ECONOMIC PROFILING ON OXIDATIVE COUPLING OF METHANE AND OPPORTUNITIES FOR INTEGRATION

An Undergraduate Research Scholars Thesis

by

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This project did not require approval from the Texas A&M University Research Compliance & Biosafety office.

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Economic Profiling on Oxidative Coupling of Methane and Opportunities for Integration

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Oxidative coupling of methane (OCM) has been investigated through catalysis, reaction engineering and various processes to achieve the valued economic performance of producing ethylene from natural gas for more than 40 years. Studies on OCM focus on the reactions' performance and catalyst options with the absences of economic analysis. More recent studies on the reaction's performance investigates the economic limitations of the reactions to add value, they are carried out on specific systems in the lack of a systematic analysis approach. These analyzed systems highlight a gap of a basic analysis that presents the economic potential as well as motivate the development of an economic screening method. A method that is quick and applicable by any system of reactions that displays an understanding of the economic performance of the reactions and the required minimum of key performance indicators such as

selectivity for profitable potential. This research will present the development of the screening method and its application to OCM reactions in the form of 'value addition/destruction maps'.

The minimum selectivity found for the OCM standalone system in an ideal scenario considering material flows was 58%, this selectivity indicates the minimum performance when considering 100% conversion of methane. The energy flow was also considered as part of the analysis, which decreased the minimum selectivity to 37%. The minimum represents the point where any lower value means that the system will never generate profit. The results were effective in the use of the developed methodology of screening, it was used to identify the economic weaknesses of OCM through the analysis and motivate the idea of integrating it with a different process to add value. The simulations of the power plant and OCM processes were completed, and then both processes were integrated and simulated to analyze the economic performance. The power plant process added value to the OCM process, however not to the extent of making it profitable, but signified the idea of integrating processes to add overall value to result in potential profit.

DEDICATION

I dedicate my work to my family who made this journey possible and Dr. Patrick Linke for his all-around advice and support with this project that developed my skills and enhanced my work.

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NOMENCLATURE

OCM	Oxidative Coupling of Methane
CO2	Carbon Dioxide
C2+	Ethylene and Ethane

1. INTRODUCTION

Oxidative coupling of methane (OCM) is a reaction that has been studied and researched for over 40 years in different areas, such as its operating conditions, catalysts, and reactor design.[1] The reaction is interesting for the conversion of methane into a more valuable product of ethylene. However, the reactions that are occur simultaneously with it, produces undesired products of mainly carbon dioxide and carbon monoxide decreasing the selectivity towards the desired product.[2] The conversion of methane into the products is also found to be low in most studies, diverting the efforts to investigate better catalysts and reactor designs.[3] The economic analysis performed on OCM is usually focused on a specified parameters or includes other integrated chemistries, making the analysis difficult to deduce what the reaction presents economically. Other economic studies investigate the performance of OCM while integrated with other reactions, such as biogas-based reactions or methane reforming.[2,4] The creation of high-level analysis of the economics of the reaction would fill in the missing gaps in the economic analysis and be useful to investigate the stand-alone reaction, resulting in economic models which will be called 'value addition/destruction maps'. These maps can provide a high-level view of the reaction performance in relation to its conversion, selectivity, energy, and product prices of the main OCM components. Therefore, creating a clear method of obtaining such maps for industrially attractive chemistries can provide a clearer picture on the minimum conditions the reaction is favorable economically and to be used to provide an understanding of how the reaction economically behaves in a general manner. The method that will be developed then can be applied to OCM with the considerations of its main components and create maps that highlight value added or destructed with the considerations of different factors. The application of the method is created to avoid extensive efforts into the research of different systems by understanding their basic economic performance and minimum performance conditions.

2. RESEARCH METHODS

2.1 Literature Review

The motivation of this work is hugely impacted by the research work completed previously on the topic, making the literature review before conducting this work an important factor for its success. The literature review consisted of looking into review papers on the reaction of OCM and its application to understand an overall picture of what the reaction offers. Research work on the OCM reactions and their performance under different conditions and catalyst assisted in gaining an understanding of where the reaction stands in the scope of its strengths and weaknesses. The papers were organized in a database sheet to put the different papers in categories for their use, categories such as experimental data or process integration were used to allocate these papers to be used for the information to carry out the project. The relevant work on the economic performance of the reaction in techno-economic models or economic analysis was a huge motivation towards the development of the described method in this paper to achieve the objectives of the research questions. Pervious work on the integration of OCM with other reactions was also relevant to the motivation of creating the standalone analysis on the reaction as well as the integrated process chosen in this paper.

2.2 Data Acquisition

The economic analysis of the developed method and maps produced used basic economic tools to achieve them. A prices databases for the different chemicals that are considered was used to find the value of them. The prices database was retrieved from a website that provides the current prices for chemicals as well as historic prices to be able to carry out sensitives of the studies. Intratec was used as the main website to attain the figures required for the analysis and all the prices used in this analysis was based on the United States chemicals prices in March 2022. These prices were used throughout the analysis to stay consistent in every section.

2.3 Chemical Engineering Fundamentals

Mass balance was an important tool to evaluate the economic analysis developed, it was used to find the amounts of material consumed and generated in the reactions system for an assumed feed. The stichometry of the different compounds in the reactions considered were used in the mass balance with the definitions of the key performance indicators to find the amounts required for the economic analysis. The main performance indicators used to carry out the analysis were selectivity and conversion.

$$Selectivity = \frac{Desired\ product}{Reactant\ In - Reactant\ Out} \tag{1}$$

$$Conversion = \frac{Reactant\ In - Reactant\ Out}{Reactant\ In} \tag{2}$$

Equations (1) and (2) represent the definitions of selectivity and conversion used in this analysis, respectively. Selectivity is defined as the ratio of the desired product to the amount of reactant consumed. Conversion is defined as the ratio of the consumption of a reactant to how much of it was fed into the process. These definitions are process performance indicators, meaning that they are applied to the overall process and not the reactor. These definitions were chosen based on the common use of them in literature for them to be easily used by anyone and to stay consistent throughout the analysis. The key performance indicators are particularly important as they play an important role in the display of the developed method of analysis and the maps produced.

Heat of reactions is the energy generated or consumed from a chemical reaction. The heat of reactions was used as part of the analysis to find the amount of energy released from reactors in the case of exothermic reactions. To quantify the energy generated in realistic manner, an efficiency of heat to power was used to translate the energy generated into an electricity value to include in the economic analysis.

2.4 The Minimum Energy of Separation Method

The method to obtain a relation between conversion and the minimum energy of separation of the products after the reactor was obtained and used by Li Wang et al.[5] The paper specifies a specific method with the necessary formulas to carry out the analysis. The method finds the difference between the Gibbs energy of mixing of the feed stream and Gibbs energy of mixing of the product streams of the separation equipment. The minimum energy of separation can then be found using the specified formulas. The following sample calculation will briefly present the method that was used in this paper to relate the conversion to the formulas with the appropriate description.

A system of reactant and products were assumed to enter a separation unit that achieved a recycle and product streams of 99.9% purity was studied using this method. The amount of product produced was set constant and explored the range of conversion which affected the flowrate of the recycle stream going through the reactor and into the separation unit.

$$\Delta_{sep}G = \Delta_{mix}G_p + \Delta_{mix}G_b - \Delta_{mix}G_f \tag{3}$$

Equation (3) represents the formula to obtain the minimum energy of separation that will be calculated by finding the individual change in energy of mixing of the recycle and product streams and subtracting the change in energy of mixing of the stream entering the separation unit.[5]

$$\Delta_{mix}G = nRT[x_1 \ln(x_1) + x_2 \ln(x_2)] \quad (4)$$

To obtain the change in energy of a specific stream, Equation (4) is used as a function of the molar flowrate and composition. To study the effect of conversion on the energy of separation, the purity as specified is constant throughout the study, making the molar flowrate the only changing variable.[5]

$$\dot{n} = \frac{\dot{n_p}}{X} - \dot{n_p} \quad (5)$$

Equation (5) presents the relation between the molar flowrate used in Equation (4) to the conversion. As conversion will be specified through a range and the product flowrate is constant, the flowrate of the reactant can be found to be used in the equations to find the minimum energy of separation.

This method is used later in the screening of the economics for level 2, which investigates the effect of the minimum energy of separation on the economics of a studied system. The general process of such study is presented by Figure (1).

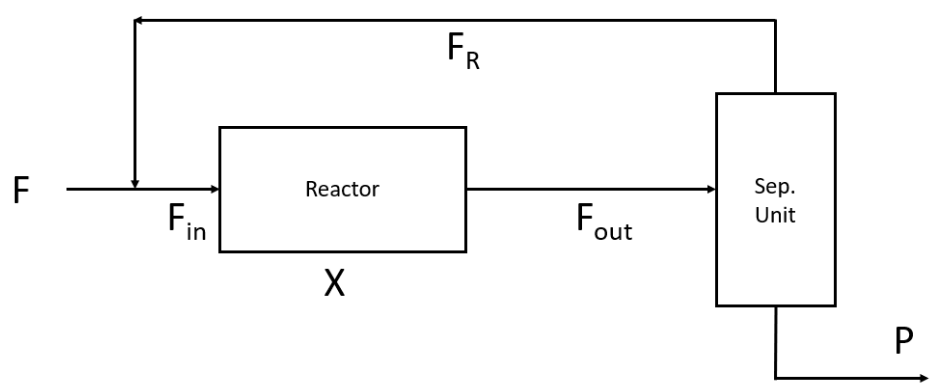

Figure 1: General process to apply the minimum energy of separation method.

2.5 Heat Integration

Heat integration was a fundamental tool that was used directly and indirectly throughout the different systems analyzed in this study. In the process simulation, heat integration was applied or was already applied on the systems studied, this was to ensure a consistent and logical investigation. The heat integration techniques applied on the process flowsheet consisted of extracting the process streams viable to be heat integrated, application of the Problem Table Algorithm, cascading to find targets, creation of grand composite curves and heat exchanger networks. All of these steps were used to carry the heat integration analysis successfully on the processes used in the analysis of the results sections. The application of heat integration in analysis was important to carry out on the economic analysis of the different process to ensure an accurate depiction of the economic performance.

