

Techno-Economic Analysis for Ethylene and Oxygenates Products from the Oxidative Coupling of Methane Process

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The interest in natural gas as an alternative feedstock for ethylene production stems mainly from its clean burning qualities, its domestic resource base, and its commercial availability. As the price of crude oil increases and an oil shortage looms, in the future, it becomes a concern for scientists trying to use natural gas as an alternative source of energy and as a feedstock in chemical industries. Methanol is one of the prime candidates for providing liquid fuels from natural gas as an alternative from traditional petroleum-based sources. In this work, a commercial-scale (210 tons/day) methanol plant, operating at steady state, which uses catalytic partial oxidation as a primary route (for synthesis gas production) from non-reacted methane coming from Oxidative Coupling of Methane (OCM) reaction has been designed. The main reason that motivates the realization of this work is to exploit the availability of unreacted methane, coming from the exit flue gas products of the OCM reactor, and thus, design an alternative process for oxygenates products, such as formaldehyde and methanol, that can make the process economically attractive and designed so as to be industrially implemented. The total project investment, based on total equipment cost, as well as variable and fixed operating costs, was developed based on mass and energy balance information taken from Aspen Process Economic Analyzer simulation results. The basis of the analysis is a world-scale conventional methanol plant that converts 368000 m³ per day of methane into 210 tons per day of methanol and generates 76 tons/day of formaldehyde. Capital and operating costs are for a remote location where natural gas is available at €12.60 per 1000 m³. Payout time for this process, with an OCM plant, is around 8 years. This analysis suggests areas for research focus that might improve the profitability of natural gas conversion. Overall, the process described here appears to be feasible for the methanol production using non-reacted methane that comes from the OCM reaction process. This process can be implemented to enable optimum utilization of the methane gas based on market demand.

1. Introduction

Methane, which is the principal component of natural gas reserves, is currently being used for home and industrial heating and for the generation of electrical power. In many aspects methane is an ideal fuel because of the existence of distribution systems in most populated centers, its ease of purification and the fact that it has the largest heat of combustion compared to the amount of CO₂ formed, among all hydrocarbons. On the

other hand, methane is an under-utilized resource for chemicals and liquid fuels. Large resources of natural gas have made methane and also the NGL components (ethane and propane) important raw materials for the chemical industry. Natural gas reserves are increasing more rapidly than those of petroleum, and it is anticipated that this trend will extend well into the 21st century, according to Holmen (2009). Large amounts of methane are found in regions that are located far away from industrial complexes and often methane is found off shore that means its transportation is uneconomical or even impossible. Because of these large reserves in remote locations, gas transport to user locations is more difficult and expensive. It is more advantageous to convert the natural gas to the useful products and transport the end product to users. Thus, several researchers are currently making great efforts to direct conversion of methane as well as to the conversion of methane to value added products, such as ethylene (feedstock for petrochemicals), aromatics (ethyl benzene) and liquid hydrocarbon fuels (methanol). With this in mind, the development of a new process that converts directly methane into liquid fuel (e.g., gasoline), rather than through synthetic gas, has been carried out by Graf (2008). The indirect routes for methane conversion are based on partial oxidation. The most used reaction is the highly energy consuming steam reforming to produce synthesis gas (CO and H₂). The synthesis gas is converted either to liquid fuels through Fischer-Tropsch or to methanol and subsequently to olefins or gasoline. These two or three steps processes require high investments in production plants.

Considerable efforts have been made for many years to develop direct conversion reactions producing partially oxidized compounds (methanol and formaldehyde) and products derived from oxidative coupling of methane (ethane and ethylene). The direct partial oxidation of methane to methanol is one of the attractive potential industrial processes for the use of abundant natural gas resources. Being an exothermic reaction, the direct conversion of methane to methanol would be superior to the conventional industrial process for the production of methanol via syngas by steam reforming of methane in terms of energy efficiency. Techno-economic evaluation, mentioned by Zhang (2002), has demonstrated that giving over 70% methanol selectivity at 8–15% methane conversion, the direct process is able to compete with the indirect one. This paper describes a feasibility study on the production of methanol and formaldehyde using the non-reacted methane coming from the OCM reaction.

2. Design of the formaldehyde and methanol plant model

The designed process is different from a commercial methanol plant based on autothermal reforming of natural gas. It uses the non-reacted methane from the OCM reaction process, a gas phase by-product stream composed by H₂O, CH₄, CO₂, CO and H₂. Although this is a by-products stream with low economic value for the ethylene production process, the amount of CO produced is attractive enough to be used in the production of synthesis gas. First this gases are purified by removing the components that may affect the conversion into synthesis gas (ethylene traces), before being used in the methanol process. The non-reacted methane is employ as a raw material for the

formaldehyde reaction. The reactor uses the selective oxidation of methane yielded essentially CH_2O , CO , CO_2 , and H_2O , which takes into account chemical kinetics obtained from the fixed-bed reactor experiment by Yang et al. (1998). Additional oxygen as oxidant is required to fulfill the reaction conditions; the CH_4/O_2 molar ratio was about 7.5/1. Oxygen is supplied, producing the equivalent of 75.9 metric tons of CH_2O per day; this lower conversion is coupled with high selectivity, according to Lintz et al. (1999). All CH_2O formed in this reactor has been purified using a distillation column. After the formaldehyde production follows the synthesis gas production using the stream coming from the top of the demethanizer column of the formaldehyde purification section. For this section the synthesis gas comes from a fixed-bed reactor for the catalytic partial oxidation of methane at conditions suitable for the production of methanol used by De Smet (2001). Addition of CO_2 (from the OCM purification process with amines) is possible in order to adjust the carbon/hydrogen ratio, which depends on the concentrations of CO and CO_2 from the non-reacted methane. The gas exiting the reformer is cooled with water generating the steam for the reformer. The synthesis gas is compressed to 30 bar by intercooled compressors before entering the synthesis reactor. The reactor operates at $250\text{ }^\circ\text{C}$ and the composition of the outlet gas is calculated assuming chemical equilibrium. The chemical equations used in the production of methanol are given in Eqs. (1) – (3), and kinetic data were taken from Gallucci (2007). The flowsheet of the process is shown in figure 1.

