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Techno-economic analysis of oxidative coupling of methane: current state of the art and future perspectives

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ABSTRACT

The oxidative coupling of methane (OCM) process, which uses natural gas as a raw material for ethylene production and has been widely investigated since the 80's, is an alternative to conventional processes based on naphtha cracking. However, many authors have shown that its viability is hampered by the low yields that can be currently achieved during the OCM reaction. In this work, the performance of the OCM reactor and its impact on the overall OCM plant have been quantified from a techno-economic point of view. It has been proven that a very high ethylene price (above 1500 €/ton C₂H₄) is obtained with the current OCM technology, which corresponds to a C₂ reactor yield of around 15%. The sensitivity analysis of the OCM process has revealed that the best reactor performance does not necessarily imply the lowest ethylene price, but there are instead other factors affecting it. With the simulation of the overall plant it has also been demonstrated that a C₂ reactor yield of at least 25-30% is the target to obtain an ethylene cost lower than 1000 €/ton C₂H₄. Finally, it has been shown that, based on the forecast of costs for natural gas and naphtha, the gap between the ethylene price obtained with conventional technologies and the one obtained with the current OCM state of the art is expected to progressively become smaller, forecasting OCM to be competitive with the traditional technologies in around 20 years.

Keywords: Techno-economic analysis; OCM technology; Ethylene prices forecasted;

- Ethylene production;

1. INTRODUCTION

The price of oil in the last years has increased more than the one of natural gas, and the forecasts indicate that this tendency will continue in the coming years. In Figure 1 the trends forecasted for both fossil fuels in different regions for the coming period are summarized:

Figure 1. Forecast for the normalized price (respect to 2016) of oil and natural gas for the coming period [1].

These projections have driven the research efforts towards diversifying the raw materials employed for the production of olefins, also known as “fuel switching” scenario. Since the natural gas resources are believed to be more abundant than the ones of oil, this raw material is one of the main alternatives to substitute, at least partially, oil in the production of hydrocarbons. Among light hydrocarbons, ethylene is the most produced worldwide because it is used as the base for the production of many plastics, reaching currently an overall production of 140-160 million tons per year [2].

The production of ethylene, which is commonly produced via either the naphtha steam cracking using oil or via the ethane dehydrogenation [3], can also be accomplished using natural gas as

raw material both via the Fischer-Tropsch process (indirect route), which involves many steps and requires multiple units, and via the direct conversion of methane, so called methane coupling, which, in presence of oxygen is called oxidative coupling of methane (OCM). This process has been investigated since the 80's [4] and allows the conversion of methane into ethylene in a single step. The overall OCM reaction is the following:

Although the reaction could be understood as a simple process, the complete reaction mechanism consists of multiple parallel and consecutive reactions. The primary reactions of the process are the following:

In a primary step, methane is converted into ethane. However, the high temperatures required to break the C-H bond, above 750 °C in most of the cases, cause the enhancement of the undesired complete and incomplete combustion reactions. These combustions will hinder the overall C₂ selectivity of this process, thus impeding the achievement of high yields towards the desired C₂ products. During the OCM secondary steps, in which ethane is converted via the oxidative and the non-oxidative dehydrogenation to ethylene, the combustion and reforming of C₂'s can decrease even further the selectivity towards the desired products. At the end, because of this complex set of primary and secondary reactions, the performance of this process is limited to low yield (either at high conversions and low selectivities or the other way round). In fact, in most of the published experimental work the yield of the process remains below 20-

25% [5], [6]. The main consequence of this poor performance is the hampering of the application of such a process to an industrial scale, making it not economically viable when compared to benchmark ethylene production technologies.

Therefore, most of the research carried out in this field has been focused on improving the C_2 's yield and to make the process feasible at larger scales. Specifically, big efforts have been made on finding novel reactor configurations, as membrane reactors [5], and more suitable OCM catalysts, meaning a better compromise between its selectivity, activity and stability [7]. These efforts are based on the fact that modelling calculations have shown promising results [8], [9], demonstrating that a proper optimization of the reactor design and operating conditions can lead to OCM reactor yields well above this 30% target (minimum to make the process economic). Nevertheless, the OCM experimental work performed in literature in the last years has not resulted in the significant improvements that are necessary to make the process economically viable. Just few of this experimental work, and with conditions not feasible at industrial scale, have reached results near the values obtained in the simulations of the modelling work [10]–[12].

