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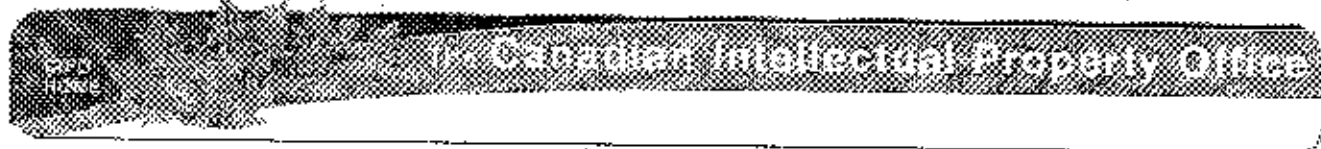
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(12) Patent:

(54) SYNTHETIC METHANOL PROCESS

(54) PRODUCTION SYNTHETIQUE DE METHANOL

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N/A

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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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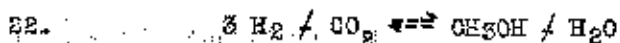
Case B

1. My invention relates to an improvement in the
 2. process of producing synthetic methanol by the reaction
 3. of hydrogen and carbon dioxide at elevated temperatures
 4. and pressures under the influence of suitable catalysts.
 5. More particularly my invention relates to a process in
 6. which the interacting gases are properly proportioned
 7. to obtain a maximum yield of methanol and a minimum
 8. yield of undesirable by-products.

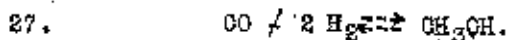
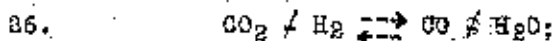
9. As is well known, methanol may be produced
 10. by the interaction of hydrogen with carbon monoxide, or
 11. carbon dioxide, or mixtures of the two.

12. I have now discovered that, in the case of the
 13. interaction of carbon dioxide and hydrogen catalytically
 14. at elevated temperatures and pressures to produce
 15. methanol, optimum results are obtained only when the
 16. carbon dioxide is present in extremely small proportion
 17. that is, in a proportion to the hydrogen present which
 18. is far less than the correct theoretical proportion.

19. The combined reaction by which it has been
 20. assumed that methanol is produced from carbon dioxide
 21. is one of the fourth order and is expressed as follows:



23. Some persons have further assumed that this combined
 24. reaction might be separated into two simple equations,
 25. thus:-



28. If the true reaction is assumed to be the simple reaction
 29. above shown, it follows from theoretical reasoning
 30. that the rate of reaction should be at a maximum when
 31. theoretical proportions of carbon dioxide and hydrogen
 32. are present in the gaseous mixture.

33. In connection with my experiments on the pro-
 34. duction of methanol from mixtures of hydrogen and carbon

Case B

1. dioxide, I have passed gases containing various pro-
2. portions of these ingredients over suitable catalytic
3. agents at temperatures of 300-500° C., and at pressures
4. in excess of 50 atmospheres. All of the gases present
5. are not reacted during one passage over the catalyst
6. and hence it is the practice to recirculate the
7. residual gases over the catalyst in cyclic fashion,
8. nothing being removed from the process except the water
9. and methanol which are formed. To maintain the volume
10. of gas, which is continually diminished by the reaction,
11. fresh gas is constantly added to the system.

12. The method of manufacture of methanol from
13. mixtures of carbon dioxide and hydrogen may be more
14. clearly described with reference to Fig. 1 of the
15. drawing which shows a suitable apparatus in cross-section
16. The gas mixture to be reacted is supplied to the process
17. at the desired pressure through the "make-up" gas pipe
18. A by the Compressor (not shown). This gas mixes with
19. the gas of the circulating system at connection B, and
20. the mixed gases pass upward into the internal passage C
21. of Heat Exchanger D. While passing through the Heat
22. Exchanger the gas is heated by thermal contact with the
23. hot gas from the methanol reaction which passes in
24. reverse direction through the annular space E between
25. the inner and outer walls of the Heat Exchanger. From
26. the Exchanger the warmed gas passes downward through
27. pipe F into the Converter (Catalyst Bomb) G. The gas
28. passes downward in the annular space between the inside
29. wall of the Converter and the wall of the Catalyst
30. Basket H then rises upward through the catalyst J and J'
31. through the perforate plate H' forming the bottom of the
32. basket H.