2.6 Economic Analysis Methods

The prices obtained from the databases were manipulated to be provided in a currency per mass unit basis to be used in the finding of the chemical amount's value, as from the mass balance the amounts of chemicals in mass basis can be found. Energy is also considered to be valued in this analysis by using the price of electricity (0.06 $/kWh) to include them in the economics of the system. Throughout the analysis, the profit calculated is based on the basic theory of the cost subtracted from the revenue, section (4.2) explains how materials and energy values fall into these categories. The two major economic parameters considered for processes in analysis is operating and capital costs, both parameters have different approaches to finding their value. The operating costs mainly consist of materials and energy flows throughout a process, which are obtained by the coupling of mass and energy balances with the prices of the respective components. On the other hand, the capital costs are mainly the costs from purchasing the equipment throughout the process, which can be estimated using the Aspen Economic Analyzer directly from the process simulation. Equipment that are not analyzed by the software can be estimated from existing similar equipment and using factors of capacity or period.

2.7 Graphical Representation

Microsoft Excel was the main software used to presents the economic maps produced in this analysis. It was used to perform the simple mathematical calculations of mass balances and economic value to retrieve the data used in the plots of the economic maps. Other plots were also produced by Excel in this study such as the investigation of the effect of conversion on the minimum energy of separation.

2.8 Process Simulation

Process simulation was an essential tool to carry out the downstream integration analysis and understand the economic performance on a process level. Aspen Plus was the main software used to analyze the performance of the different systems and use that performance to draw economic conclusions. The produced flowsheets in the simulations and results of these processes were obtained by applying process simulation techniques assisted by literature. Processes from literature were used to inspire the produced flowsheet, verify their performance for accuracy and provide inputs to the simulation. Promax examples of processes was also used to display black boxes of certain equipment in the main flowsheets that are used as part of the analysis.

3. LITERATURE REVIEW

OCM has been researched with different catalysts, reactors, and processes for decades in search of a commercially attractive performance. However, most of the work completed on OCM reports poor performance of the reaction's conversion of methane and selectivity towards C2+. The typical range of methane conversion for OCM is 3% to 50% and the selectivity towards C2+ is 18.4% to 64%, and a trend of conversion and selectivity being inversely proportional for OCM is observed.[6] A recent review of the reaction's performance challenges the success of OCM by showing a figure that presents that most OCM performances fall outside an industrially attractive region. The paper indicates that efforts to solve and make OCM's performance more attractive is in the development of the process and reactor design.[1] However, the paper does not show evidence of a route that could solve the poor performance of OCM with such description. Many trials of analyzing the economics of OCM and the exploration of integration or reactor designs with these analysis display the attempt in the search of a positive economic performance. Research work that analyzes the reaction's performance in an investigation of reactor design specified up to 12 parameters of the reactor of which included diameter, inlet gas velocity, and inlet pressure. The economic analysis of the system included opex and capex costs with studies of how the economic performance differs in ranges of temperature. The overall results of the economic analysis presented the unique performance of the specified system and its uniquely designed process.[7] Such analysis is difficult to reproduce and describes the performance of the process rather than the OCM chemistry itself. Other economic analysis studies on OCM are found in integrated systems with different processes and chemical reactions. A process uses biogas as the feedstock to the OCM process, where the system is integrated with a treatment system prior to the process to treat the biogas. The economic analysis carried out on the integrated process presents the economic performance of the overall integrated process of OCM and biogas treatment.[4] Similarly, another study explores the economic performance of an integrated system of OCM with methane reforming. It focuses on how methane reforming effects the process's performance and economics of such integration. Conclusions on the economic performance of the process are made based on the integration of methane reforming with OCM.[2] These studies may be useful to use when looking at similar specifications of a process or integrations that can be referenced to the ones studied. However, they motivate the development of a general method that can be used to analyze the chemistries taking place in a process to result in an understanding of the core performance applicable later for certain specifications or integration routes. The break-even analysis method illustration, common in use in economic analysis, motivates the display of the developed method to create a simple understandable economic map.

4. ECONOMIC SCREENING

4.1 Process Classification

The method developed in this analysis is produced as a method that can be applied to any chemistries of a process. It is deduced by investigating the process from a high-level view that classifies the process as a black box, and the flow of materials and energy in and out of this box is considered for the economic analysis. Using this method of analyzing the process provides a quick and clear understanding of how the process performs focusing only on the chemistry taking place. However, before creating the economic maps and analyzing them, the materials and energy flowing in and out of the process should be clearly identified in order to deduce the correct amounts of each, that will then be used in analysis of the economics and the value added or destroyed to the economic maps.

The materials flowing into the process would be classified usually as the raw materials that feed into the process and through different reactions produces the products. The energy that flows into the process can be where energy is required to produce the specified products, such as the energy required to maintain an endothermic reaction or energy to separate the products from other materials to meet certain purities. On the other hand, the material flowing out of the process are usually classified as products or by-products of the reactions taking place in the process. The energy flowing out of the process can be also considered as a product, examples of such energy can be the production of energy from an exothermic reaction or work from a turbine. Waste in some cases may be a product of a process, this flow of material should also be accounted for in the analysis. Finally, the process, which is classified as a black box includes the capital investment (CAPEX) and operating costs (OPEX) for which in this analysis will not be considered part of the economics. This is because the analysis is aimed to be a high-level view of the process and to follow the developed method, creating an advantage of predicting whether the chemistry itself has the chance to be profitable without including the additional costs.

4.2 Economic Identification of Materials and Energy

The pervious section explained how the materials and energy flows in and out of the process are specified, these specifications are used to identify how the materials and energy values are classified and how they contribute to the economic map. Costs and revenue are the two categories that the different classifications of materials and energy will fall into, and they either destruct or add value to the economic map, respectively. Cost is the economic factor that decreases the profitability of the process, it will contribute to the destruction of the maps. Mainly in this analysis the raw materials and energy required into the process will fall into costs, this is because raw materials and energy in is usually something bought and cash flows out. Revenue is the opposite of costs, where it increases the profitability of the process and adds value to the economic maps. The revenue from selling the product and by-products as well as any useful energy leaving the process can be considered as revenue as cash flows in. Waste as mentioned in the previous section can be considered as a product of the process, and so it will be classified as a negative revenue, hence the destruction of the added value.

To obtain the value added or destructed by the different flows of materials or energy, the prices of the corresponding material or energy from databases that provide these prices for selling or buying chemicals or forms of energy is used. Through a simple mass balance or supplied amounts of material and energy flowing in and out of the process, the value can be calculated based on the found prices and developed on the economic map through the method in the next section.

4.3 Development of Economic Maps

The economic maps present the economic performance of the process, they are aimed at showing the profitability of the process and at which point it breaks even in consideration of the economic factors defined in the previous section. The profitability region is an area on the map where the revenue is larger than the costs of the process and the break-even point is the point at which the process's revenue and costs are exactly equal, which also defines the beginning of the profitability region. Value found of the materials and energy after categorizing them into costs and revenue as specified in the previous sections will then be used to plot them on the economic map. The map is a plot of the value as a function of a certain parameter that describes the performance of the reactions in the process, these can be either the conversion or selectivity of a certain component. Specifying the map in such way is to be able to understand how the value added or destructed by the process changes by key performance indicators of the reactions, this will allow the investigation of the economic performance of the map clearly.

To develop an economic map, a certain key performance indicator should be chosen to be investigated as part of the analysis. Key performance indicators are usually represented by percentages, such as conversion or selectivity allowing the exploration of the finite range from 0 to 100 %. By specifying the value of the key performance indicator, the corresponding values of revenue and cost can be found, which then can be plotted as points on the economic map. The analysis can be done on a range of the key performance indicator to produce a model of the economic map, deducing from it the profitability region and intersection of the revenue and costs representing the break-even point. The application of this method of developing the economic models can then be applied to multiple different maps that consider different factors of addition and destruction of value. The addition and destruction of value comes from considering different materials and energy flows, that either add or destruct value depending on if it falls into revenue or costs, allowing the comparison and understanding the value of material and energy flows of the process.

4.4 Philosophy of Method (Levels)

The understanding of the different economic maps that will be produced by the use of economic screening method is important to the objective of the map. Therefore, a systematic approach is created called "levels" that classifies what each analysis of the system considers within its boundaries. These levels are created to identify and describe the chosen scenario to analyze the economics of the system and differentiates all of the different analyzed scenarios. These scenarios have different variables considered within them to carry out the economic analysis and designed in a way to satisfy one main condition. This main condition is that the minimum selectivity requirement for an analysis of a starting level is lower than the level after it, meaning that the minimum selectivity requirement increases as more levels are explored. This is because as more levels are explored, more variables of the system are considered, increasing typically the costs as the system is analyzed in more detail. This also means that the starting levels are typically quick and need minimal information to carry out their analysis and as more levels are explored the time and information required increases to carry out the analysis. This paper explores two levels in the analysis of any system to produce two different economic maps that present the philosophy clearly of the method.

Level 1 is described as the "Gross value added", the system is analyzed by only the flow of materials in and out of the process. The raw materials flowing into the process are classified as costs and the revenue comes from the products leaving out of the process. In the case of exothermic reactions, the energy released by the heat of reaction may be considered as valued energy that falls into revenue.

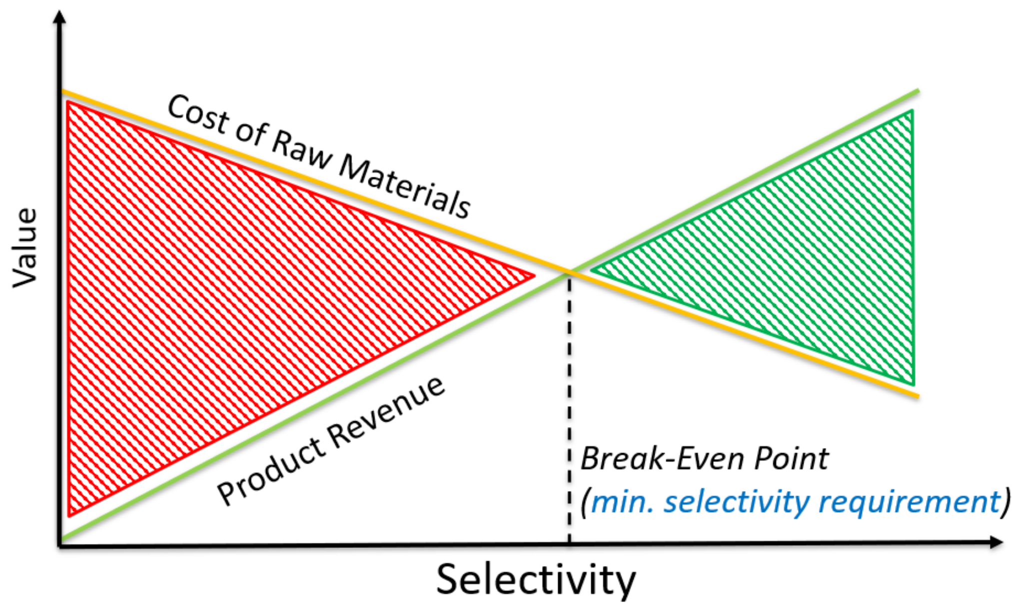

Figure 2: Conceptual economic map of level 1 analysis of value as a function of selectivity

Figure (2) presents the conceptual economic map of level 1, the green line represents the revenue and the yellow line represents the costs from the process analysis. These lines intersect and create two envelopes of interest, the red envelope is the area where value is destructed, and the process is guaranteed to make a loss. On the other hand, the green envelope represents the area where the process can be potentially profitable. The intersection of both lines is the break-even point that corresponds to the minimum selectivity requirement.