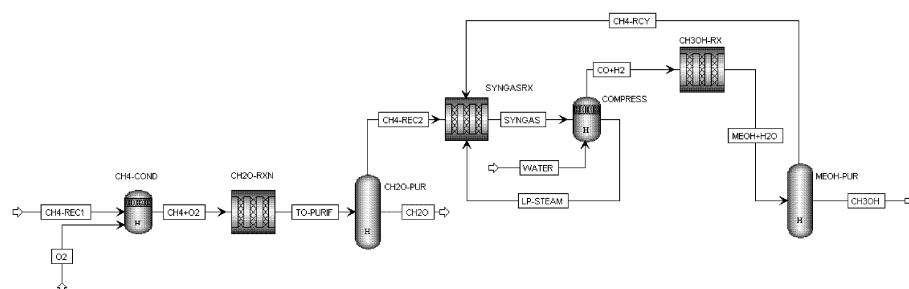


Fig. 1 Simplified flowsheet for the oxygenates plant process

The gas from the methanol reactor is cooled, and condensation of methanol and water occurs. Approximately 35% of the unconverted gas is recirculated to the synthesis reactor to get maximal methanol conversion with one reactor set. The heat generated by synthesis process is used for the distillation. Before entering the distillation column, the crude methanol stream is depressurized in a turbine generating 4019 kW of electricity

that counts for 16% of the compressor requirements. With this process, pure methanol is obtained (9308 kg/h) after water removal in the distillation column that operates at 9.6 bar.

3. Results

Table 1 summarizes the steady state flow rates of raw materials, products and by-products streams for the methanol plant concept presented in this work. For single pass reactors the methane conversion is 60% in the syngas reactor and for the methanol reactor the CO₂ conversion is 41%. Although the hydrogen required for the methanol production is generated from the reaction of synthesis gas, the initial H₂ needed can be provided from the reactor gas effluent from the OCM reaction process after separation of the ethylene. Moreover, in some recent studies Clausen (2010) suggests the use of hydrogen from electrolysis together with gasification of biomass to produce a biofuel. The investment of major plant areas for the oxygenated products plant was estimated and shown in Table 2.

Table 1 Mass flow rates of key components for oxygenated process

Raw Materials	Methanol Process (Ton/day)
Methane	1023.14
Oxygen	345.56
Products	
Methanol production	209.52
Formaldehyde production	75.86
Methanol purity (wt %)	99.70
Formaldehyde purity (wt %)	99.80
By-products	
H ₂ O	1.1
CO ₂	324.8
CO	875.9
H ₂	72.5
Non-reacted CH ₄	244.0

We found that the formaldehyde reaction and purification sections are much more expensive than the other plant sections, representing 27.9% and 39% respectively. The investment costs for the total plant are € 129 Millions and the total product sales (formaldehyde and methanol) are € 41,55 Million per year, with a methanol price of 353.8 €/ton for an annual methanol production of 72 tons in a plant located in the northern coast of the Venezuelan Caribbean Sea.

Due to high production costs caused by formaldehyde production, a second analysis was performed eliminating the production of formaldehyde and spending the total non-

reacted methane from OCM process in the methanol production; these results are shown in Table 3. The investment costs for the total plant were € 47 Million and the total methanol sales were € 25.3 Million per year, with same methanol price and production than the previous case.

Table 2 Capital expenses for oxygenates process

Process Section	Price (x10⁶ EUR)
1. Methane Conditioning	3.94
2. Formaldehyde Reaction	21.00
3. Formaldehyde Purification	29.37
4. Methane POX & Syngas	6.87
5. Gas Compressing	9.40
6. Methanol Reaction	0.82
7. Methanol Purification	3.96
Total Installed Equipment Cost	75.36
Total Direct and Indirect Costs	95.03
Contingency	17.11
Fixed Capital Investment	112.13
Working Capital	16.82
Total Capital Investment	128.95

Table 3 Capital expenses for methanol process

Process Section	Price (x10⁶ EUR)
1. Methane Conditioning	3.94
2. Methane POX & Syngas	6.87
3. Gas Compressing	9.40
4. Methanol Reaction	0.82
5. Methanol Purification	3.96
Total Installed Equipment Cost	24.99
Total Direct and Indirect Costs	31.51
Contingency	5.67
Fixed Capital Investment	37.18
Working Capital	5.58
Total Capital Investment	46.76

4. Conclusion

This analysis shows that it is possible to produce methanol from the non-reacted methane coming from the OCM process. The design of the process has taking into consideration the alternative production of valuable chemicals, such as methanol, giving added value to the OCM process, besides the ethylene production made with this use of

natural gas. This process can be implemented to enable an optimum utilization of the methane gas based on market demand. The payout period, the expected number of years required to recover the original investment in the project, is 4 years. This value indicates the length of time that the facility needs to operate in order to recover the initial capital investment (total capital cost plus working capital). For a project of 20 years, these results clearly show that it is possible an investment in the ethylene and ethanol processing technology using the scheme suggested here.

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