In any case, the target value to make OCM viable is not clear. Many authors have suggested in literature values for the C_2 reactor yield necessary to make the process competitive with the conventional technologies, and most of them agreed on a target of around 30% C_2 yield. Particularly, Roos et al. [13] in 1987 and Lange et al. [14] in 1997 proposed 24% as the minimum C_2 yield to make OCM a potential alternative to other C_2H_4 production technologies. More recently, Parishan et al. [15] and Jaso et al. [16] claimed in their works that a 30% C_2 yield is necessary to make OCM competitive, although they do not justify the value neither with a reference nor a calculation. In addition, Spallina et al. [2] compared, from an economical point of view, different OCM scenarios with the benchmark ethylene production technology (NSC).

They found a gap of at least 350 €/ton C₂H₄ between both processes in the most OCM optimistic case (1209 versus 834 €/ton C₂H₄).

As stated by Vandewalle et al. [17], it seems that there is a lack of precise and up-to-date information regarding to the overall OCM performance required to consider OCM as a feasible alternative for the C₂H₄ production. Despite the efforts made in the last decades for a maximization of the C₂ yield in a single OCM reactor, the reactor conditions which would lead to a minimization of the ethylene price via the OCM have not been yet defined. The clear definition of this target value together with the selection of the optimal reactor conditions would contribute to place the current OCM state of the art within the global ethylene production framework.

Therefore, this work aims at providing a detailed forecast of the potential of the OCM technology, focusing on the prices trend of different feedstocks used for the production of ethylene. In other words, the objective is to identify (as a function of time) the yield needed in the reactor in order to produce ethylene with OCM at a cost similar to benchmark technologies. This also allows to identify if and when the state-of-the-art OCM technology would be preferred over other technologies as a consequence of the variability in feedstock prices. To this end, a techno-economic analysis of the OCM process has been carried out, identifying the optimal reactor conditions that will result in the lowest ethylene price. This cost is then compared to the benchmark case (in Europe, the naphtha steam cracking), and the yield required in the OCM technology to fill the gap will be determined. Finally, and based on the forecasts for oil and natural gas prices, the price prediction for ethylene using different technologies will be analyzed for the coming decades.

In the coming sections, the methodology selected, the OCM reactor model and the overall OCM process technology used in this work will be described. Afterward, the results obtained at different operating conditions and process yields, as well as forecasted scenarios, will be

evaluated and discussed. Finally, the main outcomes will be summarized and guidelines on how to increase process yields will be provided.

2. METHODOLOGY

Despite of the fact that other technologies are nowadays emerging, it has already been explained that naphtha steam cracking has been historically the most common technology for the ethylene production (at least in Europe). That is the main reason why it has been considered as the benchmark technology for this work. This benchmark technology has been compared to the OCM process, whose process scheme plant has been designed and will be explained in the following sections. The methodology here presented can be extended to any other ethylene production technology, but this is out of the scope of the present work.

The core of the process will be the OCM reactor, which has been modelled in by means of an in-house developed plug-flow 1D model. From this OCM reactor, the main indicators employed to quantitatively evaluate the performance are the ones introduced in equations 5-7:

$$\text{CH}_4 \text{ conversion} \quad X_{CH_4} = \frac{F_{inCH_4} - F_{outCH_4}}{F_{inCH_4}} \quad \text{Equation 5}$$

$$\text{C}_2 \text{ selectivity} \quad S_{C_2} = 2 * \frac{(F_{outC_2H_4} + F_{outC_2H_6} - F_{inC_2H_4} - F_{inC_2H_6})}{F_{inCH_4} - F_{outCH_4}} \quad \text{Equation 6}$$

$$\text{C}_2 \text{ yield} \quad Y_{C_2} = X_{CH_4} * S_{C_2} \quad \text{Equation 7}$$

In order to integrate the OCM reactor model on the overall process, a set of assumptions are required to solve the mass and energy balances of all the process units. In this work, the same assumptions of the work of Spallina et al. [2] have been considered.

Similarly, an in-house Excel techno-economic model has been integrated in the OCM process to investigate how the different parameters affect the distribution of costs of the different units and the leveled production cost of ethylene. This ethylene cost has been calculated in the model as the sum of both capital (CAPEX) and operational (OPEX) costs, as reported in equation 8.

$$\text{Cost of ethylene} \left[\frac{\text{€}}{\text{ton}} \right] = \frac{(OPEX_{\text{variable}} + CAPEX_{C_2H_4} + C_{O\&M, \text{fixed}})_y}{(\dot{m}_{C_2H_4})_y} \quad \text{Equation 8}$$

The equations used for the CAPEX calculations are summarized in **Table 1**. The costs of all the units considered in the OCM plant, which will be later used to calculate the bare erected costs, have been estimated based on the scale-up factor correlation, shown in equation 9:

$$C = nC_0 * \left(\frac{S}{nS_0} \right)^f \quad \text{Equation 9}$$

Where C_0 is the cost of the component based on literature data, S_0 is the capacity of the scaling parameter, which is also based on literature data, S is the capacity that has to be scaled, n is the number of units to be considered and the f is the scaling factor. The prices and scaling parameters of all the units used in this work are taken from the work of Spallina et al. [2].

