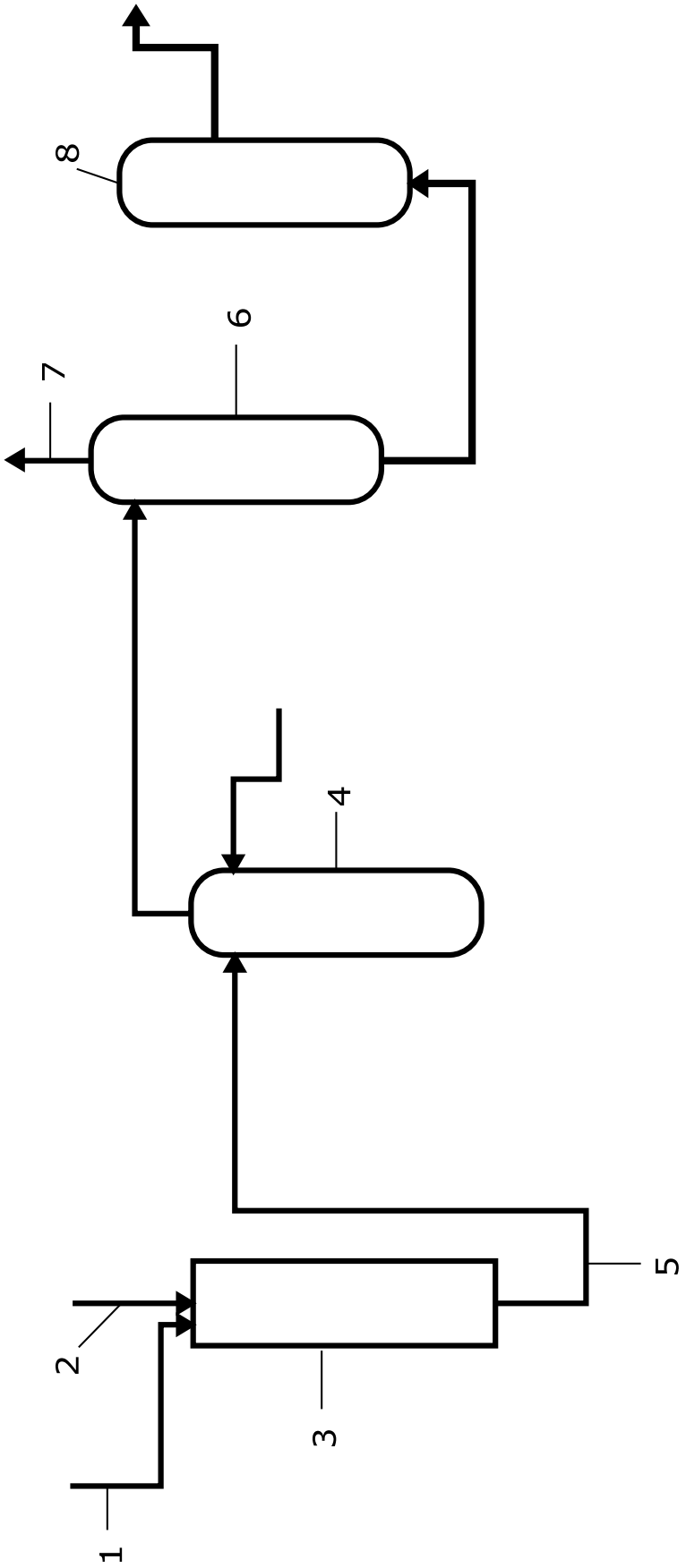

Fig. 1 D1

Document 2

Journal of Catalytic Chemistry (2008) 59, 225

Agatha Le Peu, Hester Norway,
School of Chemistry
University Of Edgestow
Edgestow
Cateweba
USA

Copper (II) Catalysts Part 3

[001] As part of our continuing work on copper (II) catalysts we have been studying the properties of copper (II) catalysts, especially copper (II) chloride catalysts, on reactions of propylene, ammonia and air. Stoichiometric mixtures of reactants (as determined using EZE-KHEM) were passed through a reaction bed of diameter 5cm and length 5m made of particles of copper (II) chloride. The flow rate was 50 l/min and the temperature was 250°C. The reaction bed was provided with outlets at 1m intervals. Samples were withdrawn from the outlets and analysed. The results are shown below.

[002] From our results we can see that the reaction is not dependent on the catalyst particle size. We are continuing to research why this is.

[003] Copper (II) chloride (Average particle diameter 100μm)

Outlet Number	0	1	2	3	4	5
Propylene	100	78	56	33	8	5
Acetic Acid	0	1	2	2	2	2
Vinyl Cyanide	0	20	40	60	84	87
Carbon Dioxide	0	1	2	4	5	5
Acetonitrile	0	0	0	1	1	1

[004] Copper (II) chloride (Average particle diameter 200μm)

Outlet Number	0	1	2	3	4	5
Propylene	100	78	54	30	12	5
Acetic Acid	0	1	2	2	2	2
Vinyl Cyanide	0	20	42	64	81	87
Carbon Dioxide	0	1	2	4	5	5
Acetonitrile	0	0	0	1	1	1

Letter from the applicant

Confederate Chemical Corp Inc.
Eagle Works
1372 Clearwater Boulevard
Springfield
Fremont
USA

Basil Don Bond
Wright, Price and Gneiss
Prince Peter Kropotkin Place
Ankh-Morpork
Latvia

Dear Mr Bond

[001] Thank you for agreeing to take over representing Confederate Chemicals Inc. before the European Patent Office. We enclose the papers our previous European Patent Attorney sent us. He told us that today is the last day to reply. We believe that there is considerable commercial potential for Confederate Chemicals Inc. to make money licensing this invention.

[002] We don't think the objections raised are too serious since the same objections were raised by the US Examiner. The US patent was granted without us needing to make any changes.

[003] D1 is an earlier patent application we made. D1 and the present application have the same inventor, Homer J Stillson. We filed the present application because we realised that our invention contains more aspects than we described in the first application. In the USA, the objections based on document D1 were withdrawn because the inventor of both applications is the same.

[004] D2 is the work of Professor Le Peu's group at the University of Edgewater. The US Examiner said that our invention was the same as that described in Professor Le Peu's paper. The inventor of our application explained to the US Examiner that he had thought of the idea before Professor Le Peu did her work. Professor Le Peu agreed and the objection was withdrawn.

[005] If you need to amend the application in order to obtain a patent you may do so. It is expensive to purchase carboxylic acids, and in particular formic acid, from chemical suppliers at the scale at which we will operate. So if you have to amend the claims, make sure that they cover processes which do not need the carboxylic acid to be bought in.

Yours sincerely,

Abe J Sampson III
Chief Executive Officer
Confederate Chemical Corp Inc.