

PATENT SPECIFICATION

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(54) PROCESS FOR THE PRODUCTION OF DIMETHYL ETHER

(71) We, SNAMPROGETTI S.P.A. (formerly known as Snam Progetti S.p.A.), an Italian company, of 16 Corso Venezia, Milan, Italy, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of dimethyl ether (DME) and is concerned with a process for the production of dimethyl ether via methyl alcohol.

Dimethyl ether may be produced by a Fischer-Tropsch type reaction through a direct synthesis from CO and H₂ according to the reaction



but the amount of by-products formed would be extremely high since there is no known selective catalyst which would be capable of carrying out the reaction exclusively in the aforesaid way.

Thus if dimethyl ether were to be produced according to the above reaction it would be necessary to separate the dimethyl ether from all the by-products formed; this, besides rendering the process complicated, would entail substantial apparatus and operating costs.

It is an object of the invention to produce dimethyl ether in a selective way, avoiding the drawbacks which would be encountered if use were to be made of the aforesaid reaction.

In accordance with the invention there is provided a process for producing dimethyl ether, which comprises reacting CO, CO₂ and H₂ in the presence of a catalytic body comprising a catalyst for the synthesis of methyl alcohol and a catalyst for the dehydration of methyl alcohol, so as to produce dimethyl ether.

The catalytic body may comprise a catalyst for the synthesis of methyl alcohol, preferably a copper containing catalyst or a

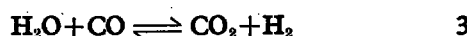
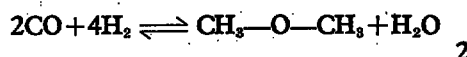
chrome-zinc base catalyst, disposed on an active carrier which is a catalyst for the dehydration of methyl alcohol, preferably alumina. Alternatively the catalytic body may be composed of alternate layers of the methyl alcohol synthesis catalyst and of the methyl alcohol dehydration catalyst, or of an admixture of the two catalyst.

The reaction may be effected at a temperature in the range of, for example from 220 to 320°C. when a copper containing catalyst is used as the methyl alcohol synthesis catalyst or from 280 to 400°C. when a chrome-zinc base catalyst is used.

The reaction may be effected at a pressure in the range of, for example from 30 to 500 kg/cm².

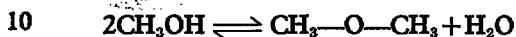
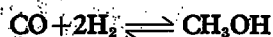
By employing the process of the invention it is possible to obtain a high conversion rate of CO, CO₂ and H₂ in the reaction, since most of the synthesized methyl alcohol, as soon as it forms, is dehydrated to DME and the catalyst bed always operates in the presence of small methyl alcohol concentrations. This fact allows most of the gases fed to the reactor to be transformed into DME plus a certain percentage of residual methyl alcohol, with the result that only a small amount of unreacted gas has to be recycled to the reactor, thus enabling the consequent economical and operative advantages to be obtained.

The chemical reactions which occur in the synthesis of dimethyl ether may be represented as follows:



Of these equations the one numbered 2 is a linear consequence of the reactions numbered 5 and 1 and the one numbered 4 depends on the reactions numbered 3 and 1.

Reactions occurring in the synthesis reactor can therefore be represented by the following chemical equations:



Even if the dehydration reaction of methyl alcohol is thermodynamically more favoured than that of the methyl alcohol synthesis, the presence of water in the reacted gas does not allow a high dehydration of methyl alcohol and also tends to reduce the percentage of transformation of fresh gas into DME per passage through the reactor.

If a relatively CO_2 rich synthesis gas (for instance one produced by steam reforming of light hydrocarbons, in which gas the amount of CO_2 is of the same order of magnitude as that of CO) is used, it is necessary to increase the amount of water to reduce the conversion of CO_2 to CO according to reaction 3 and hence the transformation of CH_3OH into DME per passage is lowered.

However, this difficulty can be avoided by using a CO rich gas having a low CO_2 concentration, which gas can be obtained, for instance, by partial combustion of relatively heavy hydrocarbons or by coal gasification, wherein the amount of CO present is in a large excess with respect to the stoichiometric amount necessary for the methyl alcohol synthesis.

By working with such a gas, it happens that the dehydration water, as soon as it forms, is consumed by the excess CO (thus producing $\text{CO}_2 + \text{H}_2$) and consequently the methyl alcohol dehydration reaction and the synthesis reaction related to the dehydration reaction take place at a very high conversion rate (up to for example 80% per passage through the reactor).

