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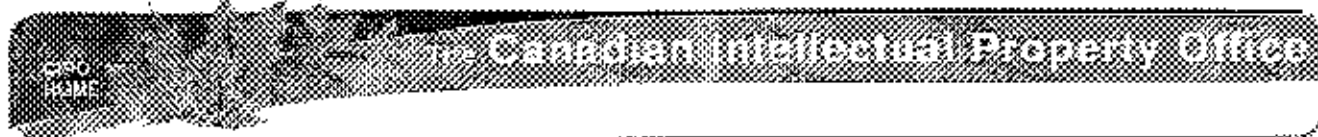
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(12) Patent:

(54) SYNTHETIC METHANOL PROCESS

(54) PRODUCTION SYNTHETIQUE DE METHANOL

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ABSTRACT:

CLAIMS: [Show all claims](#)

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

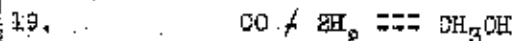
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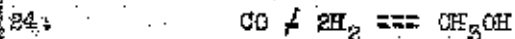
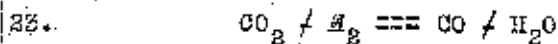
1. Our invention pertains to an improvement in  
 2. the process of producing synthetic methanol by the  
 3. reaction of hydrogen and oxides of carbon at elevated  
 4. temperatures and pressures under the influence of  
 5. catalysts. More particularly, our invention relates to  
 6. a continuous circulatory process permitting the correct  
 7. adjustment of the proportions of reacting gases.

8. As is well known, methanol may be produced by  
 9. the interaction of hydrogen with carbon monoxide, or  
 10. with carbon dioxide, or with mixtures of these two  
 11. oxides. Ordinarily in the practical operation of the  
 12. process, a mixture of carbon monoxide with smaller  
 13. quantities of carbon dioxide is employed to react with  
 14. the hydrogen, since such mixtures are the most easily  
 15. obtainable for manufacturing use.

16. The reaction by which methanol is produced  
 17. from hydrogen and carbon monoxide is thought to be the  
 18. following:-



20. When carbon dioxide reacts with hydrogen to form  
 21. methanol it has been generally assumed that the reaction  
 22. may be written in two steps, thus:-



25. From the theoretical equations involved it  
 26. might be further assumed that the optimum proportions of  
 27. reacting materials for methanol production would be one  
 28. volume of carbon monoxide to two volumes of hydrogen,  
 29. and/or one volume of carbon dioxide to three volumes of  
 30. hydrogen. However, it is well known that optimum results  
 31. are obtained in methanol synthesis when the proportion

1. of hydrogen to carbon oxides is greater than that  
2. theoretically required. (of English Patent 229,714;  
3. page 1, line 34). This is for the reason that the  
4. presence of an excess of hydrogen over that theoretic-  
5. ally required to react with the carbon oxides present  
6. tends to prevent the occurrence of undesirable side-  
7. reactions which produce free carbon, methane, water,  
8. etc., rather than methanol.

9. Methanol is produced when mixtures of carbon  
10. oxides and hydrogen in theoretical proportions, or  
11. mixtures in which there is an excess of hydrogen over  
12. that theoretically required, are passed over suitable  
13. catalysts at temperatures of from 300 to 500° C. and at  
14. pressures in excess of 50 atmospheres. In case carbon  
15. dioxide is the carbon oxide employed, there is also  
16. produced one molecule of water per molecule of methanol  
17. as was shown in the equation cited. If operating con-  
18. ditions are not correctly adjusted, or if improper  
19. catalysts are employed, side-reactions occur producing  
20. products other than methanol and water.

21. Catalysts suitable for the reaction may com-  
22. prise mixtures of metallic oxides such as are described  
23. for example, in United States Patents 1,558,559;  
24. 1,608,643; and 1,609,593; and in English Patents  
25. 229,714-5. The amount of methanol produced per hour  
26. varies with the quantity of catalyst employed, and with  
27. the space velocity of gas passage, as well as with the  
28. precise temperature and pressure.

29. The method of manufacture of methanol from  
30. mixtures of hydrogen and carbon oxides may be more  
31. clearly described with reference to Fig. 1 of the draw-  
32. ing which shows a suitable apparatus in cross-section.