Level 2 is created on the basis of the important variable that affects the overall process the most, in the case of OCM, the energy of separation required plays a major role in the economics due to the required recycle stream for reactant recovery. Therefore, level 2 considers all the variables considered in level 1 in the addition of the required energy of separation. The energy of separation is the energy required by the separation unit to separate the products from the reactants after typically a reactor. Section (2.4) explains the detailed method used to find this value of energy, while it is assumed to be the minimum theoretical energy of separation, which is the ideal case of the required separation energy.

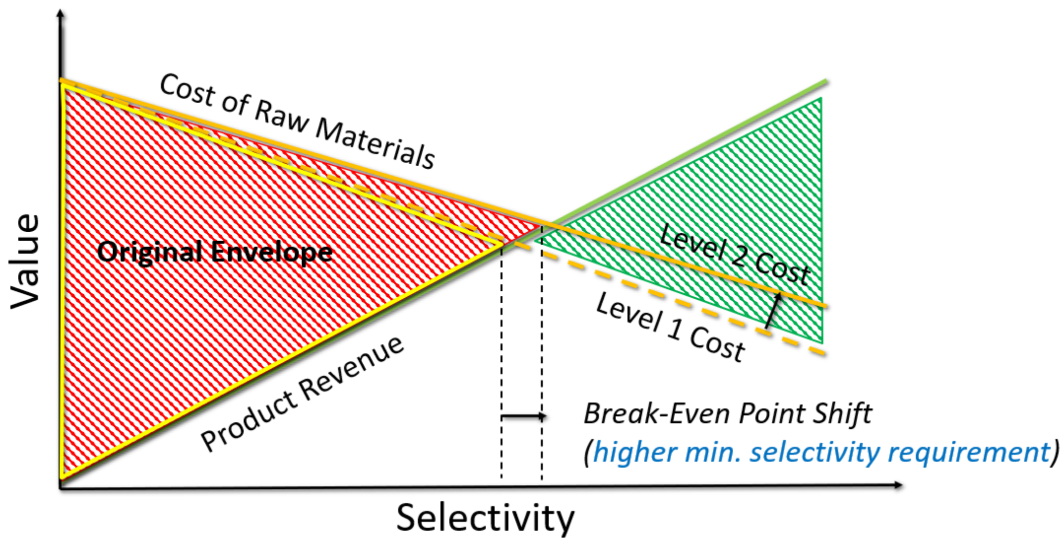

Figure 3: The shift of the cost line after level 2 analysis compared to the level 1 economic map

Level 2 economic map is a similar map to level 1 as seen by Figure (2), the shift in the cost line is only difference which can be observed by Figure (3). The shift in the cost line cuts through the profitable region resulting in a decrease of that area and the shift in the break even point. Alternatively, the revenue line can shift if the energy of separation is subtracted from the revenue, either way the result is the same. The shift in the break-even point to the right translates to a higher minimum selectivity requirement for potential profit. This observation corresponds and confirms the philosophy of the method, where as more levels are explored, the minimum selectivity required increases.

The levels can be further explored depending on the factors of processes that are relevant to different systems to explore how they affect the addition or destruction of value to these economic maps. The exploration and development in creating a set of levels that shows how the consideration of different elements within a process can affect the economic maps and interpret essential information for the understanding a specific system.

4.5 Application to OCM

The developed economic screening method can be applied on the case of OCM to understand the economic performance of the system through the produced economic maps. The flow of materials and energy in and out of the system is key to the application of the economic screening method and following the application of the method using the research methods from Section (2). The usage of the levels within the analysis will help the understanding of the economic performance of OCM along with how different variables within the process affect the performance. Two main assumptions were in place for the OCM process to stay consistent with the theme of high-level analysis.

Main Assumptions

1. Process conversion of methane was 100%
2. Three main reactions of OCM considered in analysis

The conversion of methane was assumed to be 100% to allow the study of selectivity to find the minimum in this ideal best-case scenario. The three reactions were chosen based on their dominance in the composition of the product as found by most literature and for a simpler analysis. The main products were ethylene, ethane, and carbon dioxide which are represented by Equations (6), (7), and (8), respectively.

$$C_2H_6 + \frac{1}{2}O_2 \rightarrow C_2H_4 + H_2O \tag{6}$$

$$2CH_4 + \frac{1}{2}O_2 \rightarrow C_2H_6 + H_2O \tag{7}$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \tag{8}$$

The process consists of feed and product streams as described in process classification, they are specified on the basis of the reactions presented above. Methane and oxygen are fed as raw materials into the process, ethylene, ethane, carbon dioxide and water leave the process as products. Water is ignored in the analysis as no value is set for it, making it simply a by-product of the process. The reactions are all exothermic, resulting in a net exothermic system which releases energy that can be valued as part of the analysis. The analysis is based on a ton of methane feed, this was used to carry out the mass balance and appropriate value calculations on a range of selectivity from 0 to 100 %. Methane, oxygen, and any energy considered into the process are in the costs category. Ethylene, ethane, and energy released by the system are considered into the revenue category. Carbon dioxide is also a product of the process and can be considered as a waste that introduces negative revenue in the category in the form of carbon tax. Through these identifications, the economic screening method can be applied on the OCM process through following the developed philosophy in Section (4.4).

Level 1 analysis on OCM considers the gross value added, and so it is applied on described system of OCM. However, to simplify and understand the application of the method, the first economic map will only consider the material flows and assume that only ethylene is produced in the products.

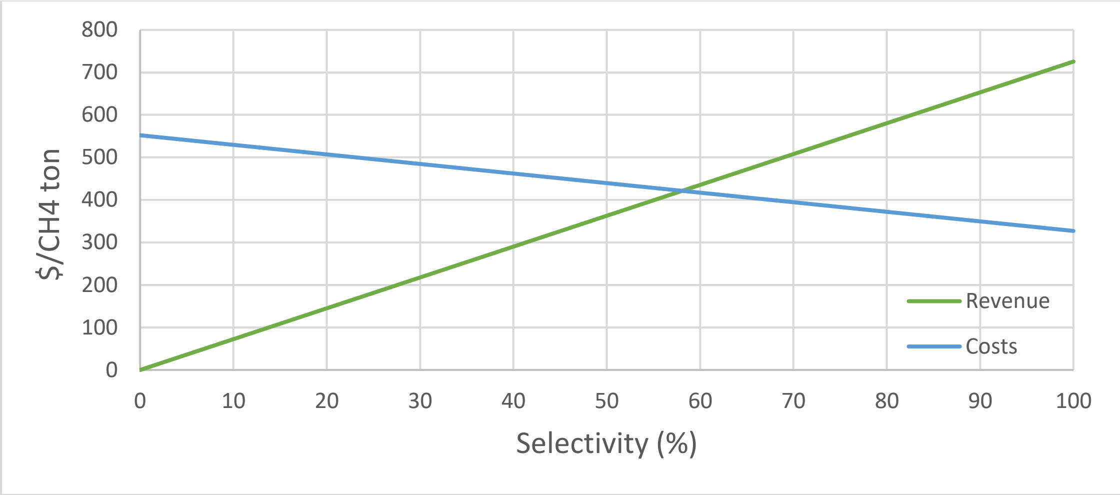

Figure 4: Level 1 economic map of OCM assuming only ethylene product

Figure (4) presents the application of level 1 on OCM assuming material flows and ethylene product only, the economic map is observed to align with the development in Section (4.4). The break-even point is found to be at approximately 58% selectivity, which can be defined as the minimum selectivity for potential profit when assumed that the process only produces ethylene. A similar analysis can be completed on the other extreme where it is assumed that only ethane is produced.

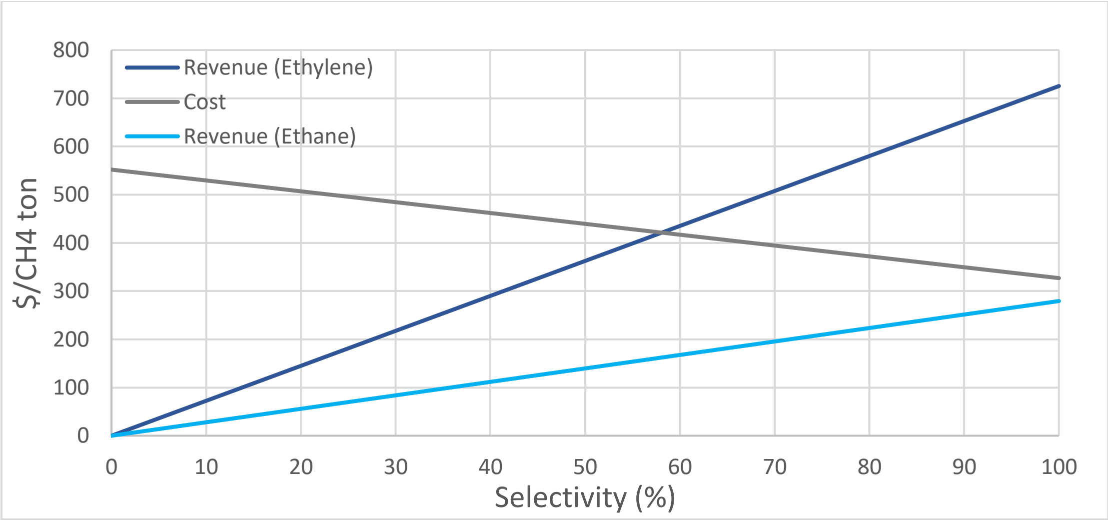

Figure 5: Level 1 economic map of OCM ethylene and ethane product assumptions

Figure (5) presents the same level 1 economic map with the addition of the assumption of producing only ethane, which is represented by the light blue line. It is observed that there is no intersection between the cost and ethane only revenue lines, which concludes that producing ethane only at any selectivity will never be profitable. The potentially profitable region is enclosed by the cost and ethylene only revenue lines after the 58% minimum selectivity point. Different ratios of ethane to ethylene production scenarios can be displayed on this economic map to understand how they fit within the potentially profitable region. This study was created with increments of 10% for the ratio of ethane to ethylene, which lie between both pure lines of ethane and ethylene.

