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# Multi-Scale Analysis of Integrated C<sub>1</sub> (CH<sub>4</sub> and CO<sub>2</sub>) Utilization Catalytic Processes: Impacts of Catalysts Characteristics up to Industrial-Scale Process Flowsheeting, Part II: Techno-Economic Analysis of Integrated C<sub>1</sub> Utilization Process Scenarios

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**Abstract:** In the second part of this paper (Part II), the potentials and characteristics of an industrial-scale Oxidative Coupling of Methane (OCM) process integrated with CO<sub>2</sub>-hydrogenation, ethane dehydrogenation, and methane reforming processes are highlighted. This novel process concept comprises a direct conversion of methane to ethane and ethylene and further conversion of the resulted carbon dioxide and remaining unreacted methane, respectively, to methanol and syngas. In this context, the selected experimental results of the catalytic CO<sub>2</sub>-hydrogenation to methanol reported in the first part of this paper (Part I), were utilized to represent its industrial-scale performance. The experimental results of the mini plant-scale operation of an OCM reactor and CO<sub>2</sub> removal units along with the experimental and industrial data available for representing the operation and performance of all process-units in the integrated process structures were utilized to perform a comparative techno-economic environmental analysis using Aspen-Plus simulation and an Aspen Economic Process Analyzer. The experimental procedure and the results of testing the sequence of OCM and CO<sub>2</sub>-hydrogenation reactors are particularly discussed in this context. It was observed that in the sequential operation of these reactors, ethylene will be also hydrogenated to ethane over the investigated catalysts. Therefore, the parallel-operation of these reactors was found to be a promising alternative in such an integrated process. The main assumptions and the conceptual conclusions made in this analysis are reviewed and discussed in this paper in the light of the practical limitations encountered in the experimentations. In the context of a multi-scale analysis, the contributions of the design and operating parameters in the scale of catalyst and reactor as well as in the process-scale represented by analyzing the type and operating conditions of the downstream-units and the process-flowsheets on the economic and environmental performance of the integrated process structures were studied. Moreover, the economic impacts of extra ethylene and methanol produced respectively via the integrated ethane dehydrogenation and CO<sub>2</sub>-hydrogenation sections were analyzed in detail. The required capital investment was found to be even smaller than the yearly operating cost of the plant. The environmental impacts and sustainability of the integrated OCM process were found to be enhanced by securing a minimum direct CO<sub>2</sub>-emission and energy-efficient conversion of CO<sub>2</sub> and the unreacted CH<sub>4</sub>, respectively, to methanol and syngas. Besides producing such value-added by-products, efficient operation of

downstream process-units was secured by minimizing the energy usage and ethylene losses. Under the considered conditions in this analysis, the specifications of the finally selected integrated OCM process structure, providing the fastest return of investments (less than 8 years), are highlighted.

**Keywords:** oxidative coupling of methane (OCM) process; CO<sub>2</sub>-hydrogenation to methanol; multi-scale analysis; techno-economic analysis; ethane dehydrogenation; downstream units; mini plant-scale experimentation

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## 1. Introduction

Having analyzed the catalytic performance of low-pressure CO<sub>2</sub>-hydrogenation system in part I of this study, its potentials as an add-on process to be used for converting the carbon dioxide generated in other upstream processes into methanol, are highlighted here in part II. Before adding the CO<sub>2</sub>-hydrogenation system to a targeted upstream catalytic process, a selective operation and lowest possible CO<sub>2</sub> generation in the standalone operation of such a process should be ensured in the first place. This should be completed by improving the efficiency of CO<sub>2</sub> separation units and the CO<sub>2</sub>-hydrogenation section in its integrated state. This is even the case for processing relatively inexpensive abundant feedstocks such as methane via Oxidative Coupling of Methane (OCM) process. Securing high selectivity towards the desired products (C<sub>2</sub>: C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>) and its crucial impact on reducing the required energy and the operating cost of the downstream separation/purification units have been emphasized to be one of the main design criteria in this process [1]. A selective catalytic reactor performance can be secured only when a selective catalyst and proper set of operating conditions as well as efficient feeding policy and heat management in the reactor-scale are established. The impacts of the design and operating parameters of the downstream-units along with the process-flowsheet configurations on the process-scale energy and economic performance should be also carefully analyzed. The interactive impacts of these aspects should be also addressed in such a multi-scale analysis, especially in developing an integrated process.

In addition to the generated CO<sub>2</sub>, extra CO<sub>2</sub> used as diluent for controlling the thermal performance of the OCM reactor [2] as well as the generated hydrogen during OCM reaction can enhance the integration potentials of the OCM and CO<sub>2</sub>-hydrogenation processes. These, along with other potentials and limitations of integrating CO<sub>2</sub>-hydrogenation within the OCM process, represented by one of the best reported selective OCM reactor performances, as well as efficient downstream units, are discussed in this paper. The overall carbon conversion performance of such an integrated process is expected to be improved in this manner. The selected experimental results reported in the first part of this study (best-reported methanol-yield in Part I for catalyst CuO–ZnO/Al<sub>2</sub>O<sub>3</sub>–MET2—using an H<sub>2</sub>/CO<sub>2</sub> ratio of 3 and 10 bar pressure), are utilized to represent the performance of an industrial-scale CO<sub>2</sub>-hydrogenation to methanol reactor in such analysis. The experimental results and the procedure of testing the coupled OCM and CO<sub>2</sub>-hydrogenation reactors are specifically discussed in Part II of the paper.

To further improve the efficiency of such integrated process, generated ethane in an OCM reactor is further converted to ethylene and the unreacted methane is converted to carbon monoxide and hydrogen (Syngas) via reforming process, all contributing to improving the sustainability of this process for producing ethylene and methanol as important intermediate chemicals. The downstream units of such integrated OCM process have been designed not only to be conceptually compatible with the integrated process structure but also to ensure their energy efficiency and minimum environmental impacts. These have been supported by the results of an extensive mini plant-scale experimental analysis. Finally, an experimentally-supported techno-economic analysis of various integrated process structures in their industrial-scale production capacity (one million tons per year ethylene production) was conducted using the Aspen-Plus simulation and Aspen Economic Process Analyzer. The performed economic-analysis starts with reviewing the specifications and performance of the reference OCM classic standalone process followed by highlighting the impacts

of further converting the unreacted methane and ethane respectively in the reforming and dehydrogenation reactors. Then, the integration potentials of the carbon dioxide hydrogenation to methanol within such OCM process structure are highlighted. In this context, specifically, the impacts of processing the undiluted or CO<sub>2</sub>-diluted feeds in the OCM reactor operating in parallel or series configurations with CO<sub>2</sub>-hydrogenation reactor, are investigated.

## 2. Conceptual Process Design and Selecting the Operating Parameters

In this of the paper, the conceptual design criteria for developing an efficient OCM process structure and an add-on CO<sub>2</sub>-hydrogenation unit to be integrated with it are reviewed. In this context, it is explained that the unreacted methane in the OCM reactor should be further converted into a reforming reactor to produce syngas and the required hydrogen for the CO<sub>2</sub>-hydrogenation unit. The ethane produced in the OCM reactor also should be converted to more valuable product ethylene in the ethane dehydrogenation (EDH) section. Selecting the operating parameters in different sections of such an integrated process is also discussed here.