33. The drawing shows the catalyst as separated
34. into two sections, J and J'. Section J is designed to
35. act as a "pre-catalyst" or purifier, to destroy or

1. absorb any catalyst poisons which may be present in the
2. gas, and thus to preserve the catalytic activity of
3. section J' for the methanol reaction. The elevated
4. temperature in the Converter G is largely maintained by
5. the heat of reaction, but supplementary heat is
6. provided for by means of electric heating elements K,
7. K', etc. embedded in an insulating jacket L which
8. surrounds G.

9. As the hot gas passes through the catalyst
10. the methanol reaction occurs, though all of the carbon
11. oxides present in the gas are not reacted at one passage.
12. The hot gas discharged from the Converter through pipe
13. M contains methanol vapors, (water if carbon dioxide is
14. present) and any reaction by-products formed, as well
15. as unreacted carbon oxides and hydrogen. This gas
16. passes through the annular space E of Heat Exchanger D
17. giving up most of its heat to the incoming gas.

18. The partially cooled gas then passes from the
19. Heat Exchanger D via pipe N to the Condenser O where
20. it is cooled. The methanol thus obtained in liquid
21. form together with any water present is deposited in the
22. Receiver P, from which the liquid may be removed through
23. drain P'. The residual, unreacted, gas rises through
24. pipe Q and passes to circulating Pump R.

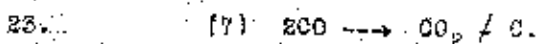
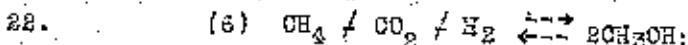
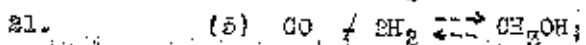
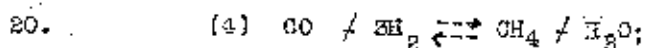
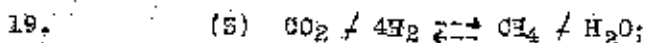
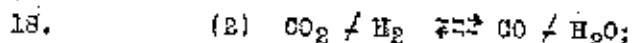
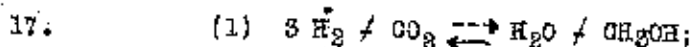
25. The circulating pump R withdraws the residual
26. gas from the Receiver P and combines it with the make-
27. up gas at connection B. In operating the process, the
28. circulating pump R serves to circulate the gas through
29. the system and to overcome pressure drops due to friction
30. in the pipes and catalyst chamber. There is of course
31. a constant diminution in the pressure of the system due
32. to the reaction of the gases to form methanol. To
33. sustain the pressure in the circulating system and to
34. replace the gases consumed by the reaction, make-up gas
35. is continually supplied under pressure through pipe A.

Case B

1. I have discovered that when methanol is
 2. produced from a mixture of theoretical proportions of
 3. carbon dioxide and hydrogen, and even when less than the
 4. theoretical proportion of carbon dioxide is employed,
 5. there is a formation of methane and carbon monoxide in
 6. the circulating gas mixture and, further that free
 7. carbon is deposited in the apparatus. Also, the pro-
 8. portion of water found with the methanol when the
 9. mixture is removed, by condensation, from the apparatus,
 10. is much greater than that that should be formed by the
 11. methanol reaction.

12. From the results thus attained it appears that
 13. there are a number of primary reactions occurring at
 14. different rates, rather than one or two simple reactions.

15. The group of reactions which occur in varying
 16. degrees is believed to be as follows:-



24. It is thus seen that the desired course of the
 25. reaction - i.e. methanol production - is attained by the
 26. advantageous reactions 1, 5, and possibly 6. On the
 27. other hand reaction 2 produces carbon monoxide and
 28. water. The carbon monoxide formed in reaction 2 may
 29. react advantageously with hydrogen to produce methanol
 30. according to reaction 5 or disadvantageously to produce
 31. carbon (Reaction 7) or methane (Reaction 4). Such carbon
 32. as is formed is, of course, removed from the process and

1. Reaction 7 is practically irreversible. The reactions,
2. advantageous or disadvantageous, which produce water are
3. also largely irreversible since water is constantly
4. removed from the process together with the condensed
5. methanol formed as the desired product.