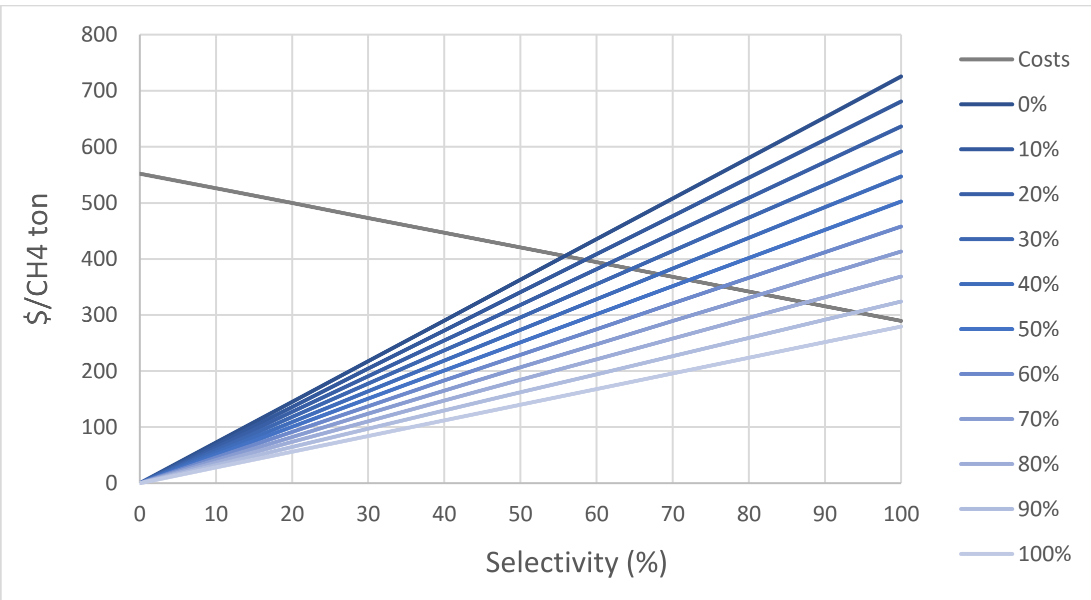

Figure 6: Level 1 economic map of OCM with different ratios of ethylene to ethane production

Figure (6) presents the level 1 economics with the display of ethane to ethylene ratios from 0 to 100 %. At 0%, only ethylene is produced and as the ratio increases to 100%, less ethylene is produced, which decreases the revenue line, cutting through the potentially profitable region and increasing the minimum selectivity (break-event point). This is observed as ethylene is a more valuable product than ethane.

The overall reactions of OCM are exothermic, which extends the level 1 economic map and analysis to include the value of energy produced within the analysis. As the energy is considered though the heat of reactions, certain efficiencies such as Carnot and heat to electricity are considered in the analysis to display the economic map to an accurate depiction of the economic performance of the OCM reactions.

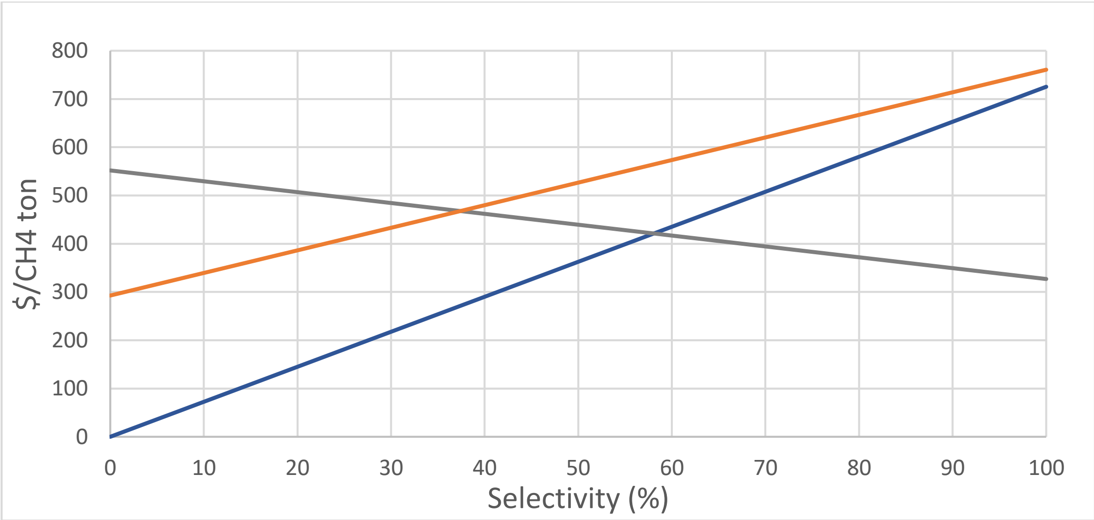

Figure 7: Level 1 economic map of OCM with energy value added from heat of reactions

Figure (7) presents the complete and final level 1 economic map with the assumption of only ethylene production to understand the economic performance on the basis of the most ideal scenario. The orange line represents the revenue of the ethylene product with the addition of 35% of the energy produced by the exothermic reactions and sold in form of electricity. The blue line is the materials only revenue that was presented in previous maps of ethylene production only. It is observed how the heat generated can add value to the OCM reactions system by the shift of the break-event point to approximately a minimum selectivity of 37%. This minimum selectivity represents the point at which any lower selectivity would never result in profit.

Level 2 explores the effect of the energy of separation required for the products and unreacted reactant on the economic performance. The minimum energy of separation was used to subtract from the revenue category of level 1 to represent level 2. The minimum energy of separation is a function of reactor conversion, and so different conversion are explored on the level 2 economic map. It should be noted that as conversion changes for the system, the level 1 material and energy flows also changed as it was assumed in level 1 that the analysis is carried out for 100% conversion.

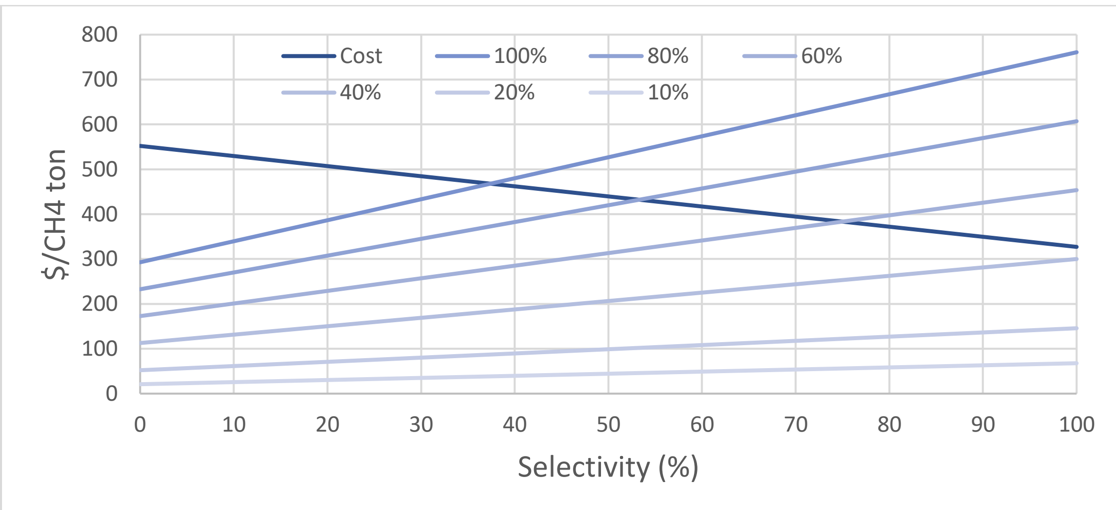

Figure 8: Level 2 economic map of OCM at different reactor conversions

Figure (8) presents the level 2 economic map that considers the energy in as minimum energy of separation in addition to all of the existing factors from level 1. As the minimum energy of separation is a function of reactor conversion, multiple conversions from 0 to 100% are explored to investigate the effect on the economic performance as presented. It is observed that at 100% reactor conversion, the minimum selectivity is equal to the level 1 minimum selectivity as no energy of separation is required since all of reactant is converted. However, as the conversion decreases, the break-even point shifts to the right corresponding to a higher minimum selectivity for potential profit. Through the found trend by the effect of energy of separation, it should be considered that this is a source of economic weakness to the overall performance, and so integrating a process to eliminate such weakness can add value to the economics of the process. Typical OCM conversions are below 40%, where the 40% revenue line on Figure (8) does not intersect with the cost line, meaning at any selectivity the system is not expected to have any potential profit. These revenue lines are also considering only ethylene production, the more valuable product, and so in reality these economic performances are poorer than what is presented.

Through the analysis of level 2, reactor conversion can be related to the minimum selectivity to create a map that displays the performance required from these key performance indicators to achieve potential profit. Through the detailed method in Section (2.4), a study on the energy of separation through a range of conversion can be produced.

