Optimal Synthesis of Downstream Processes using the Oxidative Coupling of Methane Reaction

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Abstract

Since 1993, the catalytic oxidative coupling of methane (OCM) reaction to higher hydrocarbons (C_2+) was investigated with respect to catalyst development, kinetics and mechanism of the reaction and process engineering aspects as well as economics. It has been shown in various publications over the past 30 years that the OCM is a very promising reaction as an alternative method in the production of ethylene, but two main obstacles have prevented its industrial application: one is its relatively low ethylene concentration in output gases and the second is the huge amounts of energy required to carry out the reaction.

The research work in this thesis has been done on various process schemes proposals for an industrial process for ethylene production using the Oxidative Coupling of Methane reaction. It had started from the first experimental results carried out at the pilot plant in the TU-Berlin facilities by Dr. Jašo in his fluidized bed reactor, and it was found a match between the experimental values reported for conversion, selectivity and yield and the simulation results performed using the plug-flow reactor model in Aspen Plus simulator software.

The OCM process alone was economically evaluated for different world locations in order to find the best place to get profits for this process. As a result of this evaluation two sites offer the best advantage for the potential location of the OCM plant: Middle East and Venezuela.

Considering the knowledge of the country, access to raw material costs, utilities, tax laws, domestic and export market potentials, Venezuela was selected to perform the economic evaluation process. Also Venezuela has low natural gas prices, with highest production potential in South America, and profitable sales earnings from the European market.

Of the three processes studied, electricity co-generation, formaldehyde production and oxygenates production, only the last one, formaldehyde and methanol production, proved to be economically feasible. The economic analysis has shown that it is feasible to implement a process that combines OCM reaction (for ethylene production) and oxygenates generation (formaldehyde and methanol), via synthesis gas, taking advantage of low natural gas prices offered by Venezuela. Payout period, 9 years, and profitability index of 1.1953 confirm this assertion.

This analysis shows that it should be possible to produce ethylene from the OCM reaction that is suitable to satisfy the ethylene demand worldwide as a precursor for the production of other chemicals.

Zusammenfassung

Seit 1993 wurde die katalytische Oxydative Kupplung von Methan (OCM) Reaktion zu höheren Kohlenwasserstoffen (C_2+) in Bezug auf Entwicklung von Katalysatoren, Kinetik und Mechanismus der Reaktion und Prozess-Engineering Aspekte sowie Wirtschaftswissenschaften untersucht. Es wurde in verschiedenen Publikationen in den vergangenen 30 Jahren gezeigt, dass die OCM eine sehr viel versprechende Reaktion als eine alternative Methode zur Herstellung von Ethylen ist, aber zwei Hindernisse haben ihre industrielle Anwendung verhindert: Die eine ist seine relativ geringe Ethylen-Konzentration in Gasen Ausgang und die zweite ist die große Mengen an Energie erforderlich, um die Reaktion durchzuführen.

Die Forschungsarbeiten im Rahmen dieser Arbeit wurde auf verschiedenen Verfahrensschemata Vorschläge für ein industrielles Verfahren für die Ethylen-Produktion mit der Oxydativen Kupplung von Methan Reaktion getan. Es war von den ersten experimentellen Ergebnisse bei der Pilotanlage in der TU-Berlin Einrichtungen durchgeführt von Dr. Jašo in seinem Wirbelschichtreaktor begonnen, und es wurde eine Übereinstimmung zwischen den experimentellen Werten für Umsatz, Selektivität und Ausbeute berichtet und der Simulation gefunden Ergebnisse unter Verwendung des Plug-Flow-Reaktor-Modell in Aspen Plus-Simulator-Software.

Das OCM Prozess selbst allein wurde wirtschaftlich für verschiedene Standorte weltweit ausgewertet, um den besten Platz, um Gewinne für diesen Prozess bekommen zu finden. Als Ergebnis dieser Evaluation zwei Standorten bieten den besten Vorteil für den möglichen Standort des OCM-Anlage: Naher Osten und Venezuela.