1. The gas mixture to be reacted is supplied to the process  
2. at the desired pressure through the "make-up" gas pipe  
3. A by the Compressor (not shown). This gas mixes with  
4. the gas of the circulating system at connection B, and  
5. the mixed gases pass upward into the internal passage C  
6. of Heat Exchanger D. While passing through the Heat  
7. Exchanger the gas is heated by thermal contact with the  
8. hot gas from the methanol reaction which passes in  
9. reverse direction through the annular space E between  
10. the inner and outer walls of the Heat Exchanger. From  
11. the Exchanger the warmed gas passes downward through  
12. pipe F into the Converter (Catalyst Bomb) G. The gas  
13. passes downward in the annular space between the inside  
14. wall of the Converter and the wall of the Catalyst.  
15. Basket H then rises upward through the catalyst J and J'  
16. through the perforate plate H' forming the bottom of  
17. the basket H.

18. The drawing shows the catalyst as separated  
19. into two sections, J and J'. Section J is designed to  
20. act as a "pre-catalyst" or purifier, to destroy or  
21. absorb any catalyst poisons which may be present in the  
22. gas, and thus to preserve the catalytic activity of  
23. Section J' for the methanol reaction. The elevated  
24. temperature in the Converter G is largely maintained by  
25. the heat of reaction, but supplementary heat is  
26. provided for by means of electric heating elements K,  
27. K', etc. embedded in an insulating jacket L which  
28. surrounds G.

29. As the hot gas passes through the catalyst  
30. the methanol reaction occurs, though all of the carbon  
31. oxides present in the gas are not reacted at one passage.  
32. The hot gas discharged from the Converter through pipe M

1. contains methanol vapors, (water & carbon dioxide is  
2. present) and any reaction by-products formed, as well  
3. as unreacted carbon oxides and hydrogen. This gas  
4. passes through the annular space Z of Heat Exchanger D,  
5. giving up most of its heat to the incoming gas.

6. The partially cooled gas then passes from the  
7. Heat Exchanger D via pipe N to the Condenser O where  
8. it is cooled. The methanol thus obtained in liquid  
9. form together with any water present is deposited in the  
10. Receiver P, from which the liquid may be removed through  
11. drain P'. The residual unreacted gas rises through pipe  
12. Q and passes to circulating Pump R. In operating the  
13. process, the circulating pump R serves to circulate the  
14. gas through the system to overcome pressure drops due to  
15. friction in the pipes and catalyst chamber. There is of  
16. course a constant diminution in the pressure of the  
17. system due to the reaction of the gases to form methanol.  
18. To sustain the pressure in the circulating system and to  
19. replace the gases consumed by the reaction, make-up gas  
20. is continually supplied under pressure through pipe A.

21. As a specific example of the operation of the  
22. apparatus, the following data are given.

23. Example I

24. A gas mixture consisting of approximately  
25. theoretical proportions of carbon dioxide and hydrogen  
26. (25% carbon dioxide and 75% hydrogen) was continually  
27. supplied to the apparatus at a pressure of 3500 pounds,  
28. and passed through the catalyst at a space velocity of  
29. 100,000. The catalyst employed was one containing a  
30. mixture of zinc oxide and chromic oxide, and the temper-  
31. ature of the reaction was maintained at  $420^{\circ}$  C. Under  
32. these conditions there was produced about 1.5 liters of

1. condensate per hour per liter of catalyst. This  
2. experiment is typical of the results attained when  
3. hydrogen and carbon oxides are present in theoretical  
4. proportions while passing over a methanol catalyst.

5.           On a laboratory scale one may very simply  
6. employ a gas mixture of carbon oxides and hydrogen, the  
7. latter gas being present in a proportion greater than  
8. that theoretically required. It is merely necessary to  
9. prepare a gas mixture of predetermined proportions, and  
10. pass it over a catalyst at the proper temperature and  
11. pressure. However when operating on a large industrial  
12. scale it is economically necessary to provide for the  
13. recirculation of the gases over the catalyst until  
14. a complete reaction to synthetic methanol is obtained,  
15. and when such recirculation is attempted difficulties  
16. arise if one attempts to use a gas mixture containing  
17. a proportion of carbon oxides to hydrogen that is  
18. different from that theoretically required. For  
19. example when one attempts to employ a mixture of gas  
20. containing 25% carbon monoxide and 75% hydrogen (instead  
21. of the theoretical ratio 32:68) in the synthetic  
22. methanol process while employing a system for recircula-  
23. ting the unreacted gases and supplying only sufficient  
24. make-up gas to maintain the pressure, there will be a  
25. continual change of the nature of the gas circulating  
26. over the catalyst.