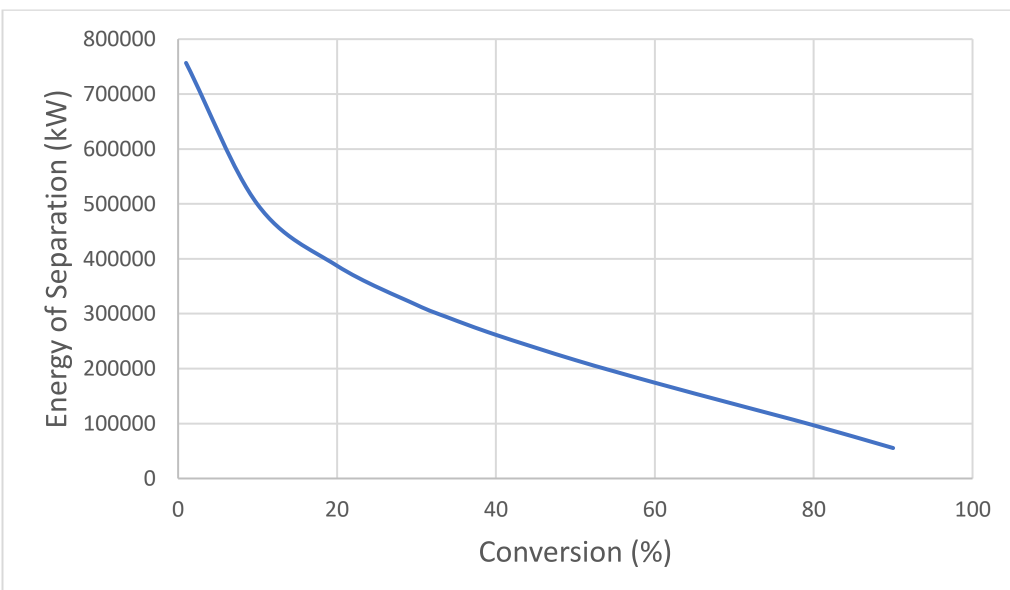

Figure 9: Energy of separation as a function of reactor conversion

Figure (9) presents the effect of conversion on the energy of separation required to separate the unreacted reactant methane from the C2+ products. It is observed that as the conversion increases, the energy of separation required decreases. This is because the flowrate in the in the recycle stream decreases, resulting in a decrease in energy required to separate it from the reactor effluent products. The energy of separation is used in the analysis of level 2 to the corresponding conversion in the analysis to create the level 2 economic map.

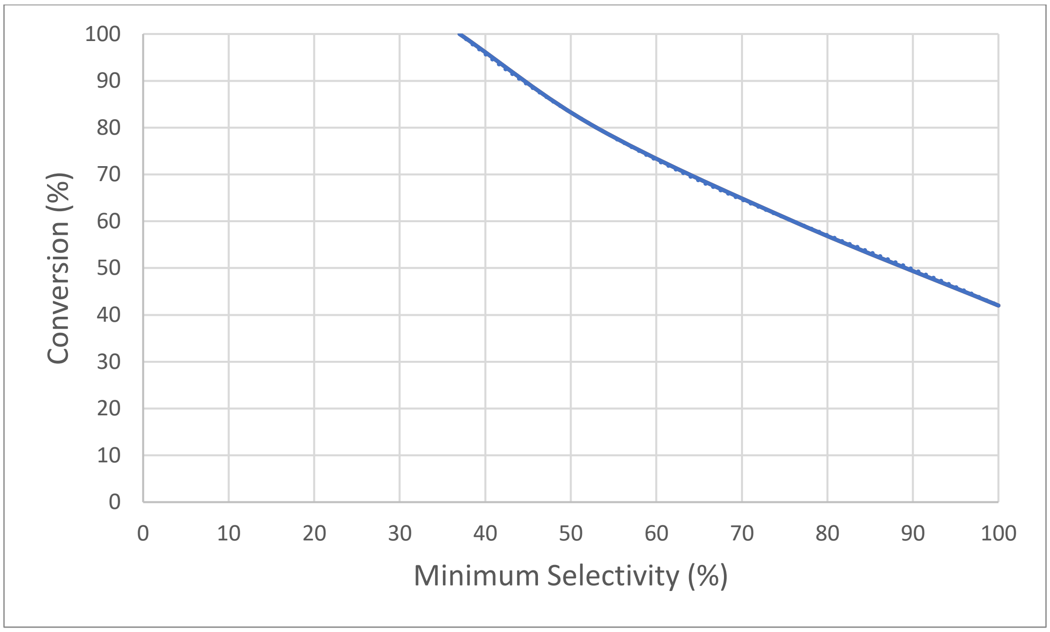

Figure 10: Reactor conversion as a function of minimum selectivity from level 2 analysis

The analysis of level 2 was completed on the assumption of ethylene production only, which describes the ideal scenario as ethylene is the more valuable product. Figure (10) presents the relation between reactor conversion and minimum selectivity required to achieve potential profit. The area above the line indicates the potentially profitable region, whereas the area below line is a region where the system is never profitable on the basis of level 2 analysis. This plot can be used to benchmark reported OCM performances to understand where existing performances typically lie in this plot.

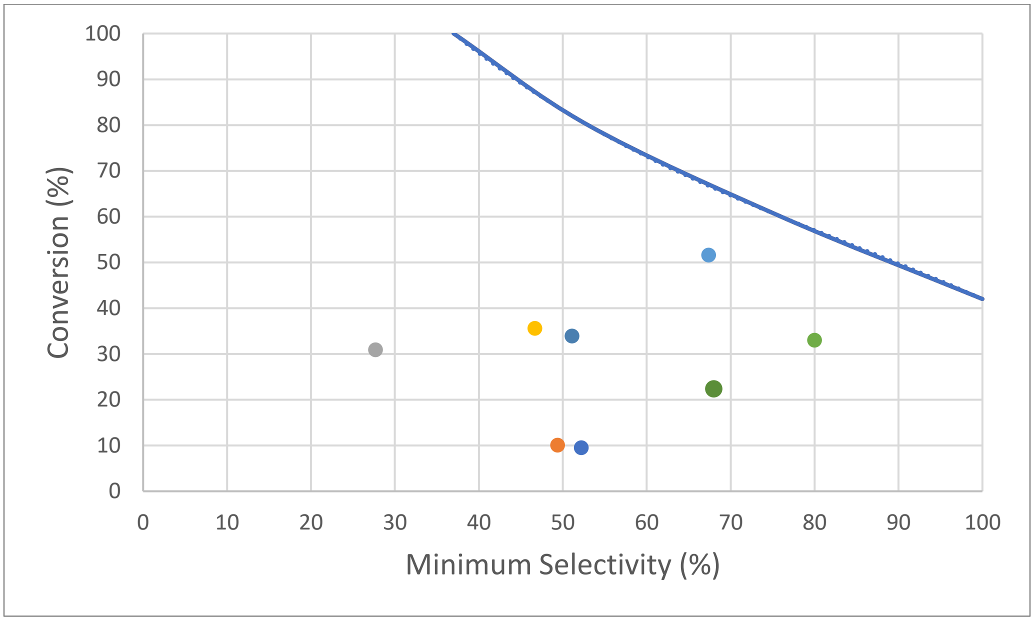

Figure 11: Benchmarking reported OCM performances on the conversion as function of minimum selectivity plot

Figure (11) presents the plot with a population of reported OCM performances, the points are plotted by using the reported achieved conversion and C2+ selectivity. The reported OCM performances were collected from different best performing sources.[1,2,8–10] As observed by the plot, all of the reported OCM performances are located below the minimum selectivity line from the level 2 analysis. This indicates that typical OCM performances are not profitable systems, which discourages the investigation of the system further and motivates integration of processes.

5. DOWNSTREAM INTEGRATION

The following sections display three different scenarios in which a power plant and OCM processes are simulated as standalone processes. The motivation of eliminating the recycle stream motivates the integrated process between both standalone simulations to explore the economic performance of the process. It should be noted that throughout these simulation, external simulations of refrigeration cycles and steam cycles to cool and recover heat from the reactor, respectively, were created and used within the study. All processes have been heat integrated using techniques described in Section (2.5) and were fed the exact same feed stream of methane for a fair comparison across the processes.

5.1 Power Plant Process

The power plant process is simply a process that burns natural gas to produce energy through turbines. The power plant process is simplified to gas and steam turbines in the integrated process to develop the simulation. To obtain an accurate representation of the gas turbine, the simulation was based and verified with a real existing gas turbine. This was performed to ensure that the final integrated process is simulated through possible efficiencies and performances of real-life processes.

5.1.1 Gas Turbine Verification

The gas turbine was based on an SGT-800 gas turbine manufactured by Siemens, the data sheet was acquired, and values were inserted into the Aspen Plus simulation.[7] The data sheet provided by the company did not include all of the values required by the simulator, hence, through trial and error as well as calculations of efficiencies, the feed of methane, turbine isentropic efficiency and excess air were estimated to achieve similar performance of the actual gas turbine.

The natural gas was assumed to have a composition of 100% methane, which allows the usage of the lower heating value of methane in the calculations of the heat available in feed stream to calculate the efficiency. The other parameters such as temperature and mass flowrate were obtained by the simulation. The important parameters were then verified with the simulation to achieve the similar performance required for the goals of the comparison.

Table 1: The verification of the simulation and real (SGT-800) gas turbine parameters

Parameter	SGT-800 Gas turbine	Simulation Gas Turbine	Percent Difference (%)
Efficiency (%)	41.1	41.7	1.4
Outlet Mass Flowrate (kg/s)	135.5	134.5	0.74
Outlet Temperature (°C)	596	596	0

Table (1) presents the performance of the simulation and real gas turbines in different parameters, this is used to verify that the simulation simulates the gas turbine accurately to an achievable performance. As observed by Table (1), the performance of the simulation is similar to the SGT-800 gas turbine due to the very small percent difference in each of the different parameters. Through this observation, the simulation is verified and can be used in further simulations to carry out the final downstream integration of the OCM process.

5.1.2 Process Description

The power plant process was created based on a simplified version of it, it consisted of two main sections, the gas turbine section, where the compression, combustion and expansion are completed for the feed gases, and the steam turbine section, where the water cycle is evaporated, expanded in a turbine, condensed and pumped to complete the steam cycle downstream of the gas turbine exhaust.

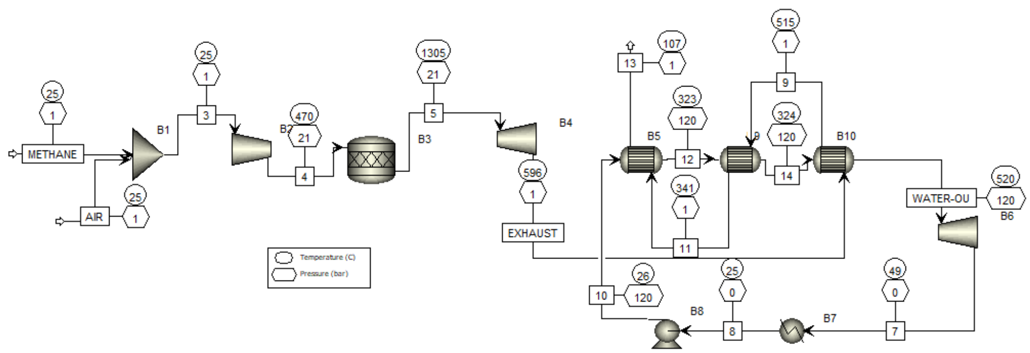

Figure 12: Process flowsheet of the power plant simulation on Aspen Plus including temperatures and pressures

The process simulation of the power plant is presented by Figure (12), the temperatures and pressures are also included corresponding to each stream. Methane and air are fed and mixed into the process, the mixture is then compressed to 21 bar to get fed into the reactor (combustion chamber). The reactor converts 100% of the methane into complete combustion products in an adiabatic condition, where the exhaust hot gases are fed into the turbine. The turbine expands the gases to 1 bar and retrieves power in the form of work. The exhaust gases are still hot on the outlet of the turbine, this is exploited through a steam cycle to retrieve the work that can be retrieved by exchanging the heat, similar to a combined cycle. The hot gases are fed as the hot stream into the heat exchangers to heat the water stream into hot vapor, three heat exchanger were used to simulate each phase of the heating process, the exhaust is fed into the last heat exchanger to heat at the highest temperature of the steam stream (superheating). The intermediate heat exchanger is the latent heat to vaporize the water to steam and the first heat exchanger is to heat the water to the boiling point, which used the end of the exhaust gases stream heat. The superheated steam at 520 C is fed into the steam turbine to retrieve power in the form of work and downstream is a condenser that condenses the vapor back to the ambient temperature water to get pumped again into the cycle at high pressure (120 bar).