In Anbetracht der Kenntnisse über das Land, um Rohstoffkosten, Versorgungsunternehmen, Steuergesetze, Binnen-und Exportmarkt Marktpotenziale, Venezuela wurde ausgewählt, um die wirtschaftliche Evaluierung durchführen zugreifen. Auch Venezuela hat niedrige Preise für Erdgas, mit der höchsten Produktion Potenzial in Südamerika, und gewinnbringenden Verkäufe Erträge aus dem europäischen Markt.

Von den drei Prozesse studiert, erwies sich Strom-Wärme-Kopplung, Formaldehyd Produktion und Oxygenaten Produktion, nur die letzte, Formaldehyd und Methanol-Produktion, wirtschaftlich durchführbar zu sein. Die wirtschaftliche Analyse hat gezeigt, dass es machbar ist, ein Prozess, der OCM-Reaktion (für Ethylen-Produktion) und Oxygenate Generation (Formaldehyd und Methanol) verbindet, über Synthesegas, unter Ausnutzung der niedrigen Erdgaspreise von Venezuela angeboten implementieren ist. Diese Behauptung bestätigt eine Auszahlungsfrist von 9 Jahre und eine Rentabilität Index von 1,1953.

Diese Analyse zeigt, dass es möglich sein sollte, Ethylen aus dem OCM-Reaktion, die geeignet ist, die Ethylen weltweite Nachfrage als Vorläufer für die Herstellung anderer Chemikalien erfüllen, ist zu erzeugen.

This thesis is dedicated to the memory of my father,

Daniel Salerno Zamudio (1928 - 2011)

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Abbreviations List

AGO: Atmosferic Gas Oil

ARCO: Atlantic Richfied Corporation

ASTM: American Society for Testing and Materials

ASU: Air Separation Unit

BASF: Badische Anilin- und Soda-Fabrik

C: Contingency

CCOP: Cash Cost Of Production

CDU: Crude Distillation Unit

DBTA: Dynamik und Betrieb Technischer Anlagen

DRM: Dry Reforming of Methane

EPC: Engineering, Procurement & Construction

FCI: Fixed Capital Investment

FT: Fischer-Tropsch process

GTE: Gas To Ethylene process

GTL: Gas To Liquids process

HETP: Height Equivalent to Theoretical Plate

HRSG: Heat Recovery Steam Generator

HP: High Pressure

HVGO: Heavy Vacuum Gas Oil

ICIS: is the world's largest petrochemical market information provider (www.icis.com)

IRR: Internal Rate of Return

IP: Intermediate Pressure

IRS: Internal Revenue Service (is the revenue service of the United States federal government)

ISBL: InSide Battery Limits

LNG: Liquefied Natural Gas

LP: Low Pressure

LPG: Liquefied Petroleum Gas

LVGO: Light Vacuum Gas Oil

MACRS: Modified Accelerated Cost Recovery System

MEA: MonoEthanolAmine

MP: Medium Pressure

MPO: Methane Partial Oxidation

MTG: Methane To Gasoline process

MTBE: Methyl tert-butyl ether [$(CH_3)_3COCH_3$]

NGL: Natural Gas Liquids

NPV: Net Present Value

OCM: Oxidative Coupling of Methane

OSBL: OffSite Battery Limit

PDVSA: Petróleos de Venezuela, S.A. (Venezuelan state-owned petroleum company)

PEC: Purchased Equipment Cost

SRM: Steam Reforming of Methane

TCI: Total Capital Investment

TDIC: Total Direct and Indirect Cost

TIC: Total Installed equipment Cost

VDU: Vacuum Distillation Unit

WC: Working Capital

WTI: West Texas Intermediate (is a grade of crude oil used as a benchmark in oil pricing)

Units List

Bbl : United States Barrel (42 gallons; 158.9873 liters)