### 2.1. Oxidative Coupling of Methane Process

Methane and oxygen are the OCM reactants catalytically reacting (usually in the temperature range of 650–850 °C) to produce ethane and ultimately ethylene. Methane as a primary reactant and ethylene as the ultimately targeted product can undergo undesired reactions to generate carbon oxides. The reaction set R-1 and -2 and reaction set R-3 and -4 respectively represent the main desired and undesired exothermic catalytic reactions of this system:



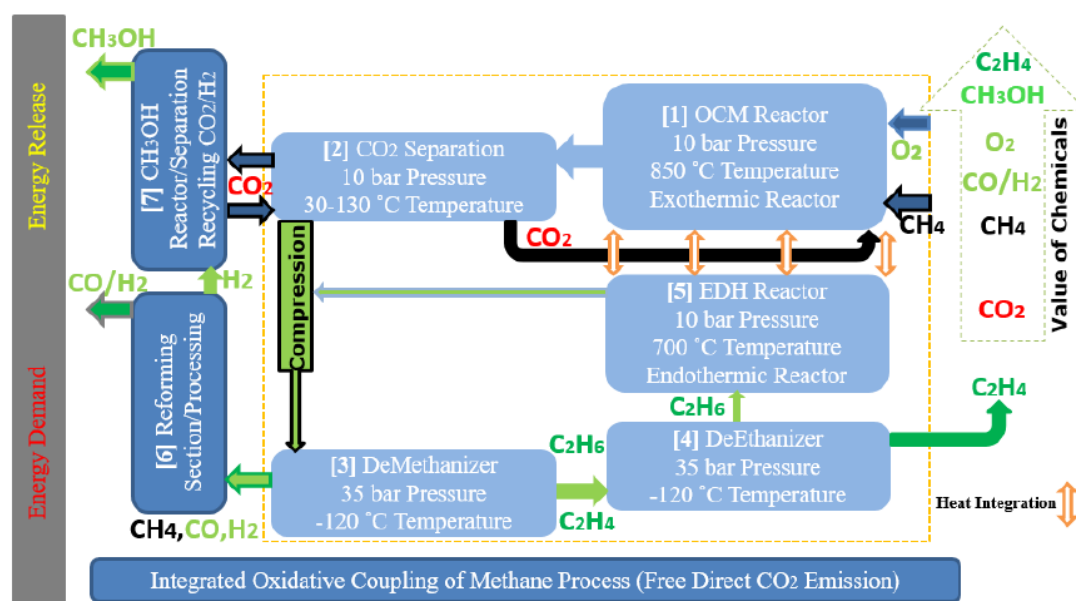
Gas-phase reactions, especially ethane dehydrogenation reaction, water gas shift (forward and reverse), and reforming reactions, also affect the OCM reactor performance. Hydrogen, water, and in lesser amount propane, propylene, etc. are the side products of the OCM reaction system. More information about the involved gas and surface reactions, distribution of the products, and the impacts of operating conditions can be found elsewhere [1]. A wide range of catalysts with different materials and structural characteristics have been suggested and tested for this system [3]. Being selective and stable are the main criteria for selecting an efficient OCM catalyst. The selectivity (S) and the yield (Y) of the desired products (C<sub>2</sub>), as well as methane conversion (X) are the main performance indicators for this catalytic reactor system as defined by Equations 1 and 2:

$$Y_{\text{C}_2} = \frac{2 \times (n_{\text{C}_2\text{H}_6} + n_{\text{C}_2\text{H}_4})}{n_{\text{CH}_4}^{\text{inlet}}} \quad (1)$$

$$S_{\text{C}_2} = \frac{Y_{\text{C}_2}}{X_{\text{CH}_4}} = \frac{2 \times (n_{\text{C}_2\text{H}_6} + n_{\text{C}_2\text{H}_4})}{(n_{\text{CH}_4}^{\text{inlet}} - n_{\text{CH}_4}^{\text{outlet}})} \quad (2)$$

The so far observed values of per pass methane conversion and C<sub>2</sub>-yield for the industrially relevant targeted range of C<sub>2</sub>-selectivity (e.g. 70%–80%) are respectively limited to below 40% and 30% [4]. Increasing the per pass methane conversion usually leads to a significant decrease in the C<sub>2</sub>-selectivity, which cannot be easily compromised due to its significant impact mainly on the operating cost of the downstream units as well as the economic performance and environmental impacts of the whole process.

Conceptually analyzing these aspects indicates that first the generated carbon dioxide and then the significant amount of unreacted methane should be separated as shown in Figure 1.



**Figure 1.** The process block-flow diagram of alternative Oxidative Coupling of Methane (OCM) process structures investigated in this research.

As seen in Figure 1, water and carbon dioxide are completely separated at first. This is crucial not only to minimize the need for using costly corrosive-resistance material but also to prevent encountering possible difficulties in the operation of the downstream units, especially the cryogenic distillation (CD) columns. In the first CD-column (3-Demethanizer), the unreacted methane and other light gases (i.e. hydrogen and carbon monoxide) are separated from C<sub>2</sub>- and heavier products. The C<sub>2</sub>-products will later be separated from each other in another CD-column (4-Deethanizer).

The operation and the design characteristics of different unit operations, as well as the whole integrated process, will be discussed in this paper. As the first step, the specifications and the selected performances of the OCM reactor and CO<sub>2</sub>-separation units in the lights of mini plant-scale experimental observations [5] are analyzed.

### 2.1.1. Reactor Section

For this study, the experimentally observed selective performance of one of the most promising OCM reactors, namely porous packed bed membrane reactor showing up to 45% methane conversion and 26% C<sub>2</sub>-yield, [2,6] using research-benchmark Mn-Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> catalyst, was used to represent the industrial-scale OCM reactor performance and operation. Nevertheless, the robust and stable operation of any OCM reactor and catalyst should be tested and assured in a pilot-plant long-term operation before any commercial industrial-scale installation and operation.

### Feed Specifications

Composition, temperature, pressure, and flow rate of the feed stream processed in an OCM reactor are designed to secure a robust-stable safe operation for maximum selective methane conversion while minimizing the undesired impacts on the operation and the costs of the downstream units. Setting the temperature, the level of dilution, and the ratio of reactants in the feed affect the thermal-reaction performance of the reactor as well as the operation of the downstream units. These parameters should be properly designed also concerning their impacts on the safe operation of the reactor in terms of avoiding the buildup of an explosive atmosphere as well as controlling the reaction temperature.