Table 2: Summary of economic performance of the power plant simulation and calculated profit

Economic Parameter	Value ($/GJ of Methane)
Costs	5.58
Revenue	10.0
Profit	4.43

The power plant simulation was found to be profitable as observed by Table (2). The revenue from the work produced and sold as electricity achieved profit over the costs of the raw materials and utilities throughout the process, the calculated profit was 4.43 $/GJ of methane fed into the process.

5.2 OCM Standalone Process

The OCM process was simulated through gathering and combining different sections of previous simulations of OCM in literature, the simulation was also based on previous research within the research group to produce the final flowsheet of the process. The OCM simulation mainly produces the desired products of ethylene and ethane from the raw materials, and the exothermic nature of the systems retrieves work that can be used within the process or to be sold as work. The simulation used values for conversion and selectivity from an existing study on the process to ensure that the simulation depicts an accurate performance of OCM. The process naturally included flash columns, compressors, coolers and distillation columns to achieve the desirable conditions at different stages, it also included amine sweetening with MDEA unit to remove the carbon dioxide that is represented by a black box on the Aspen Plus process flowsheet. The amine unit was simulated using a provided example by Promax and with adjusted parameters to fit the overall process parameters.

5.2.1 Amine Sweetening with MDEA Process

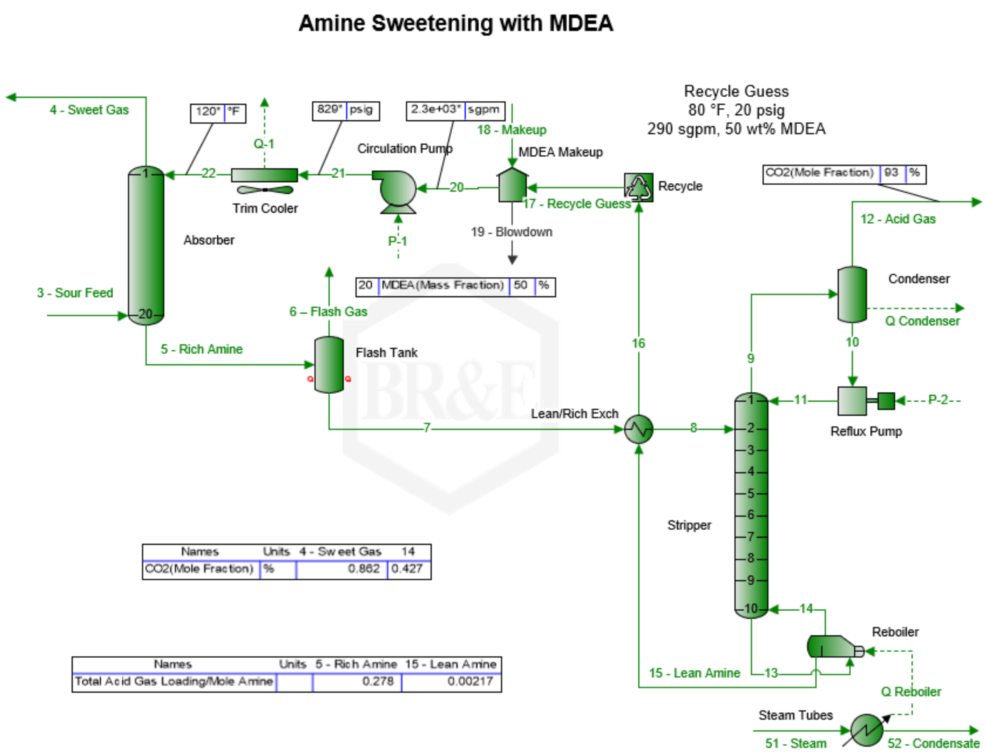

Figure 13: Amine sweetening with MDEA unit Promax flowsheet

Figure (13) presents the amine sweetening process flowsheet that is used for the simulation of the carbon dioxide removal unit. This process is fed with the sour feed from the water removal sections and through an absorber removes most of the carbon dioxide using the MDEA solvent to produce the sweet gas. The solvent with the carbon dioxide goes through the overall process containing the stripper, make up and pump to regenerate the solvent for the overall recycle. The sweet gas product is redirected to the distillation columns to separate the final products of the overall OCM process. The amine sweetening process presented by Figure (13) is represented by a black box called "CO2UNIT" on the Aspen Plus flowsheet, it is fed with the sour feed and produces the sweet gas product stream. The removed carbon dioxide from the process is represented by the "CO2" stream.

5.2.2 Reactor Performance and Conversions

The overall process of OCM was synthesized and simulated using existing performances that are realistic to best represent the overall process. This was emphasized to analyze the economic performance on the basis of achievable reactor performances, and so a set of selectivity and a conversion values for the reactor and products were used from a reported OCM performance was used as an input for the OCM simulation.

Table 3: OCM fluidized bed reactor products' selectivity performance

Component	Selectivity (%)
Ethylene	39.8
Ethane	11.3
Carbon monoxide	10.5
Carbon dioxide	38.4

The reactor conversion of methane for the system described by Table (3) was 33.9%, which was used to find the conversions of each of the reactions producing the products in Table (3). These conversion values were used as input in the simulation's reactor as the performance of OCM reactions.

5.2.3 *Process Description*

The OCM process can be described through three sections of the flowsheet that contribute towards the production of the final products. These section can be described as the reactor, water and carbon dioxide removal, and separation of products.

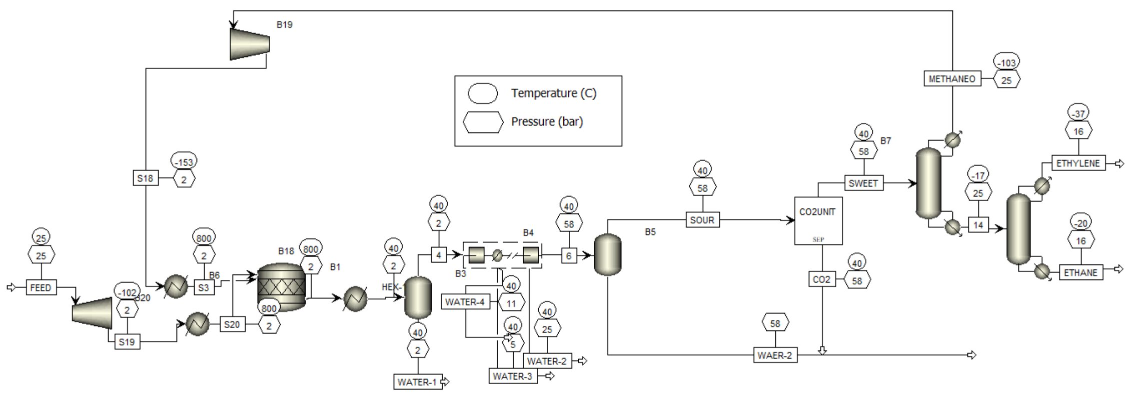

Figure 14: OCM process Aspen Plus process flowsheet

The process flowsheet presented by Figure (14) begins with feed of methane and oxygen mixture at elevated pressure, where it is expanded to achieve the reactor's pressure condition of 2 bar. The feed is heated to a temperature of 800 C using a heat exchanger that is then fed into the OCM reactor along with recycle stream at the same conditions. The isothermal reactor includes four reactions that produce ethylene, ethane, carbon monoxide and carbon dioxide through the selectivity values presented by Table (3) and water, operating at 800 C and 2 bar. The effluent of the reactor is cooled from a temperature of 800 to 40 C that is then fed into the flash column.

The flash column downstream of the reactor is used to remove most of the produced water as a liquid and the vapor stream contains all of the other products and unreacted methane. The vapor stream is then fed into a multistage compression and cooling unit to remove the water that is left in the vapor stream, the multistage unit is composed of four stages. The effluent of the unit is flashed again in a flash column to ensure that the stream is fully vaporized. The vapor stream, which can be called as the “sour” stream is fed into the black box named “CO2UNIT”, which splits the streams based on the results of the Promox simulation of the amine sweetening process presented by Figure (13). The carbon dioxide is removed as a stream and the “sweet” stream contains the products and unreacted methane.

The “sweet” stream is then fed into the separating units to separate all of the desired products and unreacted methane. Cryogenic distillation is used for both distillation columns that separate at sub ambient temperatures that use refrigeration systems for the condensers. The “sweet” stream is fed into the first distillation column (DC-1), where methane and C2+ products are separated into the product and bottoms streams, respectively. The product stream of methane is recycled back into the reactor and the bottoms C2+ stream is fed into the second distillation column (DC-2). The second distillation column separates ethylene and ethane into the products and bottoms streams as final desired products, respectively.

