Methanol from natural gas: proven and new technologies

Citation for published version (APA):

Geerts, J. W. M. H., Hoebink, J. H. B. J., & Wiele, van der, K. (1990). Methanol from natural gas: proven and new technologies. *Catalysis Today*, 6(4), 613-620. <https://doi.org/10.1016/0920-5861%2890%2985059-W>

DOI:

[10.1016/0920-5861%2890%2985059-W](https://doi.org/10.1016/0920-5861%2890%2985059-W)

Document status and date:

Published: 01/01/1990

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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METHANOL FROM NATURAL GAS. PROVEN AND NEW TECHNOLOGIES.

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SUMMARY

The world methanol consumption has surpassed 25 million tons per annum and is still growing steadily, indicating an increasing importance of methanol in the bulk chemicals market. At present, methanol is produced in a two step process: steam reforming of a hydrocarbon feedstock, followed by synthesis gas conversion into methanol.

Single step methanol production by partial oxidation of methane is a promising new catalytic process providing new opportunities for natural gas utilization. To study the economic perspective of such a new process and to set targets for further research, a process design study was carried out, based on literature data with respect to kinetics and yields. This study included investment and production cost estimates relative to those of existing plants.

The results prove that the new process is less economic, unless extremely selective catalysts are developed. Using the present data, the investment is of a similar level, while the variable costs are much higher due to the lower carbon efficiencies and the consumption of "expensive" oxygen.

INTRODUCTION

The world methanol supplies and demands are shown in Table 1 (ref. 2). A small surplus in methanol production exists, which has lead to moderate market prices.

Methanol is nowadays produced by reforming (autothermal or steam) of hydrocarbons to synthesis gas which in its turn is converted to methanol.

Among the sources of hydrocarbons: petroleum residues, naphtha, coal and natural gas, the latter is by far the most important. The important existing commercial processes: the ICI process and the Lurgi process are more or less equal (ref. 3).

Historically, about a third of the methanol produced is used to make formaldehyde, see Figure 1. A large percentage of the formaldehyde is consumed in products for housing and the automotive market. These markets are highly sensitive to changes in the economy, which explains partly the major gains and losses in the methanol production. Fast growing consumers of methanol are the acetic acid

TABLE 1
World methanol supply and demand (in million tons/year).

	1985	1986	1987 [#]
supply	18.4	21.1	24.3
demand	15.9	18.1	22.0
[#] :Prediction

Figure 1. Methanol as an important intermediate in the chemical industry.

Figure 2. Selectivity with respect to methanol and formaldehyde versus methane conversion for various catalysts (ref. 7).

production and the production of gasoline octane improvers such as Methyl-Tert-Butyl Ether (MTBE). A promising area is the direct use in fuels or a feedstock in Mobil's MTG (Methanol To Gasoline) process. Also promising is the production of Single Cell Proteins which can be used as animal food additives.

Besides the above described processes, a new not yet existing one is indicated by a dashed arrow in Figure 1. It is the direct partial oxidation of methane, the main component of natural gas, to methanol.

The direct oxidation of methane to methanol and formaldehyde has been investigated by several authors. Recent reviews have been published by Foster, Gesser and Hunter, and Edwards and Foster (ref. 4-6). Oxygen, air and dinitrogen oxide have been proposed as oxidants and a wide range of materials have some catalytic activity (ref. 7). However, high selectivities to methanol or formaldehyde are only possible at very low conversion levels of methane, see Figure 2, resulting in poor yields.

However, in the future new better catalysts will be developed. In a US patent (ref. 8) 80% methanol selectivity at 20% methane conversion is already claimed without the use of a catalyst. Therefore, starting points as stated in Table 2 were chosen for the present study.

TABLE 2
Starting points of the design study.
Single pass values.

	Case A	Case B
CH ₄ conv.(%)	10	20
Selectivities (%):		
CH ₃ OH	80	60
CH ₂ O	4	8
CO ₂	16	32

Oxygen was chosen as the oxidising agent, for it is relatively cheap. Because the methane conversion per pass is low, the surplus of methane has to be recycled. To prevent an enormous nitrogen recycle or an expensive separation of nitrogen/oxygen and methane in the recycle, pure oxygen is used.

REACTOR DESIGN

A multi tubular fixed bed was chosen as the reactor, as it is easily scaled up. Preliminary calculations showed that heat removal from this reactor would not create serious problems. The following reactions in the catalyst bed have been taken into account:

Because the literature provides very little kinetic data for these reactions, simple kinetics were assumed. The total rate has been based upon the kinetics of the first reaction only, which was assumed to be first order in both methane and oxygen concentrations. The yields of CO_2 and formaldehyde were derived from the selectivities; CO formation has been omitted since no information about the CO selectivity was available. Temperature dependence of the rate constant was estimated according to Arrhenius' law from published data. Relevant data are summarized in Table 3.