6. As illustrative of the conditions prevailing
7. when it is attempted to react carbon dioxide and
8. hydrogen in theoretical proportions the following
9. typical experiment is cited.

10. A gas mixture comprising theoretical pro-
11. portions of hydrogen and carbon dioxide (i.e. approx-
12. imately 25% carbon dioxide) was circulated over a
13. methanol catalyst containing a mixture of zinc and
14. chromium oxides for a period of 12 hours. The catalyst
15. temperature was 420° C. and the gas pressure was 3500
16. pounds. After passing over the catalyst, the gases were
17. cooled and the mixture of methanol and water formed by
18. the reaction was condensed under pressure and removed
19. from the system. The residual (unreacted) gases were
20. supplemented by fresh gas and recirculated. Under these
21. conditions there was produced 1.5 liters of liquid per
22. hour per liter of catalyst, the liquid showing 60%
23. methanol on analysis where theoretically it should
24. contain 70% by volume. An analysis of the circulating
25. gas after 12 hours of reaction showed the following
26. composition:-

27.	Carbon dioxide	21%
28.	Carbon monoxide	12%
29.	Methane	5.2%
30.	Hydrogen	61.8%

31. It should be noted that this analysis of the
32. gases circulated over the catalyst was made after the
33. process had been in operation twelve hours and should be
34. further remarked that prior gas analyses showed that a

1. practically static condition had been reached. In other
2. words, the proportions of methane and carbon monoxide
3. found in the system were no longer increasing. The
4. lowered yield of methanol in the condensate is attribut-
5. able only to the disadvantageous reactions previously
6. mentioned, which, on account of greater rapidity or
7. selective action permit the decomposition of carbon
8. dioxide and of hydrogen without a corresponding methanol
9. production.

10. The results of the experiment show that while
11. the use of a gas mixture of theoretical proportions of
12. carbon dioxide and hydrogen in the methanol process does
13. not produce a theoretical quantity of methanol, still a
14. more or less static condition is set up after a time in
15. the circulating system. This is desirable, since it
16. permits operation without constantly changing the
17. proportions of the "make-up" gas to maintain a definite
18. proportion of gases in the circulating system.

19. By experiment, I have discovered that when the
20. proportion of carbon dioxide to hydrogen is greatly
21. decreased the percentage of methanol in the condensate
22. approaches more closely the theoretical figure
23. (approximately 70%), which indicates that by the use of
24. such proportions the undesirable side reactions are
25. partially or wholly inhibited and the waste of gases is
26. thus avoided. I have discovered that when the gas
27. mixture passing over the catalyst comprises 1.5% carbon
28. dioxide and 99-95% hydrogen, the most favorable results
29. are obtained.

30. While the supplying of gases to the process
31. in these favorable proportions produces the desirable
32. result mentioned, it is obvious that difficulties would
33. be encountered on the continued operation of the process.
34. If a mixture of 3% carbon dioxide and 97% hydrogen is

Case B

1. constantly supplied to the process, all of the carbon
2. dioxide will be converted to methanol but a great excess
3. of hydrogen will remain unreacted. If the "make-up gas"
4. supplied to the process to maintain the pressure is of
5. the same composition, the result occurring on continued
6. operation will be a gradual diminution in the percentage
7. of carbon dioxide in the system until it reaches an
8. infinitesimal figure at which practically no methanol
9. will be formed.

10. In the practice of my invention this diffi-
11. culty may be easily avoided. To adjust the process so
12. that a gas of any desired proportion of carbon dioxide
13. will be present in the mixture passing over the catalyst,
14. the circulatory system in which the process operates is
15. filled with substantially pure hydrogen gas at a pressure
16. somewhat below the pressure desired for operation. The
17. circulation of this gas through the system naturally
18. produces no reaction of any kind. When this adjustment
19. has been accomplished a change is made in the gas supplied
20. under pressure to the system and instead of pure hydrogen,
21. a mixture of carbon dioxide and hydrogen in the pro-
22. portions theoretically required to make methanol is
23. supplied to the system. This gas blends with the pure
24. hydrogen in the system and at the point where the gases
25. pass the catalyst, the percentage of carbon dioxide is
26. very small.