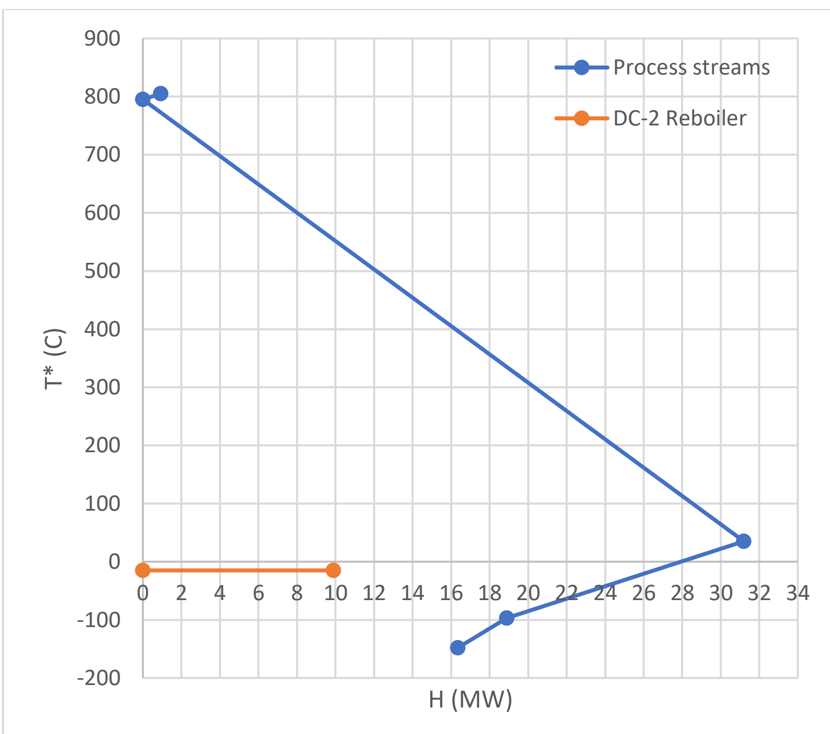

Figure 15: Grand Composite Curve of heat integrated OCM standalone process

Figure (15) presents the created grand composite curve for the OCM standalone process, which presents the process streams considered for heat integration. The small heating requirement at the 800 C point is due to the isothermal reactor, which is ignored as part of the heat integration. The only equipment integrated and supplied heat by process streams is the reboiler of DC-2 as indicated on Figure (15). Through the heat integration analysis, the other factors that affect economics, such as utility and power generation are then considered.

Table 4: Summary of cooling water requirement for the OCM standalone process

Equipment	Heat Duty (kW)
Heat exchangers	-16400
Coolers for multistage compression	-19200
CO2 unit distillation column condenser	-15100
DC-1 reboiler	-64000
DC-1 refrigeration cycle cooler	-230000
DC-2 refrigeration cycle cooler	-16600
Reactor steam cycle cooler	-139000
Total cooling duty (kW)	-500000
Total cooling water required (m^3/s)	11.2

The summarized table of the cooling requirement for the OCM process is presented by Table (4), which uses cooling water that is supplied at 25 C and returned at 35 C at a cost of 0.025 $\$/m^3$.

Table 5: Summary of power generation and consumption for the OCM standalone process

Equipment	Power (kW)
Multistage compression	-15800
CO2 unit pump	-725
DC-1 refrigeration cycle compressor	-160000
DC-2 refrigeration cycle compressor	-7460
Reactor steam cycle pump	-1870
Reactor steam cycle turbine	72400
Feed stream turbine	3790
Recycle stream turbine	1480
Total power (kW)	-108000

Table (5) presents the summary of power generation and consumption throughout the different equipment in the OCM process. The total was found negative meaning the process was overall deficit in power requiring external energy in form of electricity for this analysis.

Table 6: Summary of economic performance of the OCM process simulation and calculated profit

Economic Parameter	Value ($/GJ of Methane)
Costs	22.4
Revenue	10.8
Profit	-11.6

The costs and revenue of the OCM process were found as observed by Table (6). These parameters were used to calculate the profit, which was found to be -11.6 $/GJ of methane, suggesting that the process does not potentially profit and rather lose value through the huge energy demands of the process.

5.3 OCM – Power Plant Integrated Process

The OCM and power plant integrated process was motivated through eliminating the recycle stream of the unreacted methane of which requires huge amount of energy in separation. The elimination of the recycle stream would decrease the flow in the separation unit of unreacted methane and C2+ products, which decreases the energy requirement for the separation unit. This inspired the study of the integrated process with a profitable power plant process in the hopes of adding value to the overall process and making it potentially profitable. The integrated process simply integrates the OCM and power plant processes showcased in the previous sections by rerouting the methane recycle stream to become the feed of the power plant process. The integrated process uses exactly the same simulations from the previous sections, and so any details should be referred back to them. Heat integration is then applied to the overall process to reduce energy requirements of the process and depict an accurate calculation of the economics.

5.3.1 Process Description

The overall process is presented by Figure (16), it includes the OCM and power plant processes as one integrated process that is relatively large. The overall process can be divided into three sections to make it easier to digest and improve the understanding of the process integration. These three sections are the OCM process, the connection between both processes, and the power plant process.

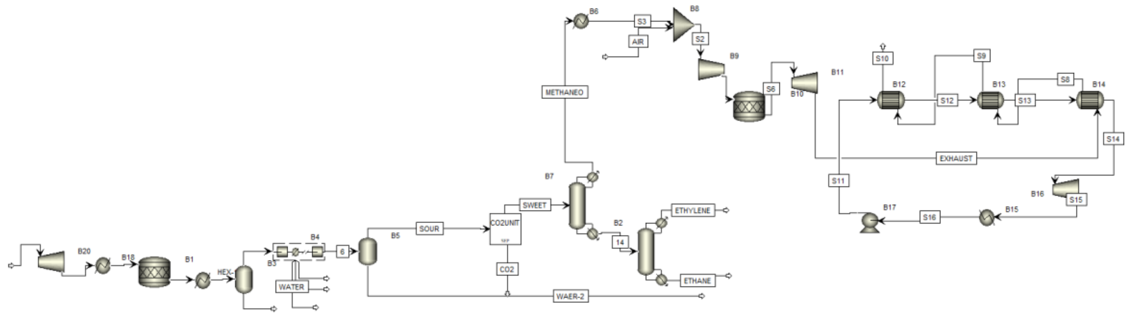

Figure 16: OCM – Power plant integrated process Aspen Plus flowsheet

The overall integrated process flowsheet is presented by Figure (16), which contains the OCM process on the left side, the connection of the unreacted methane stream leaving the first distillation column (METHANEO) to the gas turbine, and the power plant process. The specification in each of the equipment are exactly as set in the standalone simulations of each process as well as the operating conditions, conversions, and efficiencies.

5.3.1.1 OCM Process

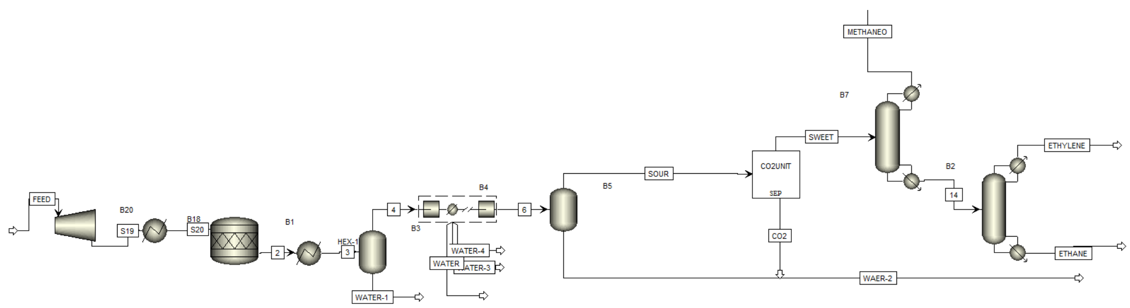

Figure 17: OCM part of the integrated process Aspen Plus flowsheet

Figure (17) displays the OCM process only of the integrated process, which is described in detail in Section (5.2.3). The process is fed with a mixture of methane and oxygen that react in the specified OCM reactions in the reactor, further into the process, the water and CO2 is removed from the streams through a series of flash columns and an amine sweetening unit, respectively. The unreacted methane and C2+ products are then separated through two distillation columns to produce streams of methane, ethylene, and ethane. The C2+ streams leave as products and the methane stream rather than being recycled is routed to the connection to be fed into the power plant process.

5.3.1.2 Connection Between Processes

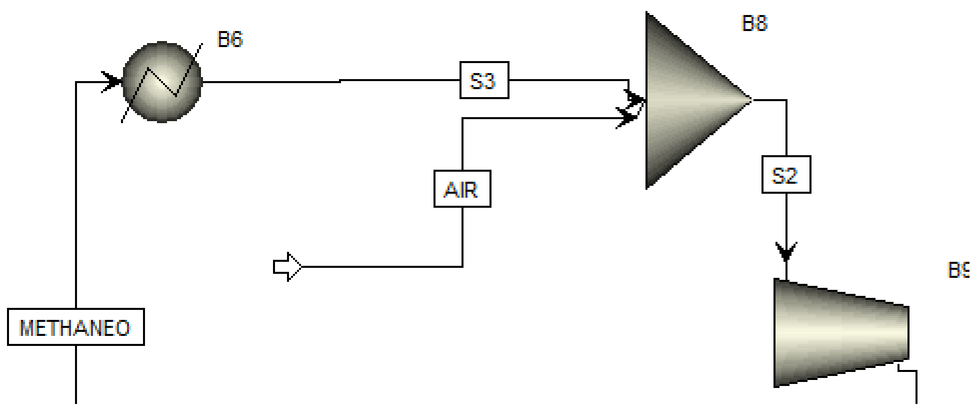

Figure 18: Connection of integrated process Aspen Plus flowsheet

The connection of both processes is presented by Figure (18), which is a simple stream connecting both processes. The methane stream leaving the OCM process (METHANEO) is heated by a heat exchanger to 25 C from -103 C and mixed with the amount of air required for the combustion in the gas turbine downstream. The mixture leaving the mixer is observed to be fed into the compressor, which is part of the gas turbine simulation presented by Figure (19).

5.3.1.3 Power Plant Process

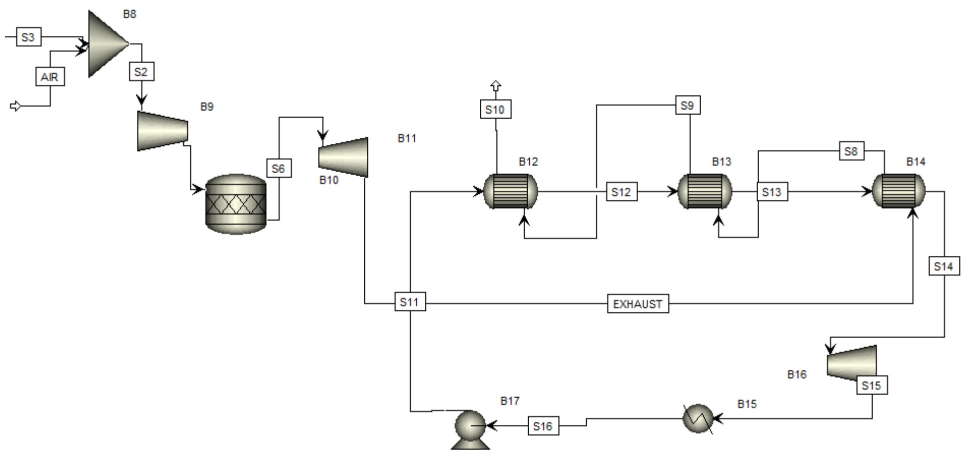

Figure 19: Power plant part of the integrated process Aspen Plus flowsheet

The power plant downstream of the OCM process is presented by Figure (19), which is described in detail in Section (5.1.2). The methane stream (S3) is mixed with air and fed into the gas turbine to generate power through the turbine. The hot exhaust gases leaving the gas turbine are fed into the steam cycle heat exchangers to vaporize the water into the steam used in the steam turbine for further power generation. The power generated by the combined cycle is a source of revenue that should add value to the overall integrated process.