Bbl/d: Barrel per day

kW: Kilo Watts

MW: Mega Watts

Nm^3: Normal cubic meter (measured at 15 °C and 1 atm)

t/d : Metric ton per day

TPD: Tonns per day

wt : Weight

Equipment Nomenclature

D: Flash Drum

E: Heat Exchanger (Shortcut Model)

F: Furnace

HX: Heat Exchanger (Rigorous Model)

K: Compressor/Expander

MK: Multi-Stage Compressor

MX: Stream Mixer

P: Pump

R: Reactor

SP: Stream Separator

T: Tower

TK: Storage Tank

Chapter 1: INTRODUCTION

Since the early 1950's, natural gas has been used as a source of energy. Oil industry, developed since late nineteenth century, has employed it as a fuel source being associated with oil fields. This gas has been burned in order to prevent accidents resulting from its improper storage, due to the large amounts found in these oil fields, particularly in remote areas where natural gas is frequently associated with crude oil but from where its transport in gaseous form is often impossible. Worldwide annual production amounts to around 2.8×10^{12} m^3, and estimated gas reserves are on the order of 150×10^{12} m^3, both values measured at standard conditions [1]. Venezuela has big quantities of proven natural gas reserves (5.52×10^9 Nm^3), being the eighth nation in the world with the largest natural gas reserves, behind Russia, Iran, Qatar, Saudi Arabia and other major world producers. For these reason the country has to take profit of these reserves and monetize them in all possible ways [2]. Venezuela's geographic location gives open access to most important oil markets, such as, European Union and United States. Historically, has sold to those regions the main part of its oil production and, few quantities are exported to Central America and Caribbean countries. In addition, Argentina, Brazil and Chile have become potential oil and gas consumers in this South American region.

For over 20 years, in the late 80's of the twentieth century, several studies have been published regarding the exploit of methane, the main component of natural gas, emphasizing its use in different projects of the chemical process industry, exploiting the immense potential of large world reserves of this hydrocarbons source. A Short overview of publications in the area of process design and operations using natural gas are given in comprehensive reviews of Preuß and Baerns [3], Gradassi and Green [4], Vora et al. [5]. The emphasis of these studies, particularly in chemical engineering, has been mainly on process design problems. Research and development funds have been invested in the last fifty years in

projects for the energetic use of methane, although there have been various studies on the extraction of other components of natural gas. For example Diaz et al. [6] mention the extraction of ethane and heavier hydrocarbons from natural gas has evolved from simple oil absorption to cryogenic expander processes. In the ambient oil absorption process, natural gas is contacted in countercurrent in a high-pressure absorber with lean oil; the oil preferentially absorbs the heavier hydrocarbons which are later removed from the oil in a low-pressure stripper. The refrigerated oil absorption process, introduced in 1957, operates at lower temperatures and allows the use of lower molecular weight oils with higher NGL recovery. Oil absorption processes were the most commonly used until 1970, and they could be used to recover up to 40% ethane from the feed gas. The first low-temperature expander plant was built in 1963, and its basic design is still in use today. It is currently the most efficient process for obtaining high ethane recovery. During the last decades, much research and development work has been devoted to the determination of the optimal operating conditions and more efficient expansion flowsheet.

The quantity of methane used as raw material for the chemical industry accounts only 5–7% of the total consumption [1]. In the long run, methane may well become the main energy source and the primary raw material for many chemical products in the 21st century with the rapid depletion of crude oil. Research and development of methane-utilizing techniques is a hot subject in the world. Basically, utilization of methane can be divided into direct and indirect methods. Indirect utilization of methane is a more ripe method compared to the direct one, according to which methane is converted to syngas first, and the resultant syngas can be converted to methanol or other products; however, there are many disadvantages, for instance, it is a complicated process, high amounts of energy are consumed, there is a high production cost, and so forth. Direct conversion of methane to valuable products seems to be attractive for overcoming the economic problem, especially partial oxidation or oxidative coupling of methane (OCM). It is promising for methane being partially oxidized to methanol and formaldehyde through one