In this study, the feed methane-to-oxygen ratio of 2 was selected to secure the highest methane conversion per pass of OCM reactor and therefore the lowest undesired impacts on the demethanizer. To highlight such an impact, processing an OCM feed with an alternative methane-to-oxygen ratio of around 4 was also studied in this research. The excess methane in this case not only resulted in

improved selective performance but also acts as a diluent (methane-diluted feed) enabling better temperature control in the OCM reactor and its thermal-reaction performance from this perspective. Using higher methane-to-oxygen ratios cannot be justified if the per-pass ethylene and ethane yield of higher than 25% is targeted (this was experimentally demonstrated in this research) because obtaining the correspondingly targeted per-pass methane conversion, in this case, becomes infeasible due to stoichiometry limitation. Using a lower methane-to-oxygen ratio than 2 is not also recommended as it significantly reduces the chance for controlling the reaction temperature and increases the possibility of building an explosive atmosphere [7]. Such risks are emboldened when lower gas dilution is used. The OCM reactor feed always contains some level of an inert gas such as nitrogen either coming from methane and oxygen sources or being additionally injected to control the reaction temperature. The OCM feed containing up to 5% nitrogen is referred to as undiluted feed in this paper. Higher nitrogen content imposes an unbearable separation cost on the demethanizer and therefore is not considered in this research.

As an alternative, CO<sub>2</sub> diluted OCM feed is recommended and analyzed in this research. There are several reasons for choosing CO<sub>2</sub> dilution. CO<sub>2</sub> is a side product of the OCM reactions and can be relatively easily separated in the downstream units and recycled back to the OCM reactor. Moreover, Biogas, which contains methane and carbon dioxide, can be also considered as an alternative OCM feed in this manner if a sizable quantity of biogas is available [5]. Having considered the above-mentioned potentials for utilizing and treating large-scale CO<sub>2</sub> streams, further process integration and minimization of the overall CO<sub>2</sub> emission are addressed in an integrated OCM process structure shown in Figure 1. Table 1 summarizes the quantity and compositions of the investigated three different feed streams processed in an industrial-scale OCM plant with one million ton ethylene annual production capacity. The corresponding reactor product composition in each case, which has been experimentally observed through the mini plant-scale OCM reactor operations, is also seen in this table.

**Table 1.** The OCM reactor inlet/outlet feed/product stream compositions with three levels and types of dilution: (a) undiluted, (b) CO<sub>2</sub>-diluted, and (c) CH<sub>4</sub>-diluted.

Component	Feed (ton/h) 25 °C (mM/h)			Product [mol %]		
	(a) Undiluted	(b) CO <sub>2</sub> -Diluted	(c) CH <sub>4</sub> -Diluted	(a) Undiluted	(b) CO <sub>2</sub> -Diluted	(c) CH <sub>4</sub> -Diluted
CH <sub>4</sub>	733 (45.7)	733 (45.7)	1131 (70.9)	30.56	24.80	49.80
C <sub>2</sub> H <sub>4</sub>	-	-	-	5.37	4.30	4.53
C <sub>2</sub> H <sub>6</sub>	-	-	-	1.57	1.40	2.05
CO	-	-	-	3.7	4.00	4.31
CO <sub>2</sub>	-	1320 (30)	-	12.95	34.90	3.23
H <sub>2</sub>	-	-	-	12.35	8.60	10.91
H <sub>2</sub> O	-	-	-	27.76	19.90	18.45
C <sub>3</sub> H <sub>8</sub>	-	-	-	400 ppm	470 ppm	0.03
C <sub>3</sub> H <sub>6</sub>	-	-	-	0.50	0.50	0.35
N <sub>2</sub>	78 (2.8)	-	173 (6.2)	3.75	-	6.30
O <sub>2</sub>	731 (22.8)	731 (22.8)	613 (19.1)	1.38	1.5	-

-: negligible or not considered

### Operating Temperature and Pressure in the OCM Reactor

The operating temperature in an OCM reactor is selected to secure a selective catalytic conversion, which is usually determined as a result of testing the OCM catalysts under a wide range of operating temperatures. In general, if the behavior of the OCM catalyst allows, running the OCM reactor in lower temperatures (below 700 °C) is preferred as it reduces the undesired contribution of the gas-phase reactions and complications of the temperature control. However, besides targeting a specific range of operating temperatures, also a desired temperature profile along the reactor should be established. These have been taken into consideration in this research also given improving the

potential of heat integration in the integrated process by operating the OCM reactor at an average temperature of 820 °C.

Operating pressure in the OCM reactor is selected not only concerning its impact on the catalysts and reactor performance but also mainly because of the required driving pressure to push the processed gas into the downstream units, specifically in CO<sub>2</sub>-removal units. The operating reactor pressure for an industrial application inevitably should be higher than atmospheric, preferably in the desired range of 5–10 bar. This is needed to avoid imposing significant cost and duty of compression needed for pressurizing the OCM reactor outlet gas, containing carbon dioxide, and to make it ready to be treated in the CO<sub>2</sub>-removal unit and CO<sub>2</sub>-hydrogenation reactor as shown in Figure 1. On the other hand, the undesired impact of elevated pressure on the performance of the OCM reactor should be also taken into consideration. Having considered these and the results of the mini-plant scale operation of the CO<sub>2</sub>-removal units, the operating pressure of the industrial-scale OCM reactor was set to be 10 bar in this study.

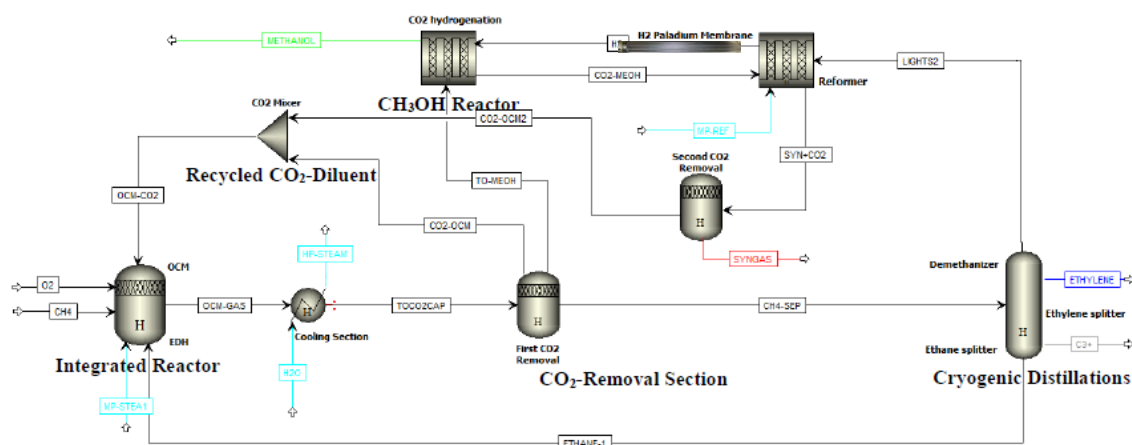
### 2.1.2. OCM Downstream Units: Carbon Dioxide Removal and Cryogenic Separation

To reduce the uncertainties around the industrial-scale operation of the integrated process as much as possible, it was decided to use the mature technologies such as amine absorption and cryogenic distillation technologies as downstream separation/purification units in this analysis. However, the performance of the energy-intensive amine CO<sub>2</sub>-separation and cryogenic distillation systems for separating the unreacted methane, and light gases such hydrogen and carbon monoxide, and down the line separating ethane and C<sub>3</sub>–C<sub>4</sub> hydrocarbons from ethylene should be optimized. These have been addressed for instance using available reference data representing the industrial-scale performance of the cryogenic distillation in ethane and naphtha cracking processes [8].