The following qualitative example will clarify this important concept. Starting from a gas having a H_2/CO ratio lower than 2, i.e. lower than the value required for producing methyl alcohol, in accordance with the conventional technique, it would be necessary to convert with steam to CO_2 and H_2 , the excess of CO and to eliminate the CO_2 produced.

By working on the contrary according to the present invention, the synthesis gas composition does not need to be adjusted because the conversion of CO to CO_2 and H_2 will take place directly in the synthesis reactor (in fact the copper or chrome-zinc base catalysts are extremely active with regard to the

water gas reaction $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$) by consuming the dehydration water as soon as it forms so allowing very high yields per passage through the catalytic bed to be obtained.

As a limit, when CO is in large excess in comparison with hydrogen, the single dehydration water may not even be sufficient to guarantee a good CO conversion and therefore it will be useful to add some steam.

It is to be observed that if the methyl alcohol synthesis is effected in a first reactor and then the dehydration to dimethyl ether of the resulting methyl alcohol is carried out in a second reactor, the methyl alcohol synthesis plant would be of conventional type and therein the conversion would be very low (10—15%). Consequently recycling would be necessary and increased costs would be involved since the plant for dehydrating methyl alcohol to dimethyl ether would require a heat consumption for vaporizing methyl alcohol, a rectification of the product and a recycle of the unconverted methyl alcohol.

It is obvious that with such a scheme the dimethyl ether cost would be higher than the methyl alcohol cost.

In the case of the present invention the dimethyl ether cost is on the contrary even lower than the cost of methyl alcohol produced according to the conventional techniques owing to the greater plant simplicity.

Dimethyl ether produced in accordance with the invention may be used as a fuel for domestic or industrial uses. This is of particular importance now that energy sources are rapidly becoming exhausted or difficult to obtain. In this connection it is considered that DME is likely to have a much wider field of use than methyl alcohol produced from natural gas.

The process of the invention may be carried out in a reactor of the type shown schematically in the accompanying drawing, in which a synthesis reactor 1 which is of the isothermal type is adapted for the removal of the reaction heat to a steam generator 2 for producing steam. The raw gas is fed through a pipe 4 and the reaction products are discharged through a pipe 5.

The following Examples illustrate the invention.

EXAMPLE 1

The gas to be transformed, which was at a pressure of 100 kg/cm^2 and temperature of about 250°C ., was fed to a reactor wherein the methyl alcohol synthesis reaction and the dehydration of the methyl alcohol occurred contemporaneously in accordance with the invention.

The characteristics of the feed gas, obtained by the known process of partial oxidation of

methane with O_2 , and of the process conditions, were as follows:

5	Flow rate	100,000 Nm ³ /h
	Composition:	
		by weight
	H ₂	62.67%
	CO	35.20%
	CO ₂	1.46%
	CH ₄	0.37%
10	N ₂	0.30%
		100.00%

Temperature 250°C.
Pressure 100 kg/cm²
Catalyst: Cu/Zn/Cr with an atomic ratio equal to 82/16/4, the carrier being alumina.

The reaction gas leaving the reactor had the following characteristics:

20	Flow rate	56,000 Nm ³ /h
		by weight
	H ₂	48.58%
	CO	8.45%
	CO ₂	17.75%
	CH ₄	0.66%
25	N ₂	0.53%
	CH ₃ OH	2.23%
	CH ₃ OCH ₃	18.48%
	H ₂ O	3.32%
		100.00%

30 Temperature 270°C.

The product obtained comprised 1,250 Nm³/h of methyl alcohol and 10,360 Nm³/h of DME.

35 This means that the conversion per passage based on CO+H₂ present was 67%.

EXAMPLE 2

40 The characteristics of the feed gas, obtained by the process of partial oxidation with O₂ of a heavy oil, and of the process conditions, were as follows:

	Flow rate	100,000 Nm ³ /h
	Composition:	
		by weight
45	H ₂	44.70%
	CO	51.90%
	CO ₂	1.78%
	CH ₄	0.27%
	N ₂	1.35%
		100.00%

50 Temperature 250°C.
Catalyst: the same as in Example 1.

The reactor gas leaving the reactor had the following characteristics:

	Flow rate	50,350 Nm ³ /h	
	Composition:		55
		by weight	
	H ₂	14.05%	
	CO	29.97%	
	CO ₂	27.30%	
	CH ₃ OH	0.91%	60
	CH ₃ OCH ₃	24.20%	
	CH ₄	0.54%	
	N ₂	2.62%	
	H ₂ O	0.41%	
		100.00%	65
	Temperature	270°C.	