2

step, [7 - 8] but it is also challenging because methanol and formaldehyde are much more active than methane. In Figure 1.1 is shown a schematic flux for the methane oxidation to formaldehyde and methanol. Up to now, great efforts have been devoted to increase the conversion of methane and selectivity to the goal products; methods of heterogeneous oxidation, [9, 10] and homogeneous oxidation [11, 12] have been developed, and significant progress has been made [10, 12]. Table 1.1 shows the results for methanol and formaldehyde production using methane.
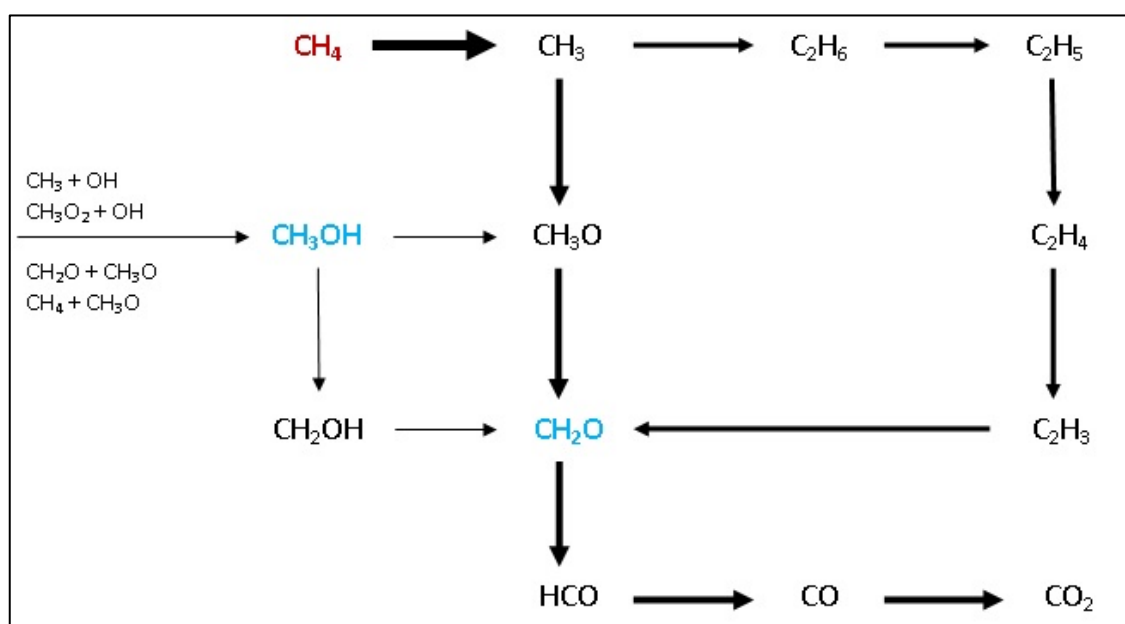
Figure 1.1 Species flux for the oxidation of methane [7]

Table 1.1: Methane conversion to Oxygenates

Catalyst	Temperature (°C)	CH$_4$ Conversion	Selectivity	Source
V$_2$O$_5$/SiO$_2$	650	40 %	40 % to HCHO	Ref. 10
No solid Catalyst used (gas phase reaction)	477	50 %	50 % to CH$_3$OH	Ref. 9