The reactor dimensions (tube length and diameter, and number of tubes) were determined by numerical simultaneous integration of the differential heat and mass balances. Heat removed through the tube walls is used to produce superheated steam at a pressure of 120 bars. Precautions were taken to prevent radial temperature profiles and pore diffusion limitation.

The basic design criterion was an approximately zero oxygen concentration in the reactor outlet to prevent consecutive oxidation reactions behind the catalyst bed. The reactor was to produce 400,000 tons/y of methanol, assuming 8000 operating hours a year.

TABLE 3
Relevant data for the reactor design
(Catalyst; ref. 9).

Kinetics:		
rate constant	8.8E5	m ³ /skmol
activation energy	7.0E4	kJ/kmol
reaction heat (A)	2.4E5	kJ/kmol
Catalyst MoO ₃ ·UO ₂ :		
spheres, diameter	2	mm
Feed (case A):		
methane	8.8	kg/s
oxygen	stoichiometric	
temperature	500	K
pressure	54	bar
Outlet O ₂ conc.	0	
Methanol prod.	400,000	tons/y

TABLE 4
The designed reactor.

Number of tubes	1500
Tube diameter	0.06 m
Tube length	3.6 m
Outlet temperature	745 K
Residence time	1.4 s
Pressure drop	0.1 bar

Figure 3. Case A. The methane conversion profiles as a function of the number of reactor tubes:

1 = 1900 3 = 1500
2 = 1700 4 = 1300 tubes.

Figure 4. Case A. Axial temperature profiles as a function of the number of reactor tubes:

1 = 1900 3 = 1500
2 = 1700 4 = 1300 tubes.

More details are reported elsewhere (ref. 1).

As an example of calculation results Figures 3 and 4 present the conversion and temperature profiles respectively inside the reactor for case A; the number of tubes is used as a parameter, while the tube diameter is fixed at 6 cm. A decrease of the number of tubes means an increasing superficial velocity. Correspondingly, a longer reactor must be used. Table 4 shows relevant reactor data that meet the demands of the design for case A.

PROCESS DESIGN

A process flow diagram has been developed, a general outline of which is presented in Figure 5. Calculations were made using the flow sheet simulation program "Process" (ref. 10).

So-called Balgzand gas is taken as feed for the plant; its composition is shown in Table 5. The higher hydrocarbons are assumed to be burned inside the reactor. Oxygen and natural gas are supposed to be delivered to the plant at 40 bar pressure.

Unconverted reactants are separated from the reactor effluent and recirculated to the reactor. Therefore, the stream leaving the reactor is cooled down to 300 K. In a vessel T1, liquid methanol is in equilibrium with and separated from a gas, which is subsequently washed with water in tower A1 for

TABLE 5
Composition of Balgzand gas in vol %.

CH ₄	88.3
C ₂ H ₆	4.3
C ₃ H ₈	0.89
i-C ₄ H ₁₀	0.11
n-C ₄ H ₁₀	0.17
C ₄ ⁺	0.108
CO ₂	1.65
N ₂	4.27
He	0.055
S (mg/m ³)	6-10

Figure 5. The flow sheet designed for the direct partial oxidation of natural gas into methanol.

R1 = Reactor C1-3 = Compressors
 A1 = Wash Tower H1-4 = Heat exchangers
 A2 = Benfield Unit T1 = Methanol Separator

main process equipment can be found in ref. 1. The 120 bar steam, produced in the reactor R1 and heat exchanger H2, is used for heating the recirculation stream and for driving both the recirculation compressor C1 and the feed gas compressors C2 and C3.

ECONOMIC FEASIBILITY

Investment estimate

The capital investment, that is required for the production of 400,000 tons of methanol per year according to the process described in the previous paragraph, has been estimated, using the well-known Miller method (ref. 11,14). In this method free-on-board-costs of shop-fabricated main process items are used as the starting point for the investment estimate. Additional costs as for installation, instrumentation, services, buildings etc. are calculated using specific factors based on experience. The way of determining such factors has been extensively described (refs. 11,14). Miller's method, having an accuracy of about 25 % is very suitable for selection of the most profitable process from alternative designs. Therefore, the method has been applied to both cases A and B of the new process, as well as to the conventional way of methanol production. For the latter process the necessary information was supplied by Methanor, a large methanol manufacturer

further methanol removal. Most formaldehyde is taken away with the water as well. The off-gas of the wash tower A1 is split into three: one part goes directly to the recirculation compressor, another part is fed to a Benfield unit for CO₂ removal, and a third part is purged to prevent accumulation of inert gases. The natural gas is directly fed into the Benfield unit to remove CO₂ and H₂S impurities. Before entering the reactor the recirculation stream is heated up to reaction temperature. Simple atmospheric distillation is applied in three columns to recover the methanol product. Detailed information about streams and

in Delfzijl, the Netherlands. A summary of the results of the calculations is presented in Table 6; more details are given in ref. 1. It appears from this table that the new single step process does not lead to a considerable reduction of investment capital when compared to the conventional process. The main costs are the distillation section and the large heat exchange batteries, which become expensive, since the limited conversion levels require large capacities, and much recycling.