27.           Since the "make-up gas" supplied to the system  
28. contains more hydrogen than is required for the reaction,  
29. and since this gas continually replaces that part of the  
30. mixture which enters into the methanol reaction (in  
31. theoretical proportions), the proportion of hydrogen in  
32. the circulating system increases as the process is con-

1. times, until eventually the proportion of carbon  
2. monoxide in the system grows so small that practically  
3. no methanol is produced. A precisely similar phenomenon  
4. occurs when one attempts to operate on a mixture of  
5. carbon dioxide and hydrogen not in theoretical  
6. proportions.

7. We have now discovered a method whereby the  
8. difficulty of operating a continuous circulating process  
9. for the production of methanol by the catalytic inter-  
10. action of carbon oxides and hydrogen in a gas mixture  
11. containing the ingredients in proportions differing from  
12. the theoretical may be obviated. By means of our improved  
13. process it is possible to obtain the economic advantages  
14. of employing an excess of hydrogen in the gases passing  
15. over the catalyst, and at the same time to maintain a  
16. static condition whereby the composition of the gas in  
17. the circulating system remains substantially unchanged  
18. during operation and whereby the make-up gas supplied  
19. to the process need not be varied in composition.

20. In accordance with our invention it is  
21. possible to operate the synthetic methanol process in  
22. such a manner that a gas containing theoretical pro-  
23. portions of carbon oxides and hydrogen may be supplied  
24. to the process as "make-up" gas, whereas the gas  
25. actually passing over the catalyst contains a great  
26. excess of hydrogen over that theoretically required.  
27. We may accomplish this result by filling the apparatus  
28. with a gas consisting of substantially pure hydrogen at  
29. a pressure somewhat below the pressure desired for the  
30. reaction. The circulation of this hydrogen through the  
31. apparatus naturally produces no chemical change. When

1. the apparatus has been filled with hydrogen at a pressure  
2. approximating the pressure required for operation, the  
3. character of the "make-up" gas is changed, and instead  
4. of pure hydrogen, a mixture of hydrogen and carbon  
5. oxides in the proportions theoretically required for  
6. methanol synthesis is passed into the apparatus.

7. The carbon oxide containing gas is blended  
8. with the hydrogen in the circulating system at connection  
9. B, and passes through the circulating system. Hence  
10. the gas passing through the catalyst J-J' contains a  
11. great preponderance of hydrogen over carbon oxides, and  
12. desirable conditions for the conversion of all of the  
13. carbon oxides to methanol are thus attained.

14. During the reaction of the carbon oxides to  
15. form methanol, the proportion of hydrogen removed is  
16. equal to the amount of hydrogen that entered the system  
17. with the carbon oxides, for these two gases were present  
18. in theoretical proportions in the "make-up" gas. It is  
19. thus seen that the introduction of a gas containing  
20. theoretical proportions of carbon oxides and hydrogen  
21. into a circulating system which contains only a small  
22. proportion of carbon oxides does not change the  
23. character of the gas in the circulating system, since  
24. the methanol reaction constantly removes carbon oxides  
25. and hydrogen in the same proportion in which they are  
26. introduced in the "make-up" gas.

27. As illustrative of the results attained by  
28. the employment of our invention, the following examples  
29. are cited.

#### 30. Example II

31. Hydrogen gas was supplied to the process  
32. through the "make-up" gas pipe A until the pressure had



1. been built up to 2000 pounds. The character of the  
2. "make-up" gas was then changed, and a mixture of carbon  
3. dioxide and hydrogen in theoretical proportions was  
4. passed into the apparatus until the pressure had reached  
5. 3500 pounds. Thereafter only sufficient make-up gas to  
6. maintain the desired reaction pressure was supplied.  
7. At a space velocity of 100,000, and a catalyst temper-  
8. ature of 420° C., 2.9 liters of condensate was produced  
9. per hour per liter of catalyst, this condensate contain-  
10. ing 60.5% methanol by volume. Analysis of the gases  
11. showed 11% carbon dioxide by volume, this condition  
12. remaining constant over twelve hours of operation. It  
13. is observed that the practice of our invention which  
14. made possible the employment of an excess of hydrogen in  
15. the circulating system produced a much improved result  
16. over Example I in which a theoretical gas mixture was  
17. employed.