Moreover, conventional amine scrubbing using methyl diethanolamine (MDEA) aqueous solution as a benchmark absorbent, was applied for CO<sub>2</sub> separation in the industrial-scale operation of the OCM process scenarios. The operating conditions in the absorption/stripping columns were selected based on the Technische Universität Berlin's mini plant-scale experimental observations, which is generally in line with the designed operation of industrial plants for similar applications, and ensuring an energy-efficient separation performance while the ethylene loss is kept below 5%. The operation of all these separation/purification units has been specially analyzed and designed in this research in the context of efficient utilizing them in the investigated integrated process structures represented in Figure 1.

### 2.2. Ethane Dehydrogenation Reactor

Integration of an industrial-scale OCM process with ethane dehydrogenation (EDH) can be established in two levels as shown in Figure 2: (a) sharing the downstream units for both processes and (b) establishing an integrated reactor and integrated process.



**Figure 2.** The process flowsheets of integrated OCM process structures simulated in Aspen (the unit names are according to Supplementary Table S-1).

In this research, the OCM and EDH reactors outlets are joined and processed together by the shared downstream unit operations. In the reactor section of an industrial-scale plant, some level of heat integration between the OCM and EDH sections, respectively considered as heat-source and heat-sink, was assumed to be established. The efficiency of such integration depends on the compositions of the feed streams and the thermal management of the furnace. In this study, the ethane generated through the OCM reaction is separated and recycled into the EDH section of the integrated reactor while being mixed with 40% steam to secure converting 50%–60% of ethane to ethylene with an ethylene selectivity of 80%–90%. This is a typical performance for an industrial-scale thermal cracker or catalytic dehydrogenation technology. In the Siluria technology, which is one of the few plants implementing OCM technology in the scale larger than the lab-scale, the reactor has been similarly designed in two compartments so that ethane is converted to ethylene right after the OCM catalytic bed [9].

### 2.3. Methane Reforming Reactor

The remaining unreacted methane, which is more than 50 percent of the inlet methane to the OCM reactor, should be separated and either recycled back to the OCM reactor or further converted to valuable chemicals. In the investigated integrated OCM process configurations in this research, the second option has been chosen. This is because the required separation of light gases (hydrogen and carbon monoxide) from unreacted methane before recycling it back to the OCM reactor imposes a significant cost, which cannot be justified having considered the range of methane prices in this study. Methanation of one mole of carbon monoxide requires more than 3 moles of hydrogen and therefore is not conceptually and economically justified also from this perspective. In this manner, the remaining unreacted methane is converted to hydrogen and carbon monoxide through a catalytic reforming reactor, where carbon dioxide and steam reforming of methane, as well as partial oxidation of methane, take place. This has been shown in Figure 2, where the top methane-rich stream of demethanizer, which also contains carbon monoxide and hydrogen, is easily handled in the reformer as it contains only the main reactant and the products of the methane reforming. By tuning the inlet quantity of CO<sub>2</sub>, steam, or oxygen and the operating conditions in the reforming section, the composition of the outlet product stream can be tuned. Therefore, the required amount of excess hydrogen can be produced in the reformer to be separated quickly afterward using the palladium membrane and supplied for hydrogenation of CO<sub>2</sub> to methanol, while securing the targeted syngas composition and its economic perspective for being ultimately converted to chemicals in downstream processes. The considered catalyst, operating conditions, reactions, and expected reaction performance in methane reformers in this research, as well as the performance of palladium membrane demonstrated in pilot-plant scale, have been reported in detail elsewhere [10]. The

selected operating pressure of 10 bar and temperature of 820 °C enable efficient integration of this system into the whole OCM process structure as shown in Figure 1.

#### 2.4. Carbon Dioxide Hydrogenation to Methanol

CO<sub>2</sub>-hydrogenation to methanol was selected here to be utilized primarily as a reactive separation of CO<sub>2</sub> in the OCM reactor outlet stream. Therefore, in such a reactor-series integrated configuration, 10 bar was chosen to be not only the operating pressure of the OCM reactor but also the operating pressure of the CO<sub>2</sub>-hydrogenation to methanol reactor under which all experiments in part I of this paper have been conducted. Accordingly, the best-performed methanol catalyst CuO–ZnO/Al<sub>2</sub>O<sub>3</sub> (MET2) and optimum operating temperature of 200 °C were then selected to represent the methanol reactor as an add-on block in the industrial-scale integrated OCM process. One of the so-far best-reported performances of pilot-plant scale operation of low-pressure CO<sub>2</sub>-hydrogenation reactor [11] is in line with the best catalytic performance observed in the experimentation reported in part I of this paper. Therefore, they have been utilized to represent the methanol reactor in the techno-economic analysis of the industrial-scale integrated process scenarios.

In the reactors-series integrated configuration, after separating methanol and water right after the methanol reactor, unreacted carbon dioxide is separated. The rest of the gas components can be handled in a downstream unit for instance in demethanizer, where the remaining unreacted hydrogen from the methanol reactor should be also separated along with the light gases coming from the OCM reactor. In such configuration, the excess hydrogen cannot be easily separated from the rest of the light gases and recycled back to the methanol reactor. This significantly increases the operation cost.

Alternatively, in the integrated process configuration shown in Figure 1, which in this paper is referred to as reactors-parallel integrated configuration, CO<sub>2</sub> and H<sub>2</sub> are supplied respectively from the CO<sub>2</sub> removal section and reforming-membrane section and enter the methanol reactor. In this configuration, methanol is simply separated as condensed product after the reactor and the remaining unreacted carbon dioxide and hydrogen can be directly recycled back to the methanol reactor. However, the methane and carbon monoxide content of such stream build up as a side product of the CO<sub>2</sub>-hydrogenation should be also handled properly. The desired values of the H<sub>2</sub>/CO<sub>2</sub> ratio in the beginning of the methanol reactor being secured via a proper supply of extra CO<sub>2</sub> and hydrogen.

In any of those integrated process configurations, the required process feed with overall H<sub>2</sub>/CO<sub>2</sub> ratios of 3 and 6 are secured by setting the feed composition of the reformer, and the separation performance of the palladium membrane unit. These will also determine the quality of the resulted syngas (H<sub>2</sub>/CO = 2.5). It has been demonstrated in the scale larger than lab-scale experimentation [11], that using such a set of operating conditions and the selected catalyst in this research for low-pressure catalytic CO<sub>2</sub>-hydrogenation process can result in one of the best so far reported methanol yield of more than 20%.