There were produced 460 Nm³/h of CH₃OH and 12,150 Nm³/h of DME.

This corresponds to a transformation of feed CO+H₂ equal to 77%.

With respect to the foregoing Example, because of the higher excess of CO, there is a higher total yield and also a higher methyl alcohol dehydration. The above conversion values appear very high when compared with the values obtainable with conventional processes for methyl alcohol synthesis, wherein conversions per passage are in the range of from 10 to 15%. The considerable advantages obtainable in a plant working according to the invention are therefore obvious.

For the transformation of methane into a more liquefiable and transportable fuel, in the process of Example 1 the complete synthesis cycle can be constituted by a first reactor with a high yield (67%) wherein most of DME is produced; subsequently, after separation of DME, residual methyl alcohol and excess CO₂, which in this case is not high, the residual gas can be fed to a second reactor for the synthesis and dehydration of methyl alcohol for further conversion.

In the process described in Example 2, for the transformation of heavy oil into DME, because of the high CO₂ excess, it will be convenient to transform most of the feed (77%) in a first reactor and, after separation of the resulting DME and methyl alcohol, to feed to a second reactor, possibly working at a higher pressure, the remaining gaseous mixture in order further to transform into DME and methyl alcohol the remaining CO and H₂, without eliminating the CO₂ obtained. It is possible to foresee that the total conversion may be 90%. The residual gas, after separation of the products, can be vented or used as a burning gas having low heat value.

Since the dehydration water is consumed as soon as it forms, there is obtained a product very concentrated in DME (95—96% by weight) which product does not require any rectification operation.

There will therefore be no need to provide expensive plants for CO conversion and for decarbonation and, possibly, for rectification.

- 5 The process according to the invention is therefore important not only for transforming natural gas into a fuel which is more easily liquefiable and transportable, but, and particularly, for transforming into a more valuable form, namely DME, coarse fuels such as
- 10 heavy oils and pit-coal, in competition with processes for the production of synthesis natural gas.

WHAT WE CLAIM IS:—

- 15 1. Process for producing dimethyl ether, which comprises reacting CO, CO₂ and H₂ in the presence of a catalytic body comprising a catalyst for the synthesis of methyl alcohol and a catalyst for the dehydration of methyl alcohol, so as to produce dimethyl
- 20 ether.
2. Process according to Claim 1, wherein the catalytic body comprises a catalyst for the synthesis of methyl alcohol disposed on an active carrier which is a catalyst for the
- 25 dehydration of methyl alcohol.
3. Process according to Claim 2, wherein the catalyst for the synthesis of methyl alcohol is a copper containing catalyst.
- 30 4. Process according to Claim 2, wherein the catalyst for the synthesis of methyl alcohol is a chrome-zinc base catalyst.
5. Process according to Claim 3, wherein the reaction is effected at a temperature of from 220 to 320°C.
- 35 6. Process according to Claim 4, wherein the reaction is effected at a temperature of from 280 to 400°C.

7. Process according to any one of Claims 2 to 6, wherein the active carrier is alumina.

8. Process according to any preceding claim, wherein the reaction is effected at a pressure of from 30 to 500 kg/cm².

9. Process according to Claim 1, wherein the catalytic body is composed of alternate layers of the catalyst for the synthesis of methyl and of the catalyst for the dehydration of methyl alcohol.

10. Process according to Claim 1, wherein the catalytic body is composed of an admixture of the catalyst for the synthesis of methyl alcohol with the catalyst for the dehydration of methyl alcohol.

11. Process according to any preceding claim, wherein the CO, CO₂ and H₂ are obtained by partial oxidation of substantially heavy hydrocarbons or coal gasification.

12. Process according to any preceding claim, wherein the CO is present in excess with respect to the stoichiometric value.

13. Process for producing dimethyl ether, substantially as described in either of the foregoing Examples.

14. Dimethyl ether whenever produced by the process claimed in any preceding claim.

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3. Process according to Claim 2, wherein the catalyst for the synthesis of methyl alcohol is a copper containing catalyst.
4. Process according to Claim 2, wherein the catalyst for the synthesis of methyl alcohol is a chrome-zinc base catalyst.
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