

TECHNO-ECONOMIC ANALYSIS FOR ETHYLENE AND OXYGENATES PRODUCTION USING THE OXIDATIVE COUPLING OF METHANE REACTION

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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 chemical process engineers 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 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, after ethylene separation, 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 $22.6 \times 10^5 \text{ m}^3$ per day of methane (at 15 °C, 1 atm) into 210 tons/day of methanol and generates 117 tons/day of formaldehyde. Capital and operating costs are for a remote location where natural gas is available at €6.82 per 1000 m^3 (Enagas, 2011). Payout time for this process, with an OCM plant, is around 9 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 CO_2 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 (Lunsford 2000; Hall 2005; Qian et al. 2009 and Vora et al. 2009) are making great efforts to direct conversion of methane to value added products, such as ethylene (feedstock for petrochemicals), aromatics (ethyl benzene) and liquid hydrocarbon

fuels (methanol) rather than through synthetic gas. With this in mind, new processes have been proposed such as direct conversion of methane into liquid fuel (e.g., gasoline) or an alternative approach: operating reactive separation of ethylene, combining separation of ethylene and production of a useful product. The separation of ethylene via alkylation of benzene to ethyl benzene has been carried out by Graf and Lefferts (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 and operational cost. 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 Oxidative Coupling of Methane (OCM) reaction right after the separation of the ethylene produced.

2. BRIEF DESCRIPTION OF THE OCM PROCESS

The OCM reaction is a highly exothermic process that is performed on metal oxide catalysts at temperatures between 700 and 900 °C. The process products are C₂H₆, C₂H₄, CO, CO₂, H₂ and H₂O. The CO_x (CO and CO₂) are formed from the complete combustion of hydrocarbons, which leads to point out the difficulties of achieving high performance in the OCM reaction process (Coronas, 1995). The complete process consists of three main sections: reaction, purification and separation section. Due to novel process design strategies, the downstream alternatives will also improve the reaction part and the catalyst design as well by means of for instance maximum carbon dioxide concentration for the reaction product. Figure 1 shows the flowsheet for this process.

2.1 Reaction Section

The reactor is continuously fed with natural gas and oxygen. The feed gas is preheated to 700 °C, catalytic partial oxidized at pressure of 115 kPa and the reaction is carried out at 850 °C. The exothermic reaction heat has to be immediately removed. The cooling of the cracked gas in the transfer line exchanger is carried out by vaporization of high-pressure boiler feed water, which is separated in the steam drum and subsequently superheated in the convection section to high-pressure superheated steam.

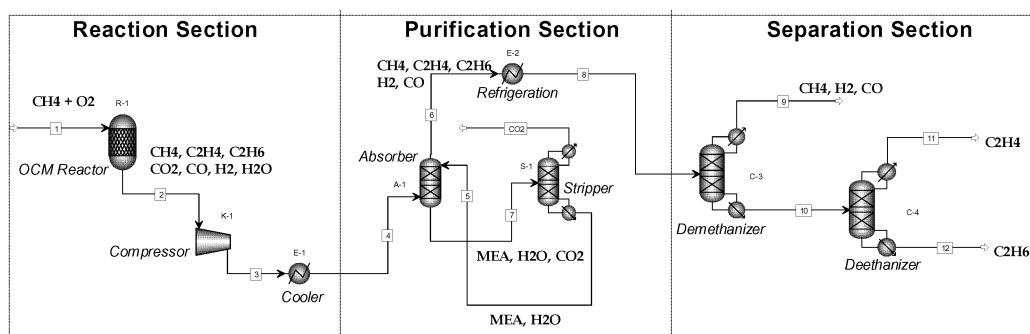


Fig. 1: Flowsheet for the Oxidative Coupling of Methane Process.

The reaction products are compressed in a multi-compaction section to 1090 kPa and cooled down to 40 °C later on. This stream is fed to the following purification section.

2.2 Purification Section

In this section the reactor effluent gasses are cooled and then are fed into the bottom stages of a series of absorber columns that uses monoethanolamine (MEA) as absorbent solution. The MEA solvent is then regenerated in stripper columns thereby releasing the CO₂ captured in a dilute stream with water vapor product. The CO₂ removal simulation model consists of an absorber and a stripper using rate-based calculation. The operation data from a pilot plant at TU Berlin were used to specify feed conditions and unit operation block specifications in the model.