In part I of this paper, a mixture of CO<sub>2</sub> and hydrogen was treated in the methanol reactor and the details of the experimentation were provided in paper-section 4 there. Here, in part II of this paper, particularly the experimental analysis of the direct sequential operation of the OCM and CO<sub>2</sub>-hydrogenation reactors (reactors-series integrated configuration) are reported and discussed. In such a reactor-series configuration, the methanol reactor is located right after the OCM reactor, and in this manner, the OCM reactor outlet gas stream directly enters into the methanol reactor. The feed-mixture to the OCM reactor was tuned by feeding nitrogen, methane, and oxygen. The OCM reactor was also operating above 10 bar pressure and 800 °C. The pipe-lines connecting the OCM reactor to the methanol reactor and gas chromatograph (GC) were kept heated at 170 °C. Similarly, the methanol reactor outlet gas mixture is heated in the line up to 170 °C and directly sent to be analyzed in GC. Mole fractions of all gas components were measured using the GC and beside performance indicators of the methanol reactor, methane conversion and yield of the OCM products were also calculated. The most challenging aspects of running such reactors-series in sequential-configuration were: (a) to synchronize the feed flows to establish the required Gas Hourly Space Velocity (GHSV)



needed in the OCM and methanol reactors while tuning the amount of catalyst used in each reactor section, (b) to ensure that oxygen is completely consumed in the OCM reactor as it deactivates methanol catalyst, and (c) to prevent hydrogenation of ethylene on the methanol reactor which was observed to be a serious issue. The first and second challenges were addressed using a proper design of experiments. In this manner, the amount of OCM catalyst ( $\text{Mn-Na}_2\text{WO}_4/\text{SiO}_2$ ) in the first reactor (6 mm ID quartz tube) and methanol catalyst ( $\text{CuO-ZnO/Al}_2\text{O}_3$  MET2) in the second reactor was set respectively to 6 and 8 g. Using these amounts of catalysts and the set feed flows, the values of GHSV in each reactor were set to be close to the targeted values under which OCM reactor and methanol reactor have individually demonstrated their best performances. However, it was observed that hydrogenation of ethylene, over the investigated catalysts and under the operating conditions tested in this research, could not be prevented. As seen in Table 2, the generated ethylene in the OCM reactor has been completely converted to ethane while passing through the methanol reactor, even under the low  $\text{H}_2/\text{CO}_2$  ratio of 3.

**Table 2.** Typical observed experimental performance of the sequence of OCM and methanol reactor (The reported percentages are the dry-based).

Reactor Outlet/inlet	$\text{CH}_4$	$\text{CO}_2$	$\text{H}_2$	$\text{C}_2\text{H}_4$	$\text{C}_2\text{H}_6$	$\text{CO}$	$\text{N}_2$
OCM Reactor Outlet (%)	43	19	18	8	2	5	5
Methanol Reactor Inlet (%)	31	13.5	41	6	1.5	3.7	3.7
Methanol Reactor Outlet (%)	34.4	10.6	36	0	11	3.4	3.5

As seen in this table and as it was observed in several experiments, in such sequential operation of the OCM and methanol reactors configuration, methanol yield is significantly lower than it was observed to be in the standalone methanol reactor operation because: (a) the feed entering the methanol reactor contains other components beside  $\text{CO}_2$  and hydrogen, (b) of limitations encountered in fully synchronizing the set GHSVs in the OCM and methanol reactors around their optimum values, (c) securing the optimum reaction conditions in general inside the methanol reactor was not always possible, (d) part of the hydrogen is consumed to convert ethylene to ethane, and (e) coke formation in the methanol reactor could become more severe in presence of other hydrocarbons.

The schematic and specifications of the utilized experimental setup were provided in Part I of this paper (Section 4.1, Figure 1). The similar procedure described in part I for preparing and running the experiments for the  $\text{CO}_2$ -hydrogenation was also applied for running the reactors in the sequential configuration.

### 3. Multi-Perspectives Process Scenarios Screening

Following aspects have been considered in a hierarchical structure of the conducted multi-scale analysis over this integrated process:

(1) In the catalyst-scale, the impacts of catalysts' characteristics of OCM and  $\text{CO}_2$ -hydrogenation system, established via different synthesis and compositions, on their performances were analyzed. The results reported in Part I of this manuscript serve in this context.

(2) In the reactor-scale, the impacts of operating conditions such as pressure, temperature, feed composition, and GHSV on the thermal-catalytic performance of the reactors were analyzed. Some of the results reported in Part I of this manuscript were used to represent the performance of the reactors in the process scenarios analyzed in Part II of this manuscript.

(3) In the process-scale, the impacts of reactor-scale performances on the process integration and techno-economic analysis are analyzed. This is the main aspect addressed in Part II of this manuscript.

Converting the generated  $\text{CO}_2$  in the OCM section to produce methanol using the hydrogen supplied by reforming the remaining unreacted methane from the OCM section and the requirement for addressing the interactive technical/economic and environmental impacts of this section, make them very interconnected. Therefore, these all have to be reflected in the multi-scale analysis of the

integrated process. Then, not only the introduced integrated process concept in this research is novel, but also the applied approach for analyzing the involved phenomena and parameters in different scales, affecting the performance of the catalyst, reactor and the process, is new and promising.

### 3.1. Simulated Process Scenarios and Designed Concepts

Having reviewed the specifications of different reactors and separation units as well as their operating conditions, their performances in industrial-scale operation were simulated in different process configurations in this research. These process scenarios and their general design and operating aspects have been listed in Table 3.

**Table 3.** List of selected simulated process scenarios and their specifications.

Scenario	Sequence Based on Figure 1	Feed			Integrated Reactors		Reforming
		CH <sub>4</sub> /O <sub>2</sub> Ratio	Dilution	EDH	Methanol-Parallel	Methanol-Series	
Standalone	1-2-3-4	2	Undil.-4%N <sub>2</sub>	-	-	-	-
OCM-EDH	1-2-3-4-5	2	Undil.-4%N <sub>2</sub>	✓	-	-	-
Int-Scen-1	1-2-3-4-5-6	2	Undil.-4%N <sub>2</sub>	✓	-	-	✓
Int-Scen-2	1-2-3-4-5-6-7	2	Undil.-4%N <sub>2</sub>	✓	✓	-	✓
Int-Scen-3	1-7-2-3-4-5-6	2	Undil.-4%N <sub>2</sub>	✓	-	✓	✓
Int-Scen-4	1-2-3-4-5-6	2	30%-CO <sub>2</sub> dil.	✓	-	-	✓
Int-Scen-5	1-2-3-4-5-6-7	2	30%-CO <sub>2</sub> dil.	✓	✓	-	✓
Int-Scen-6	1-7-2-3-4-5-6	2	30%-CO <sub>2</sub> dil.	✓	-	✓	✓
Int-Scen-7	1-2-3-4-5-6	4	CH <sub>4</sub> diluted	✓	-	-	✓
Int-Scen-8	1-2-3-4-5-6-7	4	CH <sub>4</sub> diluted	✓	✓	-	✓

-: not included in the process scenario; ✓: included in the process scenario

The sequence of process units in each process scenario configuration has been also listed in Table 3. The techno-economic-environmental performances of these process scenarios have been comparatively analyzed in this research as reported in the following paper-sections. Such comparative analysis demonstrates the impact of gas diluents as well as the contributions of extra ethylene and methanol production respectively via ethane dehydrogenation and CO<sub>2</sub>-hydrogenation reactors.