Table 1: Capital (CAPEX) costs calculations from NETL [18]

Capital costs (CAPEX)	
Plant Components	Cost (M€)
Component A	A
Component B	B
Component C	C
Component D	D
BEC (Bare Erected Costs)	A+B+C+D
Direct costs as percentage of BEC	
Total Installation Cost (TIC)	80% of BEC
Total Plant Costs (TPC)	BEC + TIC
Indirect Costs (IC)	
Engineering Procurement and Construction (EPC)	14% of TPC
	TPC + IC
Contingency	10% of EPC
Owner's Cost	5% of EPC
Total contingencies and owner's costs (TCOC)	15% of EPC

Total Overnight Costs (TOC)	EPC + TCOC
CCF (Capital charge factor)	0.1
CAPEX _{C2H4} [M€/year]	TOC*CCF

Differently, the operational expenses (OPEX) can be differentiated between the fixed, which mostly refer to labor costs, maintenance and insurance, and the variable costs, which include the feedstock, electricity, etc. Thus, the OPEX costs of the plant have been calculated as stated in equation 8:

$$\begin{aligned}
 OPEX &= \left(\sum OPEX_{variable} + \sum OPEX_{O\&M} \right) \\
 &= (OPEX_{feedstock} + OPEX_{el} + \sum OPEX_{O\&M}) \left[\frac{M\text{€}}{y} \right]
 \end{aligned}
 \tag{Equation 8}$$

For the CAPEX and OPEX calculations, some assumptions regarding the operation and maintenance (O&M) costs and the price fixed for the consumables are required. The assumed values are summarized in Table 2:

Table 2: Assumptions for the O&M costs calculations and consumables.

O&M Fixed		
Labor	M€/year	1.5
Maintenance	% TOC	2.5
Insurance	% TOC	2.0
O&M Variable		
Catalyst	€/kg	50.0
Diluent	€/kg	9.45
Catalyst Replacement	Years	5
Diluent Replacement	Years	5
Plant Lifetime	Years	25
Consumables		
Cooling Water	€/ton	0.35
Natural Gas price (Europe)	€/GJ _{LHV}	5
Electricity	€/MWh	85
CO ₂	€/ton _{CO2}	0

In addition, for all these calculations the following two assumptions have been made:

- Europe has been considered to be the scenario for all the calculations. That is, the assumptions and prices of the consumables have been taken from the current European market. Furthermore, this selection is based on the fact that the NSC is the typical process for ethylene production in Europe.
- The OCM plant has been designed to produce 31.9 kg/s of ethylene, which is the equivalent to a C_2H_4 production of 1 million-ton/year.

3. OCM REACTOR MODEL

The reactor is one of the most important units of the OCM technology since small variations in the reactor yield will largely impact the downstream separation processes. Therefore, before building up a complete process scheme, it is of high relevance to accurately describe and simulate the OCM reaction network. Because of that, a 1D reactor model has been developed using a set of assumptions within the state of the art technology. Subsequently, this reactor model is fully integrated in the overall OCM process scheme using the process design software Aspen Plus.

3.1. Assumptions

The reactor has been designed to fulfill the necessities of an industrial scale OCM process. To do so, the main reactor parameters have been defined and fixed and are listed in Table 3:

Table 3. Characteristics assumed for the simulation of the 1D OCM reactor model.

OCM Reactor characteristics		
Diameter [m]	3	
Inlet gas velocity [m/s]	1	
Bed porosity [-]	0.5	
Inlet pressure [bar]	10	
Pressure drop in the reactor [bar]	1	
Catalyst type	La ₂ O ₃ /CaO	[19]
Catalyst density [kg particle/m ³ reactor]	3600	[19]
Active weight fraction	0.27	[19]
Catalyst dilution $\left[\frac{\text{Catalyst weight [kg]}}{\text{Total solid weight [kg]}}\right]$	0.01	
Maximum axial reactor length [m]	15	
Cooling tubes diameter [m]	12.7x10 ⁻³	[20]
Cooling tubes material	Stainless steel 316	[20]