27. Since under the favorable reaction conditions
28. thus effected the carbon dioxide is converted almost
29. entirely to methanol; the amount of carbon dioxide dis-
30. appearing from the system is directly proportionate
31. to the amount of hydrogen disappearing. Consequently if
32. the gas mixture of theoretical proportions is constantly
33. supplied as make-up gas at a rate which maintains a
34. constant pressure in the system, methanol and water are

Case B

1. continually produced, and the composition of the gas in
2. the circulating system remains unchanged. In this
3. manner a most desirable "static condition" is set up in
4. which a gas of one unvarying composition remains in the
5. circulating system and another gas of a different but
6. also unvarying composition is supplied to the system at
7. the same rate at which the theoretical mixture of
8. methanol and water is formed.

9. Instead of filling the circulating system with
10. pure hydrogen at a pressure approximating the pressure
11. desired for the reaction, the gas placed in the circu-
12. lating system may contain some carbon dioxide. This
13. may be accomplished either by filling the system at the
14. pressure of operation with a gas containing a pre-
15. determined quantity of carbon dioxide, or by passing
16. pure hydrogen into the system until only part of the
17. pressure desired for operation has been attained, and
18. then adding a gas containing theoretical proportions of
19. carbon dioxide and hydrogen, until the desired pressure
20. has been attained. In this manner it is possible to
21. adjust the gas in the circulating system to any desired
22. ratio of carbon dioxide to hydrogen. Then, to operate
23. the process, the "make up gas" of theoretical proportions
24. is supplied to the system and a similar static condition
25. may be attained.

26. However if this adjustment produces a circu-
27. lating system gas which contains more than 5% of carbon
28. dioxide, a loss of gases will occur on account of the
29. undesirable reactions previously described. Large
30. quantities of methane and carbon monoxide will be built
31. up in the system and while continued operation of the
32. process will finally produce a static condition in that
33. the composition of gases in the circulating system
34. becomes unchanging in composition, the yield of methanol
35. will be much lower than that theoretically obtainable.

Case B

1. Typical results obtained by this method of
2. operation are indicated in the following tabulations:-

Table I

4. Expt. No.	6. Analysis of gases Circulating over Catalyst				Yield *	Purity **	Operation ***
	CO ₂	CO	CH ₄	H ₂			
6. 1	11.0	7.5	10	71.5	2.9	60.5	12
7. 2	6.5	7.0	9	77.5	3.4	62	11
8. 3	3.2	5.2	6	85.6	3.1	63	12
9. 4	2.0	3.2	2	92.8	2.0	66	10

10. *Liters of condensate per hour per liter of catalyst.
11. **Percent by volume of methanol in condensate (Remainder
12. being water).
13. ***Hours of operation at time of test.

14. In the experiments above reported, a pressure
15. of 3500 pounds was employed, and the "make-up gas"
16. supplied to the process was a mixture of carbon dioxide
17. and hydrogen of approximately the theoretical proportions
18. required for methanol production. The temperature
19. employed was 420° C. in each case, and a space velocity
20. of 100,000 was employed. The variance in results shown
21. in the experiments is due to variance in the gas present
22. in the circulating system before the methanol reaction
23. was started - that is before the make-up gas was
24. supplied to the process.

25. Table I indicates that as the percentage of
26. carbon dioxide in the circulating gases was reduced from
27. 11% to 2%, the per cent of methanol in the condensate
28. was increased from 60.5% to 66%. The percentages of
29. methane and carbon monoxide present in the circulating
30. system are also reduced as the result of the diminution
31. in carbon dioxide. The fact that in Experiment 4 the
32. percentage of carbon monoxide in the circulating gases

Case B

1. exceeded the percentage of carbon dioxide is of no
 2. importance, for the production of a larger percentage of
 3. methanol in the condensate than was obtained in the other
 4. experiments indicates that disadvantageous side reactions
 5. were diminished in activity. Apparently the methane
 6. and carbon monoxide were formed during the first stages
 7. of reaction before a static condition in the circulat-
 8. ing system was attained.