Starting with processing the undiluted feed, the impact of adding ethane dehydrogenation is highlighted by comparing the performances of the standalone OCM process, and the OCM-EDH process scenarios. From integrated process scenario 1 (Int-Scen-1), methane reforming section is included under the assumption that it does not impose any extranet cost but paves the way for integrating the methanol reactor in the integrated process scenarios 2 (Int-Scen-2) and 3 (Int-Scen-3), respectively, in a parallel- and series-configurations. A similar analysis is made in process scenarios 4-6 (Int-Scen-4,5,6) by treating the CO<sub>2</sub>-diluted feed in the OCM reactor. Process scenario 8 (Int-Scen-8) was investigated to analyze the contribution of methanol production about process scenario 7 (Int-Scen-7) as the integrated process configurations, where methane-diluted feed is treated in the OCM reactor.

In all of these process scenarios, it has been tried to maximize the energy efficiency of each unit operation as well as the process-scale heat integration efficiency. The performance of the OCM reactor in each scenario has been experimentally demonstrated. Simultaneously, the feasibility of the simulated scenarios has been ensured and all practical limitations for instance regarding material selection and operating conditions have been taken into consideration. Available industrial data regarding the performance of the standard carbon dioxide removal and cryogenic distillation systems were utilized for double-checking the plausibility of the simulation results.

The unit operations of the integrated process simulated in Aspen Plus® are seen in Figure 2. The dimensions and operating conditions of the industrial-scale process units have been determined according to the experimental observations, for instance, to secure the optimum GHSV and reaction temperature in the reactor units and to synchronize the operating pressure in the reactor and the CO<sub>2</sub>-removal and CO<sub>2</sub>-hydrogenation units.

In this manner, the amine scrubbing unit was simulated in Aspen HYSYS software using a 30 wt. % MDEA solution under 10 bar pressure by considering the “Acid gas” thermodynamic equations while the stripper operates at 1.5 bar pressure.

Rate-based simulation of the RadFrac cryogenic distillation columns with the operating pressure higher than 30 bar was performed to predict the dimensions and intense energy needed to separate the light gases (methane, hydrogen, carbon oxide, and nitrogen) from ethane and ethylene in a demethanizer and later separate ethane and ethane in a C<sub>2</sub>-splitter under lower operating pressure of around 20 bar.

Optimum heat integration and utilization of the heat sources and sinks in the integrated process have been targeted in this step so that significant amounts of medium/high-pressure steam and electrical power could be generated to be either used internally or considered as byproducts of the process.

Detailed information about the design and operation of these units have been also provided. As an example, Supplementary Table S-1 presents the sets of operating conditions and gas compositions entering and leaving the main unit operations indicating the performances of the reaction and separation units. The reported data in Supplementary Table S-1 correspond to the operation and performance of the integrated process scenario 5 (Int-Scen-5), which has been found to be one of the most efficient integrated process structures investigated in this research reflected in its economic and environmental impacts.

### 3.2. Economic Analysis and Results

After simulating all process scenarios listed in Table 3, fine-tuning the operating conditions, and sizing the dimensions of the equipment in operating units, their techno-economic-environmental performances were predicted using Aspen economic analyzer. These were achieved through a step-by-step sensitivity analysis and tuning the parameters to secure lower operating costs in the simulated process units. The considered costs of the products, raw materials, and utilities, as well as other specifications of the performed economic analysis, are provided in Table 4.

**Table 4.** Basic data for the techno-economic analysis: (left) operating and economic data; (Right) cost of the raw materials, utilities, and products\* (The costs and selling prices are the average local market values taken from trade companies (Eránico 2017)). \* Prices are locals for countries with significant natural gas resources with the delivery conditions required for this process.

Number of weeks per year	48	Market selling price ethylene (€/t)	900
Number of years for analysis	15	Market selling price ethane (€/t)	250
Tax rate (%/year)	10	Market selling price methanol (€/t)	220
Interested rate/Desired rate of return (%)	12	Market selling price C <sub>3+</sub> (€/t)	260
Economic Life of Project (year)	15	Market selling price HP-steam (€/MJ)	0.001
Working capital percentage (%/year)	15	Market selling price methane (€/t)	110
Operating charges (%/year)	25	Market selling price oxygen (€/t)	13

Plant Overhead (%/year)	25	Cost of fuel for heating (€/t)	60
Salvage value (%)	10	Cost of lowest cooling media (−160 °C) (€/J)	$3.5 \times 10^{-8}$
Length of start-up period (week)	15	Cost of cooling in C <sub>2</sub> -splitter (−47 °C) (€/t)	$1.4 \times 10^{-9}$
		Cost of electricity (€/kWh)	0.05

The considered costs and prices here are all for the same locality (Middle East [12]) and the subject of change from place-to-place or time-to-time. For instance, other methane sources from free-/negative-cost flare gas with the worldwide capacity of more than millions of cubic meter per hour to the relatively expensive and limited production capacity of up to thousands of cubic meter per hour biogas, have been also evaluated for industrial-scale OCM application. The price of utilities, raw materials, and the products also strongly depend on the local conditions. Therefore, the associated economic, logistic, and environmental aspects of choosing the location for implementing the OCM technology should be taken into consideration.

The main economic performance indicators of the investigated process scenarios have been listed in Table 5 along with their predicted values for each process scenario.

**Table 5.** Economic performance indicators of the investigated process scenarios (pre-specified in Table 3).

Scenarios	OCM Standalone	OCM-EDH	Int-Scen-1	Int-Scen-2	Int-Scen-3 *	Int-Scen-4	Int-Scen-5	Int-Scen-6	Int-Scen-7	Int-Scen-8
Total ethylene Produced (million Kg/year)	898	1126	1126	1126	1129	1288	1288	1275	1345	1345
Fixed Cost (million €)	267	350	548	638	506	870	1077	1148	638	668
Operating Cost (million €/year)	994	1032	1167	1399	1277	1443	1369	1961	1647	1623
Raw Material Cost (million €/year)	730	735	780	864	818	730	735	727	1115	1065
Utility Cost (million €/year)	168	196	272	398	335	570	496	1038	372	400
Total Methanol Sales (million €/year)	-	-	-	247	168	-	347	558	-	80
Total Syngas Sales (million €/year)	-	-	183	202	144	277	309	272	220	216
Total Product Sales (million €/year)	953	1089	1272	1537	1404	1522	1901	2067	1520	1596
Ethylene Loss (%)	0.8	0.3	0.3	0.3	0.3*	0.1	0.4	0.1	0.2	0.2
Total specific energy per t of Ethylene (GJ/t C <sub>2</sub> H <sub>4</sub> )	54	47	61	75	60	70	91	129	45	45
Total specific energy cost Ethylene (€/t C <sub>2</sub> H <sub>4</sub> )	170	157	241	253	267	443	385	814	277	298
Utility CO <sub>2</sub> Emission (t CO <sub>2</sub> /t C <sub>2</sub> H <sub>4</sub> )	1.10	1.18	1.86	2.96	2.39	3.39	3.76	1.64	1.91	2.17
Total specific CO <sub>2</sub> Produced (t CO <sub>2</sub> /t C <sub>2</sub> H <sub>4</sub> )	4.90	4.21	3.11	4.15	2.61	5.27	3.77	2.74	1.96	2.22
Direct CO <sub>2</sub> Emission (t CO <sub>2</sub> /t C <sub>2</sub> H <sub>4</sub> )	3.80	3.03	1.25	1.19	0.22	1.88	0.01	1.10	0.05	0.05
Pay-Back Period (year)	-	9.5	9.5	9.1	8.6	-	7.9	-	-	-

\* under the assumption that ethylene is not hydrogenated.