The diameter size has been set up based on the reactor standards for industrial scale chemical plants. Similarly, the values for inlet gas velocity, bed porosity and total pressure chosen are also well-accepted when working with industrial scale packed bed reactors. Additionally, the defined pressure drop is consistent when large scale packed beds are operated. Regarding the OCM catalyst, different alternatives can be considered as presented in several OCM reviews

available in the open literature [16], [21]–[24]. Since their characteristics vary significantly, the selection of the catalyst can strongly influence the reactor performance. For instance, La-based catalysts are very active but with a relatively low C₂ selectivity. W-based catalysts, which are considered one of the most promising options, are classified with a good C₂ selectivity but with lower activity. On the other hand, Li-based ones, widely investigated, show both good C₂ selectivity and activity but their stability under OCM conditions is too poor to carry out long-term tests. The knowledge acquired over the years on the La₂O₃/CaO catalyst, together with the fact that its kinetics is the most OCM reliable one, has been the main reason for its selection to simulate the OCM reactor in this work. Specifically, the data provided by Stansch et al. [19] in their work has been used. The kinetics defined in the mentioned work consists of a set of 10 reactions, involving 3 primary ones and 7 consecutives, including among them some undesired combustion and reforming reactions of the reactants and desired products.

In order to achieve a better heat management inside the OCM reactor, the catalyst should be diluted with inert particles to slow down the velocity of the reaction. This is a consequence of the highly exothermic reactions occurring inside the reactor, and overall results in the need of longer reactors to fully convert the oxygen introduced in the system. An accurate temperature control, derived from a proper heat management, is crucial to keep a high C₂ selectivity. A deviation from the optimal temperature, most likely by means of hotspots, would lead to a dramatic loose of C₂ selectivity, hampering the desired outcome of the reaction. Siluria Technologies, an American company which owns several OCM patents [25]–[31], has already proven the feasibility of this reactor concept in a prototype level.

The 1D reactor model developed in this work assumes isothermal conditions, where the cooling needed to remove the heat generated by the reactions is provided by evaporating high pressure water inside cooling tubes passing through the catalytic bed. The amount of cooling tubes is calculated by comparing the total heat released during the reaction and the heat that a single

tube can take. Subsequently, by fixing the inlet gas velocity of the reactants in a single reactor and the area of a single reactor (cross-sectional reactor area minus area occupied by the cooling tubes), the amount of parallel reactors required to process the amount of reactants needed to satisfy the C_2H_4 production target can be calculated. Additionally, the amount of cooling tubes required is properly considered in the techno-economic analysis when calculating the capital costs of the process.

The last assumption concerns the total length of the reactor. In this work, a reactor length is selected such that it finishes when one of the reactants is fully consumed. However, the maximum reactor length has been limited to 15 meters to avoid too long reactors that are not industrially attractive. Hence, a different reactor length is obtained for each set of operating conditions investigated.

3.2. Results of the reactor modelling

After the definition of some reactor parameters, a sensitivity analysis has been carried out on the OCM operating conditions. In particular, the operating temperature and CH_4/O_2 ratio. An overview of the yields obtained through this sensitivity analysis is shown in Figure 2:

Figure 2. C_2 yield obtained in the OCM reactor for different temperatures and CH_4/O_2 ratios.

As it can be observed in Figure 2, the optimal temperature for the OCM reactor is in between 830 and 870 °C. Lower temperatures do not activate sufficiently the methane molecules, hence limiting the CH₄ conversion and consequently the C₂ yield. At higher temperatures, the CH₄ combustions prevail, thus hampering the achievement of high selectivity towards the desired products. When giving a closer look to the effect of the CH₄/O₂ ratio, a compromise should be found. The feeding of big amounts of oxygen implies a higher CH₄ conversion at the expense of a lower C₂ selectivity. On the other hand, high CH₄/O₂ ratios yield high C₂ selectivities, although decent CH₄ conversions cannot be achieved. With all this, the best yield obtained is 15.5 %, corresponding to a CH₄ conversion of 51.1 % and a C₂ selectivity of 30.3 %. This maximum yield is reached at 860 °C with a CH₄/O₂ ratio of 1.5. These model results are consistent with many experimental work performed in literature using the same packed bed reactor configuration, and the same catalyst as the one simulated in this study [5], [19], [32].

However, the conditions giving the highest yields do not automatically imply a minimization of the cost of the plant. As it can be seen in Figure 2, other operating conditions give a yield close to the optimal one, which could significantly influence the cost of the ethylene produced when integrated in the overall process.

To illustrate this statement, Figure 3 compares the C₂ yield obtained in all the simulations presented in Figure 2 together with the required reactor length of each case.

Figure 3. C₂ yield and reactor length obtained in each of the OCM reactor simulation performed.

As depicted in Figure 3, similar yields can be reached with very different reactor lengths (which depend on oxygen amount and temperature). This implies a large variation in capital costs for similar efficiencies, as bigger amounts of catalyst and reactor volumes will be required in the simulations in which a long OCM reactor is employed. Furthermore, the need of a very energy intensive air separation unit (ASU) to produce pure oxygen for the OCM process should also be considered in the overall process and can affect considerably the final ethylene cost. In particular, the lower is the CH_4/O_2 ratio, the more oxygen needs to be supplied to the reactor, resulting in higher energy needs, and consequently in an increase in the total cost of the OCM plant.

