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(12) Patent:

(54) METHYL ALCOHOL PRODUCTION

(54) PRODUCTION D'ALCOOL METHYLIQUE

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ABSTRACT

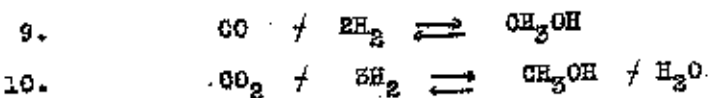
CLAIMS: Show 21 claims

*** Note: Data on abstracts and claims is shown in the official language in which it was submitted.

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- ☐ Claims Image
- ☐ Disclosures Image
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1. Our invention relates to the production of
 2. methyl alcohol by catalytic, synthetic means from
 3. hydrogen and carbon monoxide or carbon dioxide. It is
 4. well known that methyl alcohol may be catalytically
 5. prepared by reacting the above gases at elevated
 6. temperatures and pressures in the presence of a proper
 7. catalyst. The two chemical reactions which are
 8. illustrative of the reaction follow:



11. Both of these reactions are reversible and take place
 12. only at elevated temperatures and pressures.

13. A very wide variety of substances and mixtures
 14. of substances has been proposed as catalysts for the
 15. reaction. Some of these catalysts are so easily poi-
 16. soned and destroyed that they are uneconomical in use.
 17. Others are extremely expensive and still others do not
 18. produce pure methyl alcohol, but rather a variety of
 19. substances including acids and gaseous hydrocarbons
 20. such as methane.

21. It is the purpose of our invention and
 22. application to provide a workable economical process
 23. for the production of methyl alcohol from hydrogen and
 24. oxides of carbon and this purpose has been accomplish-
 25. ed by the preparation of a novel and efficient
 26. catalyst and by the discovery of proper working con-
 27. ditions for the use of this catalyst whereby methyl
 28. alcohol may be produced in good yield.

29. As a catalyst we employ a metallic alloy of
 30. zinc and copper in which the copper is present in
 31. larger proportion than the zinc. The copper-zinc
 32. alloy may also contain a small percentage of another

1. metal such as tin or manganese. The following sub-
 2. stances are typical alloys, such as are contemplated
 3. for use in our process.

4. brass - zinc, 1 part; copper, 2-5 parts

5. bronze - zinc, 1-2 parts; copper, 7-9 parts;
 and tin, 1-2 parts

6. manganese bronze - which is an ordinary
 bronze containing about .3% of
 manganese.

7. Before use as catalysts these alloys must be
 8. preliminarily activated. This may be accomplished by
 9. reducing the alloy to small particles suitable to serve
 10. as contact catalysts, for example - filings or turnings,
 11. and then subjecting the surface to an oxidizing action.
 12. This oxidation attacks the surface of the catalyst and
 13. makes it irregular and porous. On exposure to a re-
 14. ducing atmosphere, such as hydrogen gas, the oxidized
 15. surface is partially reduced to metal and the complex
 16. mixture of copper alloy and derived oxides constitutes
 17. an active methanol catalyst.

18. While our invention is directed generally to
 19. the use of activated alloys of the above type in the
 20. production of methyl alcohol, we prefer to activate the
 21. catalysts by means of a process described as "anodic
 22. oxidation". For example, the brass or bronze filings
 23. are made to serve as the anode in an electrolytic cell.
 24. Nickel or carbon may serve as the cathode, and a suit-
 25. able electrolyte is a 2% solution of sodium carbonate.
 26. For example, 30 pounds of brass filings contained in a
 27. cylindrical column 30 inches high and 4-5 inches in
 28. diameter and located 2-4 inches from a cathode of about
 29. equal size, when exposed to a current of 10 volts and
 30. 30-50 amperes for about 30 hours will result in the
 31. anodic oxidation of the entire catalyst surface to a
 32. sufficient depth to form an active catalyst.

1. This anodic oxidation results in a surface
2. change on the metal and the formation of a penetrable
3. film of oxides. If this catalyst mass is not
4. partially reduced to metallic state by heating it in
5. a current of hydrogen, a very active methyl alcohol
6. catalyst will result. We prefer to reduce the mass
7. immediately prior to methanol production by passing
8. hydrogen over it at a temperature of about 200°C.

9. While we have described in detail an anodic
10. oxidation method of activating a copper alloy to serve
11. as a catalyst for methyl alcohol production it should
12. be understood that these catalysts may be oxidized by
13. other means, such as exposure to an atmosphere of
14. oxygen at an elevated temperature. The anodic ox-
15. idation method produces a better product, but our
16. invention is not so limited, and refers broadly to the
17. use of copper alloys as methyl alcohol catalysts.

18. When carbon monoxide gas in the presence of a
19. molecular excess of hydrogen is passed over one of our
20. copper-alloy catalysts at elevated temperature and
21. pressure, methyl alcohol is produced in substantially
22. pure form. Pressures in excess of 100 atmospheres and
23. temperatures in excess of 200°C. should be employed.
24. The reaction temperature - i.e. of the catalyst mass -
25. should not exceed 600°C. There is no definite upper
26. limit of pressure except the practical limit which can
27. be attained by apparatus available.