2.3 Separation Section

This section consists of two cryogenic distillation columns. The first one is the demethanizer and the unconsumed methane is separated from the product stream (ethylene and ethane). Demethanization of OCM gas separates methane as an overhead component from C₂+ bottom components; concurrently, hydrogen is removed from the OCM gas stream and may be obtained as a product by purification before or after demethanization. The product stream consists of ethane and ethylene that is separated in the deethanizer.

3. 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 unreacted methane is used as raw material for the formaldehyde reaction. The reactor uses the selective oxidation of methane yielded essentially CH₂O, CO, CO₂, and H₂O, 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 CH₄/O₂ molar ratio was about 7.5/1. By the oxygen fed the reactor produces the equivalent of 75.9 metric tons of formaldehyde per day; this lower conversion is coupled with high selectivity, according to Lintz et al. (1999). All CH₂O formed in this reactor has been purified using two distillation columns. 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 CO₂ (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 CO₂ 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 °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 et al. (2007). The flowsheet of the process is shown in figure 2.



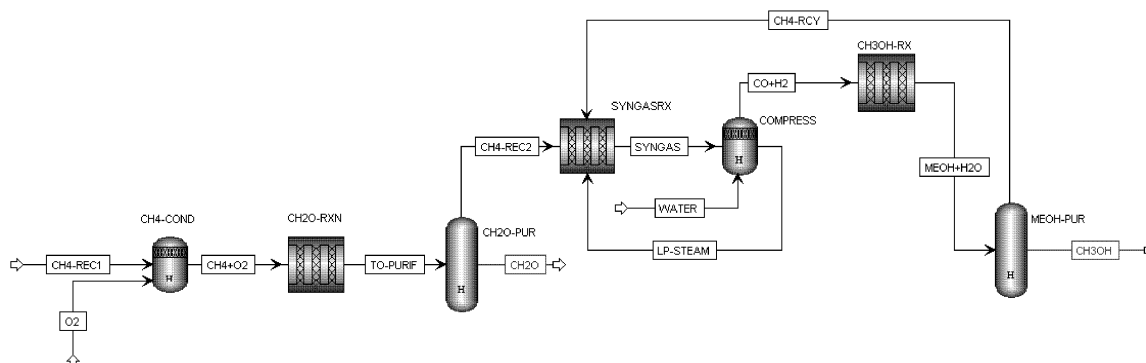


Fig. 2: Simplified flowsheet for oxygenates plant process.

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 6525 kW of electricity that counts for 23% of the compressor requirements. With this process, pure liquid methanol is obtained (8510 kg/h) after water removal in the distillation column that operates at 9 bar.

4. ECONOMIC MODEL AND DESIGN ASSUMPTIONS

The intention of this part of the project was to evaluate the economics of the OCM reaction in an industrial scale. The most important aspect was to work out the comparative economics and to identify crucial costs on this basis rather than estimating the absolute costs. In order to achieve this goal the sensitivity of the economics to the OCM process location and raw material costs was studied. A discount cash flow analysis is used to assess the process economics which are modeled using the Aspen Process Economic Analyzer. The purchased equipment cost (PEC) was estimated using data from the same Aspen software mentioned before. Total installed equipment cost (TIC) and indirect plant expenses have been set as a fraction of purchased equipment cost. Installation costs include charges for equipment installation, instrumentation, piping, electrical connections, building, warehouse and site development. Indirect expenses include costs for engineering and supervision, construction expenses, legal and contractor fees. Contingency cost is estimated as 18% of the total direct and indirect plant costs. The total direct and indirect costs along with the contingency give an estimate of the fixed capital investment (FCI) required for the project. Working capital accounts for the startup costs and is estimated as 15% of FCI. The FCI and working capital constitute the total capital investment (TCI) in the project. The prices for feedstock, raw materials and by-products have been derived from market data (e.g. ICIS chemical and oil price reports) and conservative estimates based on assumptions. It is assumed that utilities required for the plant are purchased and the wastewater treatment is carried out for a fixed price at an external facility. Labor costs are estimated based on general assumptions for employee hours required per day for the number of operating steps. Overhead expenses are accounted as a fraction of labor costs and maintenance costs are calculated as a fraction of the total purchased equipment cost. Insurance and legal fees are calculated as a fraction of installed equipment costs. These costs comprise the operating costs for the process. The discounted cash flow analysis is based on certain assumptions and takes into account cash flows over the entire plant life. In the discounted cash flow analysis the project investment is spent over three years following the assumptions stated below. The total operating costs are incurred every year and also include credit from sale of co-products (electricity, formaldehyde and methanol). The plant depreciation costs are recovered in the first eight years of operation following Modified Accelerated