Starting from the reference stand-alone OCM process, it can be concluded that the ethylene sale in the stand-alone OCM process cannot compensate for the relatively high operating cost (including the cost of the raw material) of this process and therefore, the pay-back period is longer than 10 years. Increasing the ethylene production via integrating ethane dehydrogenation reactor significantly increases the economy of the process because the ethylene selling price is three times more expensive than the ethane selling price and yet the processing cost of the recycled flow in the reactor and downstream unit is relatively insignificant. However, since high amounts of H<sub>2</sub>, H<sub>2</sub>O, and around 2%

methane is available in the EDH reactor outlet, it cannot be sent directly to the C<sub>2</sub>-splitter and therefore, also this stream should be sent to the demethanizer.

By including the methane reforming section, the fixed cost and operating cost increases at the same time the product sale increases too. However, the net profit of the whole process by including the reforming in-process scenario 1 (Int-Scen-1) does not change. This is a plausible assumption because always reforming section should be coupled with downstream syngas processing, for example, Fischer-Tropsch, methanol synthesis, etc., to secure a meaningful profit. Therefore, the payback period of this scenario is similar to the previous one (OCM-EDH). However, only by including the reforming section, the required hydrogen can be supplied for CO<sub>2</sub>-hydrogenation in other process scenarios. This has been established in-process scenario 2 (Int-Scen-2), where a CO<sub>2</sub>-hydrogenation reactor has been integrated into a parallel-reactors configuration to convert the separated carbon dioxide and hydrogen to methanol. This has led to improving the economy of the integrated process mainly due to the significant increase in the total product sale including methanol. In the integrated process scenario 3 (Int-Scen-3), the CO<sub>2</sub>-hydrogenation reactor has been implemented right after the OCM reactor to directly convert CO<sub>2</sub> while it is in the OCM products mixture which also contains some hydrogen. However, using the investigated CO<sub>2</sub>-hydrogenation catalysts and under the reaction conditions in this research, the ethylene content of this OCM gas stream can undergo hydrogenation reaction and be converted to ethane as has been experimentally observed in testing the OCM-Methanol sequential-reactors configuration. In that case, excess hydrogen cannot be separated easily and recycled back to the reactor, and also because of this, the process scenario 3 (Int-Scen-3) will not be economically viable. However, using alternative downstream units for hydrogen separation and alternative catalysts for CO<sub>2</sub>-hydrogenation (e.g. palladium-based catalysts) which are less prone to the undesired hydrogenation of ethylene, can be useful while running the OCM and CO<sub>2</sub>-hydrogenation reactors in series. In case such side effects can be avoided, the economic performance of process scenario 3 (Int-Scen-3) is promising as has been assumed and simulated for the case of undiluted feed reported in Table 5.

Changing the feed to a CO<sub>2</sub>-diluted one, similar process structures as described for scenario 1–3 were investigated in process scenarios 4–6. Inexpensive biogas, rich in methane and CO<sub>2</sub>, can be one of the targeted feedstock if available in large quantities. Such feed can be processed in the OCM reactor and CO<sub>2</sub>-hydrogenation reactor to produce a large amount of ethylene and methanol and thereby significantly increase the total product sale, which can justify considering CO<sub>2</sub>-diluted feed for an integrated OCM process. However, in this case, CO<sub>2</sub>-hydrogenation reactor should be used in parallel to the OCM reactor (comparable to Int-Scen-5) because in the other two process configurations (Int-Scen-4,6) the gas flow and load of carbon dioxide in the CO<sub>2</sub>-removal section and the hydrogen content of the gas stream entering demethanizer impose significant processing costs. The serious challenge of undesired hydrogenation of ethylene to ethane in these process configurations should also be highlighted in this comparative analysis. In the parallel reactor configuration, however, the unreacted carbon dioxide in the methanol reactor is easily separated in a flash column and recycled back to the methanol reactor to minimize its net generation–consumption–separation–recycle in the integrated process.

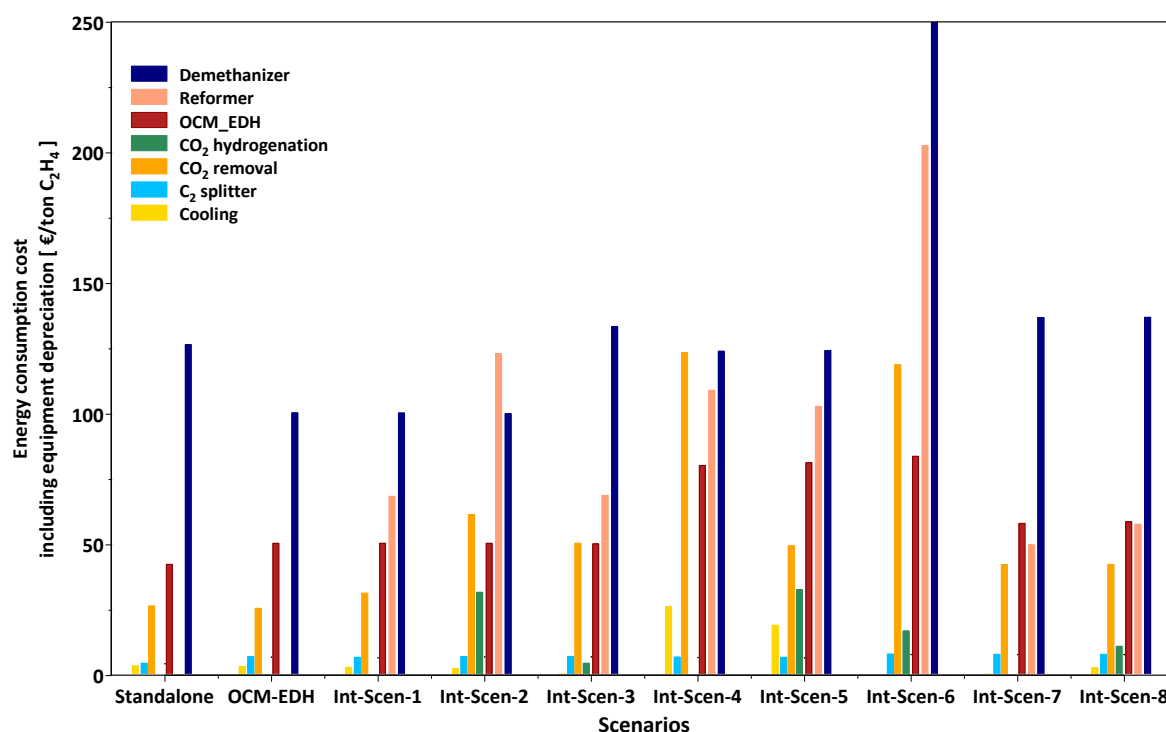
The process configuration (Int-Scen-5) with the detailed performance data reported in Table 4, has shown the best performance in terms of the shortest pay-back period and minimum net CO<sub>2</sub>-emission. Such process configuration remains promising even if the methanol reactor operates sub-optimally. This has been proven in this research by even considering the methanol reactor performance much below its highest methanol yield (proven to be achievable somewhere else [11]), and still the performed economic analysis resulting in an acceptable economic performance for this integrated process.