18. Example III

19. Hydrogen gas was supplied to the process  
20. through the make up gas pipe A until the pressure had  
21. been built up to 1800 pounds. A gas mixture containing  
22. theoretical proportions (32:66) of carbon monoxide and  
23. hydrogen was then passed into the apparatus until the  
24. pressure had reached 3500 pounds. Thereafter only  
25. sufficient "make-up" gas to maintain the desired reaction  
26. pressure was supplied. At a space velocity of 50,000  
27. and a catalyst temperature of 420° C., 1.2 liters of  
28. condensate per hour per liter of catalyst was produced,  
29. this condensate containing 93% methanol. The gas  
30. mixture passing through the circulating system showed  
31. 14% carbon monoxide, on analysis. This method of  
32. operation provides an improved result since when similar

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Case C

1. reaction conditions were employed and a gas mixture of
  2. theoretical proportions was passed over the catalyst a
  3. yield of only 0.7 liters of condensate per hour per
  4. liter of catalyst was obtained.
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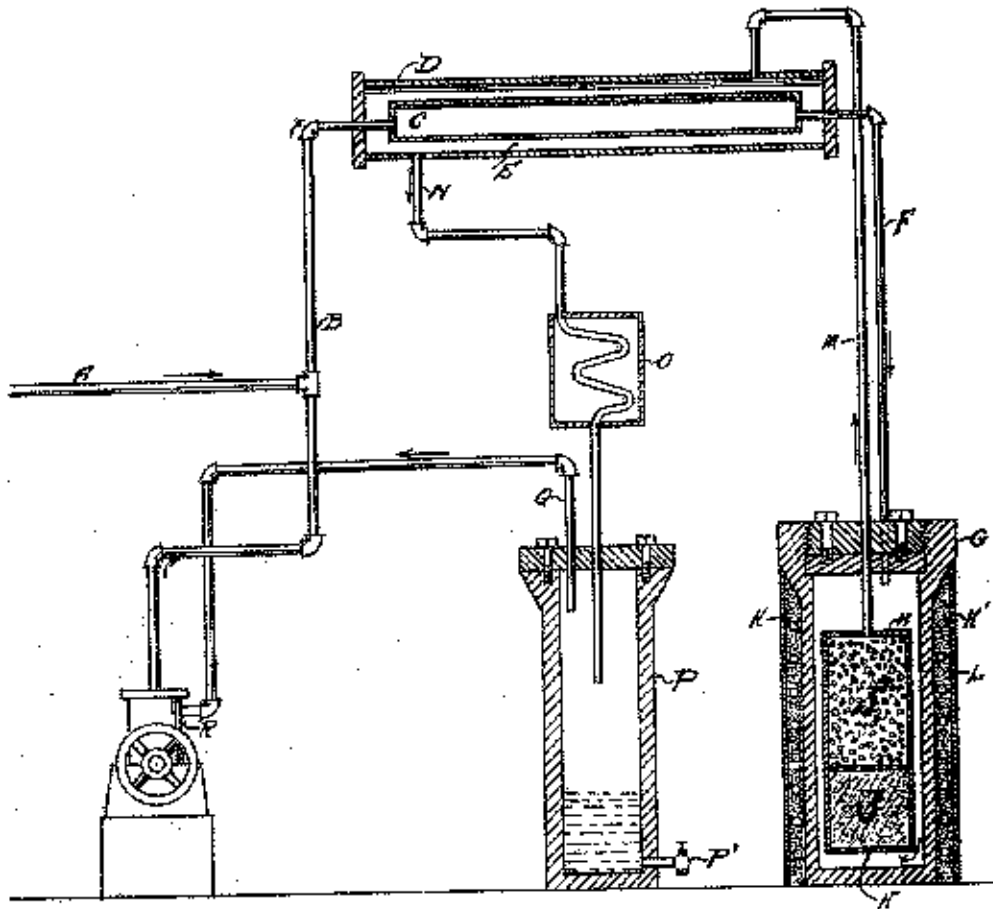
6. Now having described our invention, we claim  
8. the following as new and novel.

7. 1. In a process for the production of methanol  
8. by the catalytic interaction at elevated pressure of  
9. carbon oxides with hydrogen, the step which comprises  
10. circulating a gas containing a ratio of hydrogen to  
11. carbon oxides far greater than the theoretical propor-  
12. tions required for the reaction, while maintaining the  
13. reaction pressure by adding a gas containing carbon  
14. oxides and hydrogen in substantially theoretical  
15. proportions.

16. 2. In a process for the production of  
17. methanol by the catalytic interaction at elevated  
18. pressure of carbon dioxide and hydrogen, the step which  
19. comprises circulating a gas containing a ratio of  
20. hydrogen to carbon dioxide far greater than the  
21. theoretical proportions required for the reaction, while  
22. maintaining the reaction pressure by adding a gas  
23. containing carbon oxides and hydrogen in substantially  
24. theoretical proportions.

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Synthetic Methanol Process.  
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APPLICANTS

Certified to be the drawing referred to  
in the specification hereunto annexed.

June 14<sup>th</sup> 1927

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ATTORNEY