9. While Experiment 2, employing 8.5% carbon
 10. dioxide in the circulating system, gave the largest
 11. yield of condensate per hour, this is not the consider-
 12. ation of prime importance in the economy of the process.
 13. Any desired yield of condensate per hour may be obtained
 14. by increasing the apparatus and the amount of catalyst
 15. employed. The greatest economy and efficiency of
 16. operation is attained when all of the gases removed from
 17. the process enter into the production of the theoretical
 18. mixture of methanol and water, rather than disadvantag-
 19. eous side reactions. For example, the same volume of
 20. condensate per hour as was obtained in Experiment 2 may
 21. be obtained in Experiment 4 by merely doubling the amount
 22. of catalyst employed, and modifying the apparatus accordingly.

Table II

24.	Expt. No.	Analysis of Gases Circulating over Catalyst				Yield *	Purity **	Time of Operation ***
25.		CO ₂	CO	CH ₄	H ₂			
26.	5	11	15	9	66	2.45	63	12
27.	6	7.2	13	6	73.8	1.95	65	12
28.	7	3	2.5	1	93.5	1.85	69	10

29. *Liters of condensate per hour per liter of catalyst.

30. **Per cent of volume of Methanol in condensate
(Remainder being water)

31. ***Hours of operation at time of test.

32. In the experiments reported in Table II a

Case B

1. pressure of 3500 pounds was employed and the "make-up"
2. gas supplied to the process was a mixture of carbon
3. dioxide and hydrogen of approximately the theoretical
4. proportions required for methanol production. In each
5. case a temperature of 390° C. and a space velocity of
6. 60,000 was employed.

7. Table II confirms Table I in showing the
8. favorable effect obtained by employing a gas mixture
9. containing only a small proportion of carbon dioxide.
10. Since the temperature employed (390° C.) is a more favor-
11. able one, the purity of the methanol thus produced is
12. greater; for example, Experiment 7 produced a condensate
13. containing practically the theoretical proportions of
14. methanol and water.

15. My process is in no way dependent on the use of
16. a specific catalyst. In general, any catalyst suitable
17. for synthetic methanol production may be employed in the
18. process, these catalysts ordinarily consisting of
19. mixtures of metallic oxides such as are described, for
20. example, in United States Patents 1,558,559; 1,608,643;
21. and 1,609,593; and English Patents 229,714 and 229,715.

22. My invention is in no way dependent, for its
23. operation, on the employment of the specific apparatus
24. disclosed in the drawing and it is obvious that many
25. manipulative variations might be made without departing
26. from the spirit thereof.

27. My invention is not dependent on the mainten-
28. ance of a static condition within the circulating system
29. whereby make-up gas of theoretical proportions is
30. passed into a system of circulating gas originally
31. composed of substantially pure hydrogen, this process
32. being the subject matter of Application Serial No.

33. ~~filed~~

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Case B

1. For example, the favorable result attendant on the use
2. of a very small proportion of carbon dioxide in the
3. methanol synthesis may be accomplished by passing a gas
4. of the proportion of 3% carbon dioxide and 97% hydrogen
5. into the system under pressure, circulating it to make
6. methanol, gradually adding carbon dioxide to the system
7. to replenish the carbon dioxide converted to methanol,
8. and, occasionally adding some hydrogen to maintain the
9. correct proportions of materials in the circulating gas.
10. Or, alternatively, the circulating system may be dis-
11. pensed with and a gas of the correct proportions may be
12. passed through a number of catalyst beds in series,
13. pressure being maintained in the system, so that a
14. preponderance of the gas entering the system is convert-
15. ed to methanol and water by one passage, the residual
16. gases being recovered for use in another passage.