Cost Recovery system method (MACRS). The annual sales of ethylene follow the selling price in €/1000 kg and annual plant output from the process. The difference between these annual costs and the annual sales of ethylene give the net revenue in the respective year. Income tax is incurred at the rate between 15% - 35%, depending on plant location, on the taxable income derived after covering the losses forwarded from the previous operating year. Deducting the income tax from the net revenue gives us the annual cash income for each operating year. These revenue streams from the operating years and the investment costs are discounted to the 2010 year of reference following a 10% internal rate of return. The sum of these costs and revenues in the year of reference give us the net present value (NPV) of the project. The following items are some of the major assumptions critical to the analysis (Brown, 2007):

- The process has been modeled to utilize $22.6 \times 10^5 \text{ m}^3$ per day of methane (at 15 °C, 1 atm) which is assumed to be produced on-site in remote gas field locations.
- The detailed reaction kinetics for the OCM reaction was taken from Stansch et al. (2007). The reactor size is estimated using residence time and catalyst bulk density.
- The plant operates on a continuous basis for 8000 h every year.
- The methane price is assumed to be different, depending on plant location, between 6.82 and 88.37 €/1000 m³. The oxygen price (for the formaldehyde production) also depends on the location and it is in the range between 17 and 19 €/1000 kg.
- The plant is 100% equity financed and the lifetime is assumed to be 20 years.
- The construction period is assumed to be 3 years, with 32% of the capital investment spent in 1st year, 60% in year 2 and 8% in year 3.
- The start-up time is assumed to be 18 weeks during which period the revenues have been assumed to be 50% of normal capacity.
- The income tax rate depends on plant location and it is in the range between 15% - 34% and the plant is depreciated following the IRS Modified accelerated Cost Recovery System (MACRS).
- The Internal Rate of Return (IRR) for this project is set at 10%.
- All the costs and prices are updated to 2010 dollar value using appropriate indices.

5. RESULTS AND DISCUSSIONS

5.1 Process Analysis

Before deciding what to do with the amount of non-reacted methane in the OCM process, we performed an economic analysis to compare the costs associated with recycling of this methane. Table 1 summarizes the economic overview of this analysis. Economic analysis of both alternatives are based on a total annual production of 240000 metric tons of ethylene with a selling price of 1135 €/ton. Operating and Utilities costs differences represent 4.2% and 4.8% respectively, and both values are for the unreacted CH₄ no-recycling alternative. Since the differences between raw material costs for both alternatives represent only 3%, and the Project Capital Cost are 7.8% more expensive for the recycled case, the decision was made to use the non-reacted methane in the production of oxygenated products, such as formaldehyde and methanol, in order to give added value to the OCM reaction process.

Table 1: OCM Process Economic Results

Investment (Millions €)	OCM Process without CH ₄ Recycling	OCM Process with CH ₄ Recycling
Total Project Capital Cost	170.67	183.94
Total Operating Cost	266.05	255.34
Total Raw Material Cost	83.77	81.31
Total Utilities Cost	154.89	147.71
Total Products Sales (C ₂ H ₄)	272.40	272.40
Payout Period (Years)	12.16	10.54

Table 2: OCM and Oxygenated Process Economic Results

	OCM Process Alone	OCM & Oxygenated Process Proposed
Raw Materials	(metric ton/day)	
Methane	2593.2	2593.2
Mono Ethanol Amine	676.7	676.7
Products		
Ethylene	396.0	396.0
Formaldehyde	---	117.1
Methanol	---	204.2
Ethylene purity (mass %)	99.6	99.2
By-products		
H ₂ O	1438.9	229.2
C ₂ H ₆	19.6	25.7
CO ₂	1675.2	518.8
CO	126.5	1512.9
H ₂	72.0	108.6
Non-reacted CH ₄	1421.1	502.2