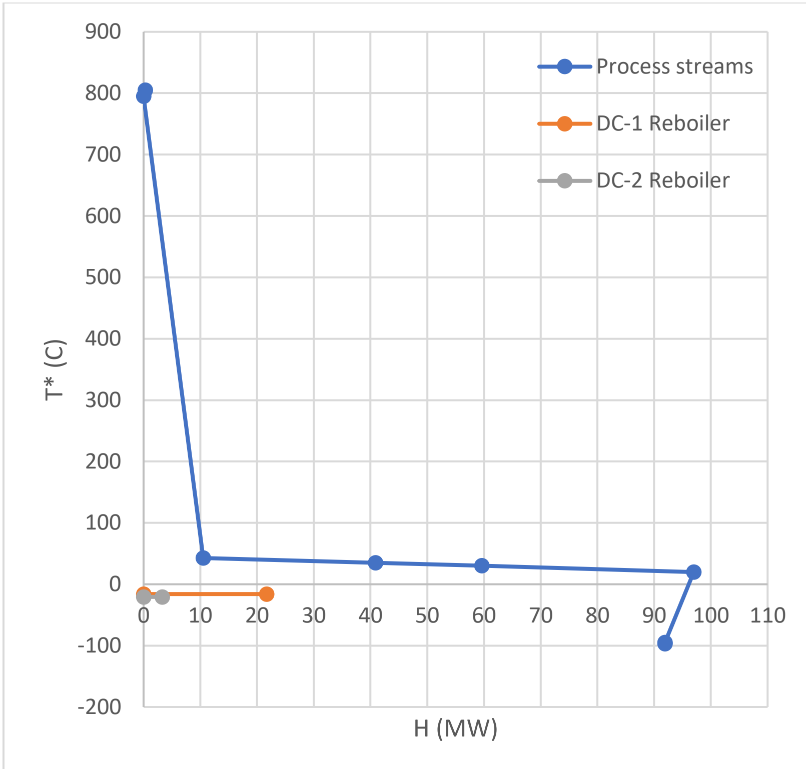

Figure 20: Grand Composite Curve of heat integrated OCM – Power plant integrated process

The heat integration for the integrated process produced the grand composite curve presented by Figure (20). Similar to the OCM standalone process, the heating requirement at the 800 C point is ignored. Both DC-1 and DC-2 reboilers are integrated and supplied heat with process streams. After the process was heat integrated, the utilities and other economic factors are considered.

Table 7: Summary of cooling water requirement for the OCM – Power plant integrated process

Equipment	Heat Duty (kW)
Heat exchangers	-91900
Coolers for multistage compression	-6300
CO2 unit distillation column condenser	-5970
DC-1 refrigeration cycle cooler	-78200
DC-2 refrigeration cycle cooler	-5590
Reactor steam cycle cooler	-69600
Steam cycle cooler	-87000
Total cooling duty (kW)	-344000
Total cooling water required (m^3/s)	3.86

Table (7) presents the cooling water requirement throughout the overall integrated process. Cooling water was used mostly for all of the equipment the required cooling duty, cooling water is typically supplied at 25 C and returns at 35 C with a cost of 0.025 $/$m^3$.

Table 8: Summary of power generation and consumption for the OCM – Power plant integrated process

Equipment	Power (kW)
Multistage compression	-5150
CO2 unit pump	-505
DC-1 refrigeration cycle compressor	-54200
DC-2 refrigeration cycle compressor	-2520
Reactor steam cycle pump	-1440
Reactor steam cycle turbine	36200
Feed stream turbine	2460
Power plant power generation	140000
Total power (kW)	115000

The integrated process's power demands and generation from different equipment throughout the process are summarized in Table (8). The total power is found to be a positive value meaning the process is in power surplus that is sold as revenue in the form of electricity.

Table 9: Summary of economic performance of the OCM – Power plant integrated process simulation and calculated profit

Economic Parameter	Value ($/GJ of Methane)
Costs	8.29
Revenue	7.45
Profit	-0.839

The objective of the integrated process was for the power plant process to add value to the overall integrated process, and while the process did add value by using the generated power to cover energy demands throughout the overall process and decrease costs significantly compared to the OCM standalone process, it did not generate profit as presented by Table (9). The calculated profit was a negative value of -0.839 $/GJ of methane, which means the costs were still above the revenue generated.

Table 10: Summary of profits through all of the explored process simulations

Process	Profit ($/GJ of Methane)
Power Plant	4.43
OCM standalone	-11.6
OCM – Power Plant integrated	-0.839

Throughout the economic analysis performed on all three process simulations, it is observed that there is an improvement in the profit calculation from integrating the power plant process with the OCM process as presented in Table (10). The expectation was that the power plant would make the OCM process profit generating, which was not the case as profit is negative for the integrated process, however it significantly added value as a result of the process integration. This presents that such process integration can help value destructing processes, motivating the search of more valuable processes to be integrated with the OCM process to result in a potentially overall generating profit process.

6. CONCLUSION AND FURTHER WORK

The developed method was observed to be effective in its use on the OCM process. The OCM process was analyzed using the economic screening method and the economic performance was understood through the interpretation of the economic maps. The level 1 economic map presented a minimum selectivity of 58% for materials flow and 37% for materials and energy generation through the exothermic reactions flows, both considered only ethylene production. Any performance of the OCM system below the minimum selectivity is concluded to never profit. The level 2 analysis considered the minimum energy of separation as part of the analysis, which produced a plot of conversion as a function of the required minimum selectivity for potential profit. Reported OCM performances in literature were all in the value destruction area. The OCM process was found not to be profitable after the applied method, as observed as well by the benchmarked plot. The results of the method resulted in the motivation of integrating it with a process that can eliminate the huge energy requirement for separation, a power plant was found to be the most suited process for this integration. The objective was achieved of developing an economic screening method to produce economic maps, where the economic weaknesses of a set of reactions can be identified and motivate integration opportunities.

The OCM and power plant processes were simulated as standalone processes and then integrated and analyzed for the economic performance. The processes were then compared to understand how the integration of processes affected the value added to the process. It was found that even though the integrated process did not result in making the overall process profitable, the integration of the power plant process added value to the OCM process. This confirms that the identification of economic weaknesses through the economic screening method and searching for process alternatives for integration does help improve the overall economics of an integrated process.

In future, the economic screening method can be further developed in the realm of exploring further levels that analyzes the process in more detail. More level consideration would analyze different aspects of the process that could affect the economic performance and present how they affect the economic maps. Through such analysis, the weaknesses can help improve the search of processes for integration to eliminate the weaknesses and improve the economics. Price fluctuations of the materials and energies considered should be explored as well to investigate how the economic maps and minimum selectivity changes for each of the levels. Areas rather than lines to represent the revenue and costs can be plotted to create areas of historic price fluctuations. The inputs of the simulations, specifically the conversion and selectivity used for the OCM reactor can be studied further with using better reported OCM performances to analyze how the economic performance changes. Finally, areas of investigating a systematic method to finding processes to help economic performance in integration should be addressed as it can significantly improve the performance of processes and utilization of efforts and time.

REFERENCES

1. Barteau MA. Is it time to stop searching for better catalysts for oxidative coupling of methane? *J Catal*. 2022;408:173-178. doi:10.1016/j.jcat.2022.03.006

2. Godini HR, Xiao S, Jašo S, et al. Techno-economic analysis of integrating the methane oxidative coupling and methane reforming processes. *Fuel Processing Technology*. 2013;106:684-694. doi:10.1016/j.fuproc.2012.10.002

3. Gambo Y, Jalil AA, Triwahyono S, Abdulrasheed AA. Recent advances and future prospect in catalysts for oxidative coupling of methane to ethylene: A review. *Journal of Industrial and Engineering Chemistry*. 2018;59:218-229. doi:10.1016/j.jiec.2017.10.027

4. Penteado AT, Kim M, Godini HR, Esche E, Repke JU. Techno-economic evaluation of a biogas-based oxidative coupling of methane process for ethylene production. *Front Chem Sci Eng*. 2018;12(4):598-618. doi:10.1007/s11705-018-1752-5

5. Wang L, Violet C, DuChanois RM, Elimelech M. Derivation of the Theoretical Minimum Energy of Separation of Desalination Processes. *J Chem Educ*. 2020;97(12):4361-4369. doi:10.1021/acs.jchemed.0c01194

6. Galadima A, Muraza O. Revisiting the oxidative coupling of methane to ethylene in the golden period of shale gas: A review. *Journal of Industrial and Engineering Chemistry*. 2016;37:1-13. doi:10.1016/j.jiec.2016.03.027

7. Cruellas A, Bakker JJ, van Sint Annaland M, Medrano JA, Gallucci F. Techno-economic analysis of oxidative coupling of methane: Current state of the art and future perspectives. *Energy Convers Manag*. 2019;198:111789. doi:10.1016/j.enconman.2019.111789

8. Nguyen TN, Nakanowatari S, Nhat Tran TP, et al. Learning Catalyst Design Based on Bias-Free Data Set for Oxidative Coupling of Methane. *ACS Catal*. 2021;11(3):1797-1809. doi:10.1021/acscatal.0c04629

9. Ohno T, Moffat JB. Cation effects in the oxidative coupling of methane on phosphate catalysts. *Catal Letters*. 1992;16(1-2):181-190.

doi:10.1007/BF00764369

10. Bhatia S, Thien CY, Mohamed AR. Oxidative coupling of methane (OCM) in a catalytic membrane reactor and comparison of its performance with other catalytic reactors. *Chemical Engineering Journal*. 2009;148(2-3):525-532. doi:10.1016/j.cej.2009.01.008