The last process scenarios (Int-Scen-7,8) treating OCM methane-diluted feeds are not economically viable because of the significant cost associated with separating the extra unreacted methane in the demethanizer in these processes. This neutralizes the positive impact of using the methane-diluted feed on the selectivity of the OCM reactor and thereby increase the ethylene production. Increasing the product sale by producing syngas and methanol (Int-Scen-8) cannot also

compensate for such a negative impact. Using more energy-efficient downstream units while minimizing the loss of ethylene in all process scenarios should be prioritized. For instance, even losing more than 2%–3% of ethylene in the downstream unit could unravel the economic prospect of the best-integrated process.

Summing all the types of energy utilized in different sections of each process scenario reported per ton of produced ethylene is defined as “Energy consumptions (GJ/t-C<sub>2</sub>H<sub>4</sub>)” and the calculated cost associated with this is referred to as “Energy consumption cost (€/t-C<sub>2</sub>H<sub>4</sub>)” in this paper. Similarly, the whole CO<sub>2</sub> produced in different sections of the process is defined as “Total specific CO<sub>2</sub> produced (t-CO<sub>2</sub>/t-C<sub>2</sub>H<sub>4</sub>)” and the ultimate quantity of CO<sub>2</sub> emitted from the process is defined as “Total net specific CO<sub>2</sub> produced (t-CO<sub>2</sub>/t-C<sub>2</sub>H<sub>4</sub>)”, all calculated per ton of ethylene-product. These values have been also provided in Table 5 as performance indicators of different process scenarios. As shown in this table, process scenario 5 (Int-Scen-5) has shown the best performance also in this regard.

To track the main sources of the energy cost in the investigated process scenarios, the energy consumption cost for different sections of each process scenario has been shown in Figure 3.



**Figure 3.** Section-wise “Energy Consumption Cost” for the investigated process scenarios (the process scenario numbers are according to Table 3).

As seen in this figure, the main source of energy cost in all process scenarios is the demethanizer and cryogenic cycle. This shows that a proper design of some of the operating parameters such as methane-to-oxygen ratios and dilution in the OCM reactor can significantly affect the economic performance of the whole process.

Finally, the details of the operating costs in a different section of the selected process scenario (Int-Scen-5) are provided in Table 6.

**Table 6.** The cost items in different sections of the selected OCM process scenario (all in (€/t C<sub>2</sub>H<sub>4</sub>) and according to the section numbers in Figure 1).

OCM-EDH Reactor (1,5)	Reformer Methanol Reactors (6,7)	CO <sub>2</sub> Removal (2)	Demethanizer (3)	C <sub>2</sub> -Splitter (4)
81	136	50	124	7

All costs are reported in Euro per ton of ethylene produced. The reported costs here include the utility cost per ton of ethylene in which the equipment cost has been depreciated and included in the calculation (€/t-C<sub>2</sub>H<sub>4</sub>). As seen through the data reported in Table 6, the operating cost in demethanizer is the main source of operating costs in the OCM process. The required compression of the gas streams and the internal compression duty for providing the low-temperature utility refrigerant in the cryogenic cycle are the main source of energy and operating costs. The costs associated with these aspects in all process sections, both in the form of operating cost as well as the depreciated fixed cost of the required equipment have been taken into calculation.

Again, it becomes clear that increasing the ethylene production capacity due to integrating the OCM with the EDH reactor reduces the separation costs per ton of ethylene. Therefore, the integration of the OCM process with ethane cracking units is especially promising.

#### 4. Conclusions

The impacts of the parameters such as temperature, pressure, gas composition, and dilution on the catalyst selectivity and the performance of OCM and CO<sub>2</sub>-hydrogenation reactors and thereby on the whole process-scale performance were analyzed using a multi-scale analysis approach. In this context, using representative models of industrial-scale operation of several alternative integrated OCM process scenarios, supported by available industrial-scale and mini plant-scale data, their techno-economic-environmental performance indicators were comparatively analyzed. It was found that the observed improvement in the ethylene selectivity in the reactor-scale due to methane dilution equivalent to using methane-to-oxygen ratio of 4 will impose an intolerable operating cost on process-scale using conventional downstream units. The same is true for the impact of nitrogen dilution which was determined to be even more restricted (below 5%). OCM membrane reactor, in which an inorganic membrane (preferable an oxygen selective membrane) enables the fine distribution of oxygen along the catalytic bed, can secure selective conversion of methane and the above-mentioned requirements. For the CO<sub>2</sub>-hydrogenation section, the focus was on its low-pressure operation and its integration with the rest of the process.

Further converting the unreacted methane and the generated undesired carbon dioxide and less desired ethane in the OCM reactor to value-added chemicals was the main motivation for integrating ethane dehydrogenation, methane reforming and CO<sub>2</sub>-hydrogenation sections in the OCM process. Parallel to securing more ethylene production, methanol production, and syngas production, and ultimately paving the way for alternative integrated gas conversion technologies for producing value-added chemicals, utilizing more efficient downstream units for minimizing the energy usage and ethylene loss found to be the priorities for further developing these technologies. In this context, for instance, tightening environmental regulations for minimum greenhouse emission and ever-growing CO<sub>2</sub> tax can be addressed by the proposed zero direct CO<sub>2</sub>-emission OCM process. Methane and hydrogen can be also supplied from renewable resources. The performed analysis in this research enables us to reflect these requirements and potentials in the design and operation of efficient catalysts, reactors, and integrated process flowsheets. The promising techno-economic environmental performance indicators of the selected integrated process namely zero direct CO<sub>2</sub>-emission and promising less than an 8-year pay-back period, should outweigh the relative complexity of such an integrated process structure and the uncertainties associated with each of its process-blocks. Nevertheless, to ensure establishing such an integrated OCM process as a competitive technology for being implemented in the industrial scale, the stability and selectivity of the catalysts involved should be improved and the difficulty of the reactors' operations should be addressed.

The analyses provided here in this paper concerning the performance of the operating parameters is valid for most of OCM and CO<sub>2</sub>-hydrogenation catalysts and reactors.

**Supplementary Materials:** The following are available online at [www.mdpi.com/2073-4344/10/5/488/s1](http://www.mdpi.com/2073-4344/10/5/488/s1), Table S-1: Set of operating conditions and simulated compositions of the main streams in the integrated process scenario 5 (Int-Sec-5).

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