The steady state flow rates of raw materials, products and by-products streams are summarized in Table 2. Both simulated processes (OCM alone and proposed alternative) consume a 2593 t/d pure methane as feed-stock, resulting in a production of 396 t/d of 99% purity ethylene. The difference in water production in both processes can be explained because the alternative process goes through more equipment to produce steam to be the raw material for the syngas reaction before its final use in the methanol reactor. The CH₄/O₂ molar feed ratio in the OCM reactor for the original and alternative OCM process is 1.7; as a result in both processes a gas phase by-product stream composed by H₂O, C₂H₆, CO₂, CO and H₂ is obtained. Although this is a by-products stream with low economic value, the flow of CO and H₂ are sufficiently attractive to separate it from the mixture and used it as synthesis gas in a methanol synthesis reactor. The non-reacted methane in the initial process is 2.8 times higher than the alternative, because it is employed in the production of synthesis gas and formaldehyde. The CO₂-enriched stream obtained after the amine process section together with the CO₂ and H₂O formed as by-products of both, formaldehyde and OCM reaction, can be used for the methanation of carbon dioxide reaction by hydrogen reduction (Brooks et. al., 2007), and then recycled back to the syngas reactor. As shown in Table 2, the final CO₂ emissions in the alternative process are 3 times lower than OCM process because it is used in the methanol production process. All these improvements in the process can result in a more favorable economic analysis. In the case of the OCM process the nitrogen obtained from the air separation unit, which is at 95% wt. purity, can be sold for many applications in a wide variety of areas including its use as purge-gas in the reactors

when carrying out the catalyst regeneration and as feedstock for ammonia plants as raw material for the production of nitrogen based fertilizers.

Table 3: Plant Location Economic Analysis

Plant Location	Project Capital Cost (Millions €)	Operating Cost	Raw Material Cost	Utilities Cost	Ethylene Sales	Payout Period (years)
Germany	179.77	328.81	139.96	154.89	272.40	More than 15
Vietnam	194.06	286.96	164.39	92.39	193.00	More than 15
Russia	292.50	295.68	113.52	150.75	316.22	13
China	194.72	252.46	125.80	99.46	261.69	13
Venezuela	195.43	229.35	73.56	130.86	272.36	8
Qatar	196.03	199.03	70.06	106.70	246.89	7

Table 4: Capital expenses for both processes using OCM reaction

Process Section	Price (Million EUR)	
	OCM Original Process	OCM-OXY Process
1. Air separation Unit	44.37	38.11
2. OCM Reactor	24.44	22.99
3. Gas Compression	30.88	21.79
4. CO ₂ Removal	11.89	72.31
5. C ₂ H ₄ Separation	8.71	8.62
6. Methane Conditioning	---	2.01
7. Formaldehyde Reaction	---	47.29
8. CH ₂ O Separation	---	20.47
9. Syngas Production	---	7.65
10. Syngas Compression	---	13.07
11. Methanol Reaction	---	0.78
12. CH ₃ OH Separation	---	4.04
Total Installed Equipment Cost	120.29	259.21
Total Direct and Indirect Costs	167.02	326.86
Contingency	29.31	58.47
Fixed Capital Investment	180.47	352.67
Working Capital	29.31	63.48
Total Capital Investment	195.43	403.06
Lang Factor	5.7	5.7

5.2 Economic Analysis

Before starting the economic study of the OCM process a preliminary analysis of possible plant locations should be developed. Natural Gas (methane) is a commodity which price varies strongly from one region to another. Moreover, not only the price of raw materials is affected by the location of the plant but also the costs associated with the production, namely: steam, refrigeration, electricity, fuel, wages, etc., affecting strongly the profitability of a petrochemical project. Table 3 shows the operating costs of different regions. Due to low natural gas prices

in Venezuela, which has the highest production potential in South America, and the highest ethylene sales for the European market, this geographical location has been chosen for economic analysis of this project.

Table 5: Operating expenses for both processes using OCM reaction

Operating Expenses	OCM Alone Process (millions EUR/year)	OCM Alternative Process (millions EUR/year)
Methane feed	0.95	0.98
Utility costs	130.86	246.15
Labor costs	1.03	0.32
Overhead and maintenance	3.92	7.18
Others	20.85	25.37
Total expenses before credit	157.61	279.99
By-product credit (CH ₃ OH + CH ₂ O)	0.00	81.41
Net total expenses	157.61	198.58

The capital expenses for the production of ethylene and oxygenates products for both processes are summarized in Table 4. The common sections to both processes are: Air Separation Unit, OCM Reaction, Gas Compression, CO₂ Removal and Ethylene Separation. The differences in capital costs results show that the alternative process is two times more expensive than the OCM process alone; this is evidently due to the alternative process uses a lot more equipment for the production of oxygenated products. Looking deeply the operating expenses, shown in Table 5, we can notice that the cost of the utilities (refrigeration, cooling water, steam) are the major contributor to the operating expenses that accounts for the 82.5% of the total operating costs for the OCM original process and 87.9% for the OCM alternative process. In order to decrease utility costs in the OCM alternative process the condensed water coming from the OCM reactor is used to generate HP steam (30 bars) for the reboilers in the demethanizer and ethylene-ethane separation columns. The other costs represent general and administrative costs incurred during production such as administrative salaries/expenses, R&D, product distribution and sales costs. The by-product sales in the alternative process include the formaldehyde and methanol production.