28. At pressures and temperatures within the range
29. described, methanol will be produced in every case by
30. the use of our copper alloy catalysts. The yield will
31. vary with the pressure, temperature, and rate of gas

1. flow over the catalyst. In general we prefer to use
2. pressures between 100-200 atmospheres and a temperature
3. of 250-300° C.

4. Where pure carbon monoxide gas is used we
 5. prefer to use an excess of hydrogen in the relation of
 6. one molecule of carbon monoxide to five molecules of
 7. hydrogen. A gaseous mixture of carbon monoxide with
 8. carbon dioxide or pure carbon dioxide gas may be also
 9. employed, but in this case more hydrogen must be used
 10. as some is consumed in producing water according to
 11. the reaction



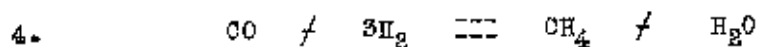
13. In the case where a substantial quantity of
 14. the oxide of carbon employed is carbon dioxide, we
 15. prefer to use a much larger excess of hydrogen - for
 16. example twenty molecules of hydrogen per molecule of
 17. carbon dioxide.

18. When a mixture of carbon monoxide and hydrogen
 19. in the proportion of one volume of the former to five
 20. of the latter is passed over our copper-alloy catalyst
 21. at a pressure of 200 atmospheres and a temperature of
 22. 280°C. at a speed of about 10 cubic meters of gas per
 23. kilogram of catalyst, about 15% of the carbon monoxide
 24. present is converted to methyl alcohol, which, on cool-
 25. ing the gaseous mixture, is condensed to liquid form and
 26. thus removed from the process. The residual gas mix-
 27. ture is continually recirculated over the catalyst and
 28. from time to time carbon monoxide and hydrogen is added
 29. to maintain approximately the original percentage
 30. composition of gases.

31. Carbonyl forming metals such as iron, nickel,
 32. and cobalt must not be present in the catalyst or used

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1. in constructing the catalyst chamber as the presence of
2. these metals results in the formation of methane in
3. accordance with the following equation:-



5. The apparatus for conducting the reaction may well be
6. made of steel internally lined with copper.
7. While we have described the use of pure carbon
8. oxides and hydrogen as the raw materials for methyl
9. alcohol production, it should be understood that small
10. percentages of gaseous hydrocarbons such as methane and
11. inert gases such as nitrogen may be present in the
12. gaseous mixture without bad results.

13. Now having fully described our invention, we
14. claim the following as new and novel.

15. 1. A process for the production of methyl
16. alcohol which comprises passing a gaseous mixture of
17. oxides of carbon and hydrogen over a copper alloy cata-
18. lyst at an elevated temperature and pressure.

19. 2. A process for the production of methyl
20. alcohol which comprises passing a gaseous mixture of
21. oxides of carbon with a molecular excess of hydrogen over
22. a copper-zinc alloy catalyst containing some oxides, at
23. an elevated temperature and pressure.

24. 3. A process for the production of methyl
25. alcohol which comprises passing a gaseous mixture of
26. oxides of carbon with a molecular excess of hydrogen over
27. a copper alloy catalyst containing some oxides, at 250-
28. 300° C. and at a pressure in excess of 100 atmospheres.

29. 4. A process for the production of methyl
30. alcohol which comprises passing a gaseous mixture con-
31. sisting of 1 volume of oxide of carbon and 5-20 volumes

1. of hydrogen over a copper-zinc alloy catalyst contain-
 2. ing some oxides, at 250-300° C. and at a pressure in
 3. excess of 100 atmospheres.

4. 5. A process for the production of methyl
 5. alcohol which comprises passing a gaseous mixture con-
 6. sisting of 1 volume of carbon monoxide and 5-20 volumes
 7. of hydrogen over a copper-zinc alloy catalyst containing
 8. some oxides, at a temperature of 250-300° C. and at a
 9. pressure in excess of 100 atmospheres.

10. 6. A process for the production of methyl
 11. alcohol which comprises passing a gaseous mixture con-
 12. sisting of 1 volume of carbon monoxide and 5 volumes
 13. of hydrogen over a copper-zinc alloy catalyst containing
 14. some oxides, at 280° C. and at a pressure of about 200
 15. atmospheres.

16. 7. In a process for the production of methyl
 17. alcohol, the step which comprises leading a gaseous
 18. mixture of carbon monoxide and hydrogen at elevated
 19. temperature and pressure over a catalyst consisting of
 20. an alloy containing copper and zinc, partially oxidized.

21. 8. In a process for the production of methyl
 22. alcohol, the step which comprises leading a gaseous
 23. mixture of carbon monoxide and hydrogen at elevated
 24. temperature and pressure over a catalyst consisting of
 25. an alloy containing copper and zinc which has been
 26. activated by anodic oxidation and subsequent partial
 27. reduction.

28.- 9. In a process for the production of methyl
 29. alcohol, the step which comprises preparing a suitable
 30. catalyst by anodically oxidizing the surface of a
 31. copper-zinc alloy and partially reducing the surface by
 32. contact with hydrogen.