Summing up, a maximization of the OCM reactor performance will not directly imply a minimization of the total plant costs, as upstream and downstream processes have a large influence on the cost of ethylene. Therefore, all these variables should be properly accounted for in the optimization of the C_2 yield, as they can play a very important role in the economics

of the process. In the next section, a detailed description of the overall OCM process and the economic evaluation of all the cases simulated at a reactor level will be highlighted. This preliminary economic evaluation will help defining the optimized reactor parameters that minimize the ethylene production costs.

4. OCM PROCESS

The developed reactor model has been integrated and linked with the OCM plant designed in Aspen Plus. This integration allows the optimization of the OCM technology by paying special attention to the influence of the reactor variables on the process economics.

4.1 Plant description and assumptions

The OCM plant used for this work has been previously described by Spallina et al. [2]. In Figure 4, a scheme of the simulated plant can be seen.

Figure 4: OCM process flow diagram [2].

In this technology the oxygen is first purified in a cryogenic air separation unit (ASU). This oxygen is mixed afterwards with desulfurized natural gas, and both are fed in the reactor, where the very exothermic OCM reactions take place and where the desired products of the plant are formed. High pressure water is evaporated inside the cooling tubes integrated in the reactor to compensate the heat produced during the reaction, hence assuring isothermal operation. To restrict the consecutive gas-phase reactions, in which the desired products can further react leading to a significant decrease of the reactor performance, the outlet of the reactor is rapidly

quenched with a dry recycled stream and further cooled down in a series of heat exchangers, where high-pressure steam is also produced. Subsequently, the steam in the products stream is condensed and separated in a flash unit, and the CO_2 is removed from the cooled gas stream by means of an amine-based acid gas removal unit. Afterward, the gas is pressurized, and it enters in the cryogenic distillation units, where first the light gases are separated from the C_2 's in the de-methanizer distillation column. Thereafter, the ethane and the ethylene are separated in the de-ethanizer, which works at milder conditions compared to the de-methanizer. To reach these cryogenic temperatures, a refrigeration cycle is required. The pure ethylene is obtained from the top of the de-ethanizer, while the bottom stream, which contains mostly ethane, is recirculated to the reactor where it can be further converted into ethylene.

The light gases coming from the top of the de-methanizer, containing mainly unreacted CH_4 , CO and H_2 , are sent to a reactor for methanation in which the CO and H_2 are converted back to CH_4 . The outlet of this unit, formed mostly by methane, is then divided; part of the flow is directed to a boiler, where methane is burnt to provide heat and high pressure steam to the plant, while the rest of the stream is recirculated to the OCM reactor to maximize the conversion of CH_4 . This syngas stream could be used in different ways, such as for FTS process or split before the methanizer, or used for H_2 production or electricity production. The optimization of the processing of this stream has been left out from this study.

The main assumptions and the methods used for the calculation of the different units in this work are adopted from the ones given in the work of Spallina et al. [2]. The size of the plant is also the same as the one taken from Spallina et al. [2], having an outcome of 31.9 kg $\text{C}_2\text{H}_4/\text{s}$ with a purity of 99.5% which allows also direct comparison with literature results.

4.2 Results

4.2.1 Optimization of OCM process

Among the different approaches that can be taken (energy consumption minimization, CO₂ emissions minimization etc.), the price of ethylene has been selected as the target to be minimized during the sensitivity analysis of the plant. The same parameters than in the previous section, that is, reactor temperature and CH₄/O₂ ratio, have been varied for this optimization. The results of the simulations are presented in Figure 5:

Figure 5: OCM reactor yield and overall C₂H₄ cost for the results of the simulations carried out when varying temperature (from 800 to 880 °C) and CH₄/O₂ ratio (from 1 to 6).

In Figure 5 the OCM reactor yield and the ethylene cost from the OCM plant are combined. As anticipated in the previous section, the results of this analysis reveal that the configurations giving the cheapest ethylene are not necessarily the ones corresponding to the highest reactor yield. Actually, the lowest price (1541 €/ton C₂H₄) is obtained at 850 °C and CH₄/O₂ ratio of 3, while the best reactor conditions are achieved at 860 °C and CH₄/O₂ ratio of 1.5 (C₂ yield of 15.5%). In more details, the cost of a single reactor, which mainly relates to the cost of the reactor vessel and the cooling tubes, is affected by the reactor operating conditions. However,

different reactor conditions lead to a variation in the composition of the reactor outlet stream, which can afterwards influence the size and consequently the cost of all the separation train. Thus, a compromise between the costs of all these units and not just a reactor optimization, needs to be found to optimize the ethylene price.