The volatility of the market for oil and natural gas trades, mainly because the political situations of the producing countries, makes the prices always changing. For this reason, the value for the actual C₂H₄ prices is higher for the 3rd quarter 2011 than last year (around 35%). However selling by-products compensates any future fluctuation for these high price ethylene sales for this process. Finally, the payout period, the expected number of years required to recover the original investment in the project, is 8 years for OCM process in Venezuela and 9 years for the OCM & Oxygenates process in the same country.

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 investment in the ethylene processing technology using the scheme suggested here. Figure 3 shows the cash flows for the OCM alternative project for the 20 years period.

6. CONCLUSIONS

This analysis shows that it should be possible to produce ethylene from the OCM reaction that is suitable to satisfy de ethylene demand worldwide as a precursor for the production of other chemicals. The development of integrating the OCM process technology, including reactor considerations, and a materials survey under severe OCM reaction conditions have been conducted in this project. The inclusion of alternative processes to the traditional OCM process to increase its profitability is indeed feasible. Nevertheless, a bigger capital investment is required, and the benefits obtained from this are still overcome by the margins and pay out time periods of the OCM process, due to the increase on capital expenses and operative costs.

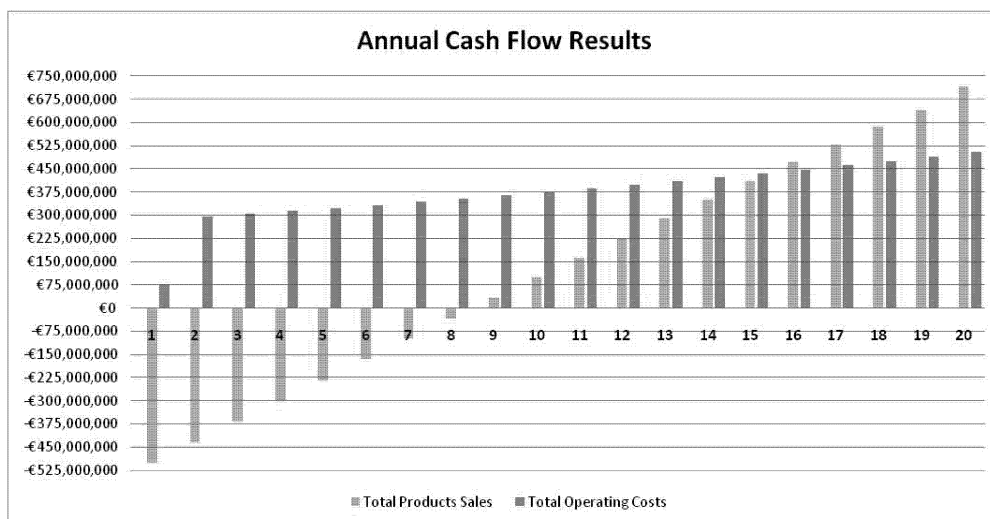


Fig. 3 Cash flow for the Ethylene, Formaldehyde and Methanol process using OCM reaction

As shown in the results of this analysis, the price of methane is the key factor for the success of an OCM process in the ethylene market. For instance, international companies are moving now to countries that provide low feedstock prices (natural gas) in order to obtain greater margins due to this cost advantage. Producers located in mature markets like Europe will have a hard time in the following years, due to the costs advantage of the other markets and globalization. Middle East represents the best option for every project, even with the strong competition expected in that region during the coming years. The recent discovery of huge offshore gas reservoirs in the northern coast region near Carupano, Venezuela and the new trade agreements between this country and China, for the exportation of natural gas, oil and chemicals, could open the way for new projects in that region. Nevertheless, the lack of infrastructure and investors protection could affect its value.