1.1. Natural Gas Processing

Natural gas is produced at the well site in compositions of considerable variety. The objectives of natural gas treatment are correspondingly diverse. Besides its primary constituent methane, with relatively small amounts of ethane, propane and higher paraffins, natural gas may contain various amounts of impurities: nitrogen, carbon dioxide, hydrogen sulfide and water vapor, which occur in varying quantities leading to several problems during production and transportation. Two objectives must be met in treating natural gas: a) adjustment to the required quality standards, b) the recovery of byproducts. The main objective worldwide is production of a sales gas of pipeline standard. In this respect, both the extent of removal of undesirable components and the range of conditioning measures are predetermined. The processing of natural gas, prior to transportation and use as fuel or chemical feedstock, consists mainly of removing the excess of CO_2, and H_2S, in addition to some other sulfur compounds such as COS and mercaptans. Particularly in North America (United States and Canada) and in some countries in South America (Venezuela, Bolivia and Argentina) ethane and propane are also often separated from natural gas; these paraffins are then used as feedstocks for the production of ethylene and some propylene via pyrolysis. As mentioned above, the separation processes and natural gas purification depend on their composition; however, the overall process can be outlined as shown in Figure 1.2. According to this schematic, a natural gas stream containing N_2, CO_2, and C_1 through n-C_4 is processed in a refrigeration system to remove the heavier hydrocarbons. The lean, dry gas produced will meet a pipeline hydrocarbon dew point specification. The liquids removed from the rich gas are processed in a depropanizer column, yielding a liquid product with specified propane content. More specific details are shown in reference [1].
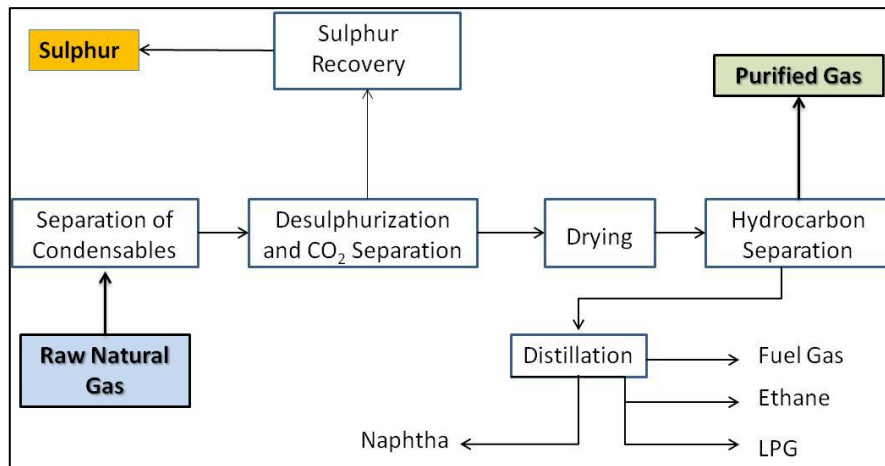
Figure 1.2 Basic operations of natural gas processing [1]

1.2. Uses of Methane as Chemical Feedstock

A use of natural gas for electrical power generation, directly or via NGL, is well established and only a small proportion of natural gas is used as chemical feedstock. Another technology that would meet with quick adoption is a means to ''activate'' the methane in natural gas. Producing ethylene from methane in addition to or instead of ethane would greatly increase the available feedstock. Hydrogen production along with the ethylene could also be a benefit for the chemical industry. Hall [13] presents a schematic diagram of a possible arrangement for two processes: gas to liquids (GTL) and gas to ethylene (GTE) and is shown in Figure 1.3.

The most important chemical processes by means of methane as raw material are the production of synthesis gas for manufacture of ammonia, methanol and oxoaldehydes via hydroformylation. As an example of power generation using natural gas recently research done by Adams et al. [14], shows an electricity generation process using natural gas and solid oxide fuel cells at high electrical efficiency (74% Higher Heating Value) and zero atmospheric emissions. The process contains a steam reformer heat-integrated with the fuel cells to provide the heat