TABLE 6
Investment estimates for the conventional process and the direct partial oxidation process (in million US \$).

	Convent.	Direct ox.
Battery Limits	40	35
Utilities	41	36
Total Direct Costs	81	71
Indirect Costs	20	18
Contingencies	4	5
Fixed Capital	106	93
Land	5	5
Working Capital	15	15
Total Cap. Invest.	126	113

Profitability

The profitabilities of both the conventional and the direct partial oxidation process were determined using Holland's method (ref. 12-14). This method is based on assumed relationships between costs and plant capacity and complexity. The total expenses are formed by the total manufacturing expenses (= all costs due to production), the depreciations (= 10% of total fixed capital) and the general expenses (= administrative costs, distribution, selling, research & development). The total manufacturing expenses are built up of the direct manufacturing expenses (= sum of raw materials, catalysts, utilities like electricity and water, labour, maintenance, and laboratory charges, minus byproduct credits) and the indirect manufacturing expenses (= overhead, package and storage, local taxes, and insurance). The annual profit after taxes is the revenues from sales minus the total expenses and minus the income taxes that have to be paid.

The natural gas price in the Netherlands is related to the oil price and the amount of consumed gas. Contract prices for large consumers are confidential

TABLE 7
Profitability of the conventional process and cases A and B of the direct partial oxidation process (in million US \$ at Jan. 1988)

	Conv.	Case A	Case B
Total Cap. Inves	126	113	113
Direct Manu. Exp	56.3	84.9	115.8
Indir. Manu. Exp	6.0	6.0	6.0
Depreciations	11.0	9.8	9.8
General Expenses	13.8	18.6	23.9
Total Expenses	87.1	119.2	155.5
Rev. From Sales	70.2	67.5	65.6
Annual Profit	-16.9	-51.7	-89.9

information. In this study, a price of US \$137.25/ton was assumed for gas delivered to the plant at 40 bar.

Oxygen will be supplied from a pipeline, also at 40 bar pressure, for a price of US \$ 49.75/ton. Calculations and enquiries proved that the costs for on-site production of oxygen are similar. The number of operators who actually run the plant was calculated to equal 27, including shifts. The vent streams are burned to produce electricity with an efficiency of 50 % and at a price of US \$0.05/kWh. Besides electricity, the revenues from sales exist mainly of methanol. Which January 1988 price of US \$ 175.6 per ton was used.

In Table 7 the costs, at January 1988 price levels, are summarized for the conventional process and case A and B of the direct partial oxidation process. The profitabilities of both processes were negative at January 1988. For the conventional process this was confirmed by the Methanor company. However, the profitability of the direct partial oxidation process is even worse than the one of the conventional process. Extra costs for oxygen and a poorer methane utilization account for these differences, see Table 7, because the raw materials form the major part of the direct manufacturing expenses. For the same reason, a high selectivity per pass is preferred over a high methane conversion per pass, compare case A and B. Figure 6 shows calculations of the minimum selectivity at complete methane conversion needed for the new process to be profitable if only raw material costs are taken into account. It appears from the figure that an overall methanol selectivity of at least 75% is required. This is a very high selectivity level compared with performances reported in the literature, see Figure 1. Although the price ratio between methanol and natural gas has increased since January 1988, the targets for a profitable new methane to methanol process will be difficult to reach.

CONCLUSIONS

In conclusion, a new production route to methanol by direct partial oxidation of natural gas is chemically a very interesting one, because in principal a 100 % carbon efficiency can be achieved. The process is quite feasible using conventional technologies. However, a much better catalyst performance has to be

Figure 6. Costs per ton of natural gas converted versus selectivity with respect to methanol.

achieved to meet the selectivity levels required for a profitable process.

ACKNOWLEDGEMENT

The financial support, which was provided by the European Communities under contract no. EN3C-0038-NL, and by the Netherlands Organization for Scientific Research (NWO) is gratefully acknowledged. The students W.J. Coppens, H. Geurts, T. Janssens, G.J. de Koning, Ch. Pijls, M.A. Schulten, E. Verdurmen and P. Vissers have contributed to this article.

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