Further work is needed in order to reduce total investment cost especially costs for compressors, furnaces and reactor operation at enhanced pressure should be considered. The investment costs for the reactor are still influenced by uncertainty in the reactor construction. The economic evaluation showed that the minimum performance of the OCM catalyst is more than 30% methane conversion and 80% C_2^+ selectivity under some inverse correlation of conversion and selectivity. Based on this economic studies the above consumptions were confirmed that further catalyst improvement is required with respect to an increase of C_2^+ selectivity and this would be certainly beneficial for process economics. The economic analysis of the processes studied here has shown that it is feasible to implement a process that combines OCM reaction (for ethylene production) and oxygenates generation (formaldehyde and methanol), via synthesis gas, taking advantage of low natural gas prices offered by Venezuela. Furthermore, in general, the OCM technologies were confirmed to be more economically feasible in the case of installation to deal with a natural gas containing large hydrocarbons deposits.

Acknowledgment

The authors acknowledge support from the Cluster of Excellency "Unifying Concepts in Catalysis" coordinated by the Berlin Institute of Technology and funded by the German Research Foundation – Deutsche Forschungsgemeinschaft.

7. REFERENCES

- Brooks, K.P., Hu, J., Zhu, H. and Kee, R.J., 2007, Methanation of carbon dioxide by hydrogen reduction using the Sabatier process in microchannel reactors, *Chemical Engineering Science*, 62, 1161-1170.
- Brown, T., 2007, *Engineering Economics and Design for Process Engineers*. CRC Press, Boca Raton.
- Coronas J., 1995, Síntesis de Hidrocarburos por Acoplamiento Oxidativo de Metano. Utilización de Reactores de Membrana. Doctoral Thesis, Universidad de Zaragoza, Departamento de Ingeniería Química y Tecnologías del Medio Ambiente (in Spanish).
- Clausen L.R. Houbak N. and Elmegaard B., 2010, Technoeconomic analysis of a methanol plant based on gasification of biomass and electrolysis of water, *Energy*, 35, 2338-2347.
- ENAGAS, Ente Nacional del Gas, MENPET – Venezuela, Precios y Tarifas del Gas Natural. (<http://enagas.gob.ve/info/areasimportancia/preciosytarifas.php>). Last time accessed Aug 2011.
- Gallucci F. and Basile A., 2007, A theoretical analysis of methanol synthesis from CO₂ and H₂ in a ceramic membrane reactor, *International Journal of Hydrogen Energy*, 32, 5050-5058.
- Graf P. and Lefferts, L., 2008, Reactive separation of ethylene from the effluent gas of methane oxidative coupling via alkylation of benzene to ethylbenzene on ZSM-5, *Chemical Engineering Science*, 64, 2773-2780.
- Hall, K.R., 2005, A new gas to liquids (GTL) or gas to ethylene (GTE) technology, *Catalysis Today*, 106, 243–246.
- Holmen A., 2009, Direct conversion of methane to fuels and chemicals, *Catalysis Today*, 142, 2-8.
- Lintz H.-G, Schwittay, C. and Turek, T., 1999, One-Step Conversion of Methane to Formaldehyde. AIDIC Conference Series, Vol. 4, 309-316.
- Lunsford, J.H., 2000, Catalytic conversion of methane to more useful chemicals and fuels: a challenge for the 21st century, *Catalysis Today*, 63, 165–174.
- De Smet H.R.S. de Croon H.M.J. Berger R.J. Marin G.B. and Schoten J.C., 2001, Design of adiabatic fixed-bed reactors for the partial oxidation of methane to synthesis gas. Application to production of methanol and hydrogen-for-fuel-cells, *Chemical Engineering Science*, 56, 4849-4861.
- Qian, Y. Liu, J. Huang, Z. Kraslawski, A. Cui, J. and Huang, Y., 2009, Conceptual design and system analysis of a poly-generation system for power and olefin production from natural gas, *Applied Energy*, 86, 2088–2095.
- Stansch, Z., Mleczko, L. and Baerns, M., 1997, Comprehensive Kinetics of Oxidative Coupling of Methane over the La₂O₃/CaO Catalyst. *Ind. Eng. Chem. Res.* 36, 2568-2579.
- Vora, B., Chen, J.Q., Bozzano, A., Glover, B. and Barger, P., 2009, Various routes to methane utilization—SAPO-34 catalysis offers the best option, *Catalysis Today*, 141, 77–83.
- Yang C., Xu N. and Shi J., 1998, Experimental and Modeling Study on a Packed-Bed Membrane Reactor for Partial Oxidation of Methane to Formaldehyde. *Ind. Eng. Chem. Res.* 37, 2601-2610.
- Zhang Q., He D., Li J., Xu B., Liang Y. and Zhu Q., 2002, Comparatively high yield methanol production from gas phase partial oxidation of methane, *Applied Catalysis A: General*, 224, 201-207.