To study more in detail the origin and the behavior of these costs, a disaggregation of the units costs is reported in Figure 6.

Figure 6: Detailed cost of the units of an OCM plant, CAPEX, (left) and disaggregated ethylene cost, CAPEX AND OPEX, (right) for the minimum C₂H₄ price case at different temperatures.

In the left part of the graph, the CAPEX cost is detailed. Because of the energy intensive units that are required to separate products like oxygen from nitrogen, C₂ from methane or ethylene from ethane (cryogenic temperatures are required in these 3 examples), the biggest contribution to the CAPEX is given by the refrigeration cycle, which includes all the pumps, compressors, condensers and evaporators that need to be integrated to assure a proper functioning of the

mentioned units. In any case, the influence of CAPEX on the final ethylene price is much lower than the one of the OPEX, being the price of the raw material (natural gas) and the electricity required for the process the main contributors.

In addition, it can be clearly understood that the actual OCM process cannot compete in any case with the conventional C_2H_4 technologies. Although the price of ethylene can remarkably fluctuate depending on the region and on the resources available, its current value does not exceed 1000 €/ton. In particular, the C_2H_4 price calculated by Spallina et al. [2] for the benchmark technology (naphtha steam cracking with a naphtha price of 450 €/ton) was 834 €/ton, that is, almost half of the C_2H_4 price obtained with OCM.

In particular, the expensive ethylene price derived from the OCM process is mainly caused by the low C_2 yield attained within the OCM reactor. The techno-economic evaluation shows the consequences of this poor yield. Firstly, big amounts of electricity need to be imported to operate all the separation train units to separate the very large and broad variety of by-products that are formed in the reactor, thus impacting notably both OPEX and CAPEX. Another important cost contribution relates to the feedstock that the process employs. A big quantity of natural gas is required to meet the ethylene production target since most of it is not converted into the desired product but into CO and CO_2 , having this effect a major impact on the process OPEX.

4.2.2 Sensitivity analysis on the reactor performance

From the previous section it is obvious that OCM is not economically viable with the current state of the art. Nevertheless, large research effort is still spent on this topic. Thus, it would not be surprising to see further improvements on the process performance in the coming period.

To quantify the relevance of the improvement of the reactor performance on the overall ethylene price, the yield of the OCM reactor has been modified (by changing the reactor rates as a way to simulate improvements in the reaction path) and the updated ethylene price obtained with such a modification has been analyzed.

To do so, the OCM simulation giving the lowest ethylene price has been taken as base case. Its conditions are summarized in Table 4:

Table 4: Main characteristics of the base case simulation obtained with Aspen.

Base case simulation	
Temperature [°C]	850
Pressure [bar]	10
CH ₄ /O ₂ [-]	3
Reactor length [m]	1.56
CH ₄ conversion (%)	31.8
C ₂ selectivity (%)	43.8
Ethylene price (€/ton)	1541

From this base case, the reaction rates of the primary OCM reactions (according to the kinetics provided by Stansch et al. [19]) have been manually modified to increase the CH₄ conversion and/or the C₂ selectivity. With this strategy, both an improvement on the OCM reactor performance and a decrease on the C₂H₄ final price are expected in every simulation. In Figure 7, the different OCM simulations are represented and the change in the overall process performance for each of them is quantified:

Figure 7: C₂H₄ “Iso-C₂H₄ prices” obtained from the OCM process for different reactor C₂ selectivities and CH₄ conversions.

As explained in previous sections, in Figure 7 it can be observed that a certain ethylene price derived from an OCM process can be obtained with different reactor performances. It is clear that a significant increase in C₂ yield in the OCM process plant is needed to become competitive with the conventional ethylene production technologies. A yield of 30% at conditions applicable at industrial scale is the target to decrease the ethylene price below 1000 €/tonC₂H₄, which can be set as the objective to be competitive with the conventional technologies. Two main technical options can be considered to reach this target in the coming years; the development of a novel reactor configuration and the improvement of the characteristics of the OCM catalyst. Many reactor designs have been attempted at small scale, showing some advantages respect to the conventional packed bed in terms of reactor performance [5]. For instance, membrane reactors are known to be better in terms of reactor performance because of the better methane-oxygen contact [33]. The application of the membrane reactor would keep

a high C_2 selectivity in the reactor, increasing simultaneously the CH_4 conversion. However, these novel technologies are not yet mature, thus impeding their implementation at a bigger scale in the coming future. In addition, the process scheme should be changed if the reactor configuration is modified; aspects like the cost of a more complex reactor design or the suppression of the air separation unit (in the case that a dense membrane reactor is used) should be considered to have a detailed and accurate analysis of the system.