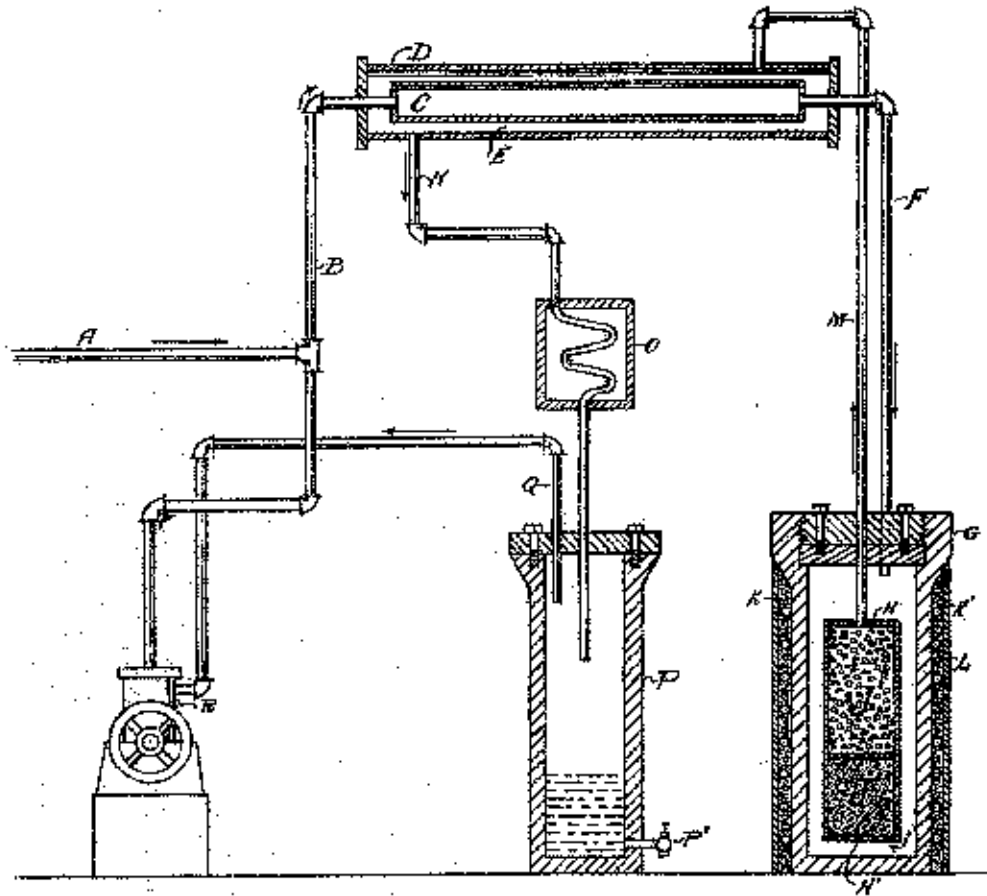
17. Now having fully described my invention, I
18. claim the following as new and novel.
19. 1. In the process of manufacturing methanol
20. by the interaction of hydrogen and carbon dioxide in the
21. presence of a catalyst and under the influence of
22. elevated pressure and temperature, the step which
23. comprises maintaining the proportion of carbon dioxide
24. in the gas contacting with the catalyst below that
25. proportion theoretically required for reaction with all
26. of the hydrogen present.
27. 2. In the process of manufacturing methanol
28. by the interaction of hydrogen and carbon dioxide in the
29. presence of a catalyst and under the influence of
30. elevated pressure and temperature, the step which
31. comprises maintaining the concentration of carbon
32. dioxide in the gas contacting with the catalyst below 11%.
33. 3. In the process of manufacturing methanol

Case B

1. by the interaction of hydrogen and carbon dioxide in the
2. presence of a catalyst and under the influence of
3. elevated pressure and temperature, the step which
4. comprises maintaining the concentration of carbon
5. dioxide in the gas contacting with the catalyst below 5%.
6. 4. In the process of manufacturing methanol
7. by the interaction of hydrogen and carbon dioxide in the
8. presence of a catalyst and under the influence of
9. elevated pressure and temperature, the step which comprises
10. maintaining the concentration of carbon dioxide in the
11. gas contacting with the catalyst at substantially 2%.

286289
Synthetic Methanol Process.

286289



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

June 10th 1927

Terre Haute, Indiana,
U.S.A.

William J. Edmonds

APPLICANT

Bruce K. Brown

ATTORNEY