necessary for reforming. The fuel cells are powered with H_2 and avoid carbon deposition issues. 100% CO_2 capture is achieved downstream of the fuel cells with very little energy penalty using a multi-stage flash cascade process, where high-purity water is produced as a side product.
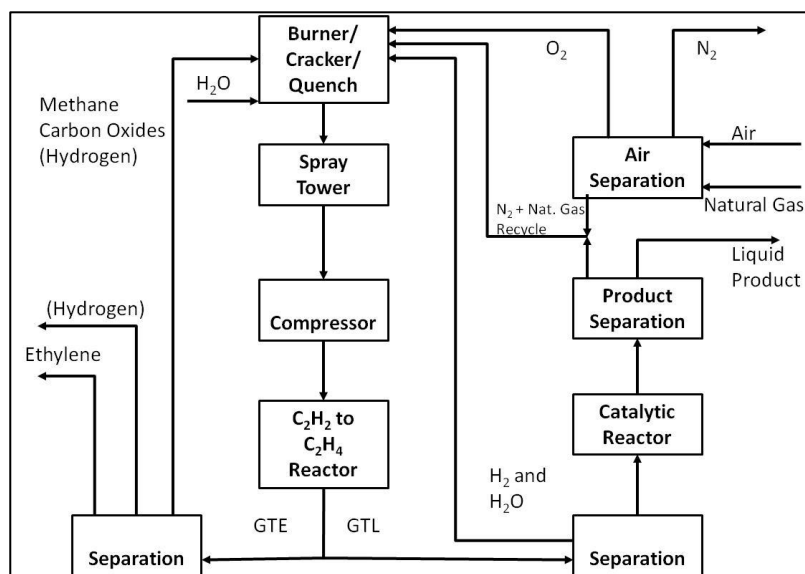
Figure 1.3: Schematic diagrams of GTL and GTE process of natural gas [13]

Indirect methane conversion processes uses synthesis gas and, despite being over 50 years, still remains valid and continually shows to be a promising option in the future. Synthesis gas can be converted into hydrogen for ammonia and fuels: a) through the Fischer-Tropsch reaction in α-olefins, waxes and fuels; b) through methanol in olefins (ethylene, propylene), gasoline, acetic acid, formaldehyde and MTBE chemicals, just to mention some end products of the currently most important petrochemical processes.

At the beginning of XXI century, the Venezuelan state company PDVSA Gas conducted a feasibility study of using natural gas to produce liquid products in a way that would address the issues of site, process, product selection and rates, and technology so that the company could develop a suitable strategy to use GTL Technology as an optional route to monetize the country´s large natural gas reserves. The GTL products of interest to PDVSA Gas are: LPG, Naphta, Linear

Paraffins, Kerosene, Diesel, Waxes, High VI (Viscosity Index) Lube Oils and Oxygenates (methanol, ethanol, n-propanol and n-butanol) [15].

In the direct methane conversion a number of approaches include oxidative coupling, oxyhalogenation, aromatization and selective oxidation to methanol, among other processes, depending on the selected catalyst. Of these methods, oxidative coupling has received significant attention and the best result to date approaches 30% conversion of methane and about 80% selectivity to C_2+ hydrocarbon products [5]. In recent years, efforts were therefore more likely to achieve through new reactor designs yield gains, but has also led to no noticeable gains. The reaction system has been investigated in many works [16 - 19], so that a relatively secure knowledge exists on which sub-processes taking place and which of them could be limiting. The most studied reactor types are: conventional catalytic fixed-bed reactors, plug-flow reactors with distributed oxygen addition, counter-current moving bed chromatographic reactors, fluidized-bed reactors and various types of membrane reactors.

1.3. Fundamental of the Oxidative Coupling of Methane Reaction

Oxidative coupling of methane is a complex system of heterogeneously catalyzed and non-catalytic gas-phase reactions. The dependence of primary reaction steps on temperature and partial pressures of reactants is well recognized. Fundamental understanding of the complex heterogeneous–homogeneous reaction network of the OCM reaction has progressed significantly since its infancy in the early 80's of the twentieth century [20]. Since then, the oxidative coupling of methane leading to C_2+ hydrocarbons, ethane and ethylene, has received much attention. Numerous papers have been published each year, but determining how to convert methane to C_2+ hydrocarbons with high selectivity is difficult because complete oxidation of CH_4, C_2H_6, and C_2H_4 to CO_2 and H_2O must be suppressed [21]. In past decades, significant work has been reported