The other alternative to increase the OCM reactor yield is the improvement of the catalyst performance. If the performance of the catalyst is sufficiently increased, there would be no need of changing the reactor configuration to become competitive at large scale. There are two main factors affecting the behavior of the catalyst; its activity and its selectivity. The selectivity influences mostly the primary reactions, and it has a major contribution to the overall process performance. A more selective catalyst would decrease the percentage of undesired products, enhancing the production of ethane (in the primary step) and resulting at the reactor outlet in an increase in the ethylene yield even though the undesired gas-phase consecutive reactions (C_2 combustion and reforming) could still play a role. However, high selectivities are commonly related to relatively low CH_4 conversions. Similarly, a more active catalyst would increase the CH_4 conversion, although in most of the cases it originates a significant decrease of the C_2 selectivity.

In literature it can be found that in a conventional lab-scale packed-bed reactor, the yield that can be currently achieved with a stable catalyst, commonly W, La or Sr based, remains around 15-20% [5]. Therefore, the challenge is the development of a better OCM catalyst, either by increasing its activity and/or its selectivity, such that the overall reactor yield reaches the target fixed to be competitive with the conventional ethylene technologies.

To study more in detail how the different parameters affecting the ethylene cost change when the OCM reactor performance is improved, three different cases have been evaluated. The first

one is the so-called reference case, which accounts for the conditions derived from the process performance optimization. Subsequently, in Case 2 the reactor performance has been improved by increasing the C₂ selectivity while keeping the same CH₄ conversion as in the reference case. For Case 3, the CH₄ conversion has been increased and the C₂ selectivity has been kept as in the reference case. The objective behind this comparison is to determine whether an increase in conversion is preferred over an increase in selectivity, or vice versa, for further OCM catalyst improvements. The details of the 3 cases are listed in Table 5:

Table 5. Simulations selected to analyse the effect of the reactor performance improvement in the ethylene cost distribution.

	Reference case	Case 2 (higher C ₂ selectivity)	Case 3 (higher CH ₄ conversion)
CH ₄ conversion (%)	31.8	31.8	40.8
C ₂ selectivity (%)	43.8	56.2	43.8
C ₂ yield (%)	13.9	17.9	17.9
Ethylene price (€/ton)	1541	1223	1460

The ethylene cost distribution in the cases selected is presented in Figure 8:

Figure 8. Cost distribution of an OCM plant, CAPEX, (left) and disaggregated ethylene cost, CAPEX AND OPEX, (right) for the reference case, case 2 (higher C₂ selectivity) and Case 3 (higher CH₄ conversion).

It can be seen in Figure 8 that both CAPEX and OPEX show better results when the C₂ reactor yield is improved by increasing the C₂ selectivity rather than by increasing the CH₄ conversion (Case 2 has lower costs than Case 3). The variation in the separation train units cost (CAPEX) is originated by the fact that the outlet of the OCM reactor is influenced by the achieved C₂ selectivity and CH₄ conversion, getting in each case a specific by-products distribution. Particularly, Case 2 will have a separation train with more unreacted CH₄ while Case 3 will face more undesired carbon products (CO and CO₂). Actually, the low CAPEX cost obtained in Case 2 relates mainly to the cost of the refrigeration cycle, which accounts for all the energy required for the cryogenic units, and of the methanizer. The low productivity of undesired carbon (mainly CO) because of the high C₂ selectivity achieved in the OCM reactor will originate a lower methanizer cost, since this unit is meant to convert back the CO into CH₄. Furthermore, the increase in ethane and ethylene mol fractions at the inlet of the cryogenic distillation columns, as consequence of increased selectivities, will result in lower amounts of condensable gases at the condenser of the de-methanizer. This will lead to lower energy requirements in the condenser which will results in the need of less power consumption compressors for the refrigeration cycle, with a positive impact on both CAPEX and OPEX.

Another remarkable cost change is associated with the OCM reactor. The cost of this unit in Case 2 and 3 is much smaller than in the reference case. The endothermic C₂H₆ dehydrogenation becomes more important when more C₂H₆ is produced during the primary reactions, as it happens in Cases 2 and 3. As a consequence, the overall system is less exothermic, thus reducing the required number of cooling tubes with a concomitant decrease in the cost of this reactor.

Correspondingly, the OPEX is also largely influenced by the reactor performance. A better reactor performance leads to a reduction in the carbon footprint of the process, since less natural gas is needed to achieve the same production capacity. However, even if the total electricity consumption is also decreased when increasing the OCM reactor performance (especially in Case 2), it still remains as a strong factor on the final ethylene price and it evidences the need to import electricity. This power generation is still associated with large CO₂ emissions derived from the electricity production, and could be understood as a drawback of this process.

Summing up and knowing that an increase of the OCM reactor performance is always beneficial for the process, it has been demonstrated that the effect of increasing the C₂ selectivity has a larger (and positive) impact in both the CAPEX and the OPEX of the process than when the CH₄ conversion is increased (reaching the same C₂ yield).

4.3 OCM forecast

Different aspects such as location, politics or economics, can have a large influence on the ethylene market price. Therefore, it remains challenging to properly predict the ethylene price in the coming future. However, based on the historical ethylene price trend for the last 30 years (in US, since there was no data available from Europe) [34], a linear trend line has been extrapolated to foresee the ethylene price for the coming years. The results of this analysis are plot in Figure 9:

Figure 9: Historical ethylene price (black) [34], ethylene price forecast based on historical data (red) and ethylene price forecast using OCM (blue) for the coming period.

In Figure 9 it can be seen that in the near future, with the currently achieved C₂ yield of 14%, conventional OCM can become competitive with the traditional process because the naphtha price is expected to increase faster than the natural gas one. When considering accurate the predictions for natural gas [1] and cost of ethylene for the coming years from benchmark technologies, the currently developed OCM technology (C₂ yield=14%) for the ethylene production will be able to compete with the conventional technologies from 2030-2035 in EU. Since the increase in the oil price is supposed to be steeper than the one of natural gas (see Figure 1), and the price of ethylene in each technology is strongly affected by the cost of the feedstock used, the increase in the ethylene price when using conventional technologies is also supposed to increase faster than when applying OCM. Additionally, OCM could become competitive even before if some improvements in the process performance are achieved. In Figure 10, the OCM reactor yield required at each of the coming years to reach with OCM the same ethylene price than with conventional technologies is presented:

Figure 10: OCM reactor yield necessary to achieve the same ethylene price with OCM as with the conventional ethylene production technologies in Europe for the next period. The green area represents the C₂ reactor yield that can be currently achieved with OCM.

Because of the explained trend of the different fuels cost from which ethylene can be produced, the OCM performance required to make this technology competitive is expected to decrease in the coming years.

This can be translated into the fact that a technological breakthrough in the OCM technology, that is, a significant increase in the current OCM performance, would make OCM viable for its application at industrial scale even before than 2035. As extensively stated in previous sections, two are the most likely options to achieve this breakthrough; reaching a high maturity level with a novel reactor configuration which can provide a higher C₂ reactor yield, and/or with the development of a better catalyst which would also result in the desired reactor performance increase.

It should be in any case considered at this point that other already fully-developed technologies, like ethane dehydrogenation, can play a very significant role in this future scenario (especially if natural gas becomes much convenient than naphtha), competing also to be the most cost-

effective alternative to naphtha steam cracking. Actually, ethane dehydrogenation has been already implemented in some regions whose characteristics make the process especially convenient.

5. CONCLUSIONS

The results reported in this work show that the OCM reactor has a big influence on the ethylene price when produced with that technology. It has also been demonstrated that the cheapest ethylene does not need to be obtained necessarily with the highest C₂ reactor yield. Moreover, by using the most common OCM reactor technology, the packed bed, and by assuming the most trustable OCM kinetics, it has been demonstrated that the current OCM state of the art is not competitive with the traditional C₂H₄ production technologies.

In order to understand how to close the existing gap between OCM and benchmark technologies, the OCM reactor performance has been manually modified to increase the reactor yield and to see the effect that this change can have on the behavior of the overall plant. As a result, a C₂ reactor yield of at least 25-30%, at conditions applicable at industrial scale, is nowadays needed to obtain an ethylene price below 1000 €/ton_{C₂H₄}, which could be set as the threshold to be industrially competitive. This can be translated into the fact that a breakthrough in the OCM technology is required to reach this C₂ yield, either by means of an improvement of the catalyst characteristics and/or the development of novel reactor configurations. In this work, it has been demonstrated that an improvement in the selectivity of the catalyst towards the products is more beneficial than an increase in feedstock conversion. In addition, it should be somehow considered that the improvements should be mature and validated for long term tests to ensure a proper industrial application of such a reaction system. Considering that the assumptions formulated are relatively accurate, it can be highlighted that the OCM technology is supposed to become competitive in a period of around 20 years if, as predicted, the oil price has a steeper increase than the one of natural gas. If the foreseen situation is accomplished, a “fuel switching” scenario for the ethylene production with the emergence of some alternative technologies, like OCM, will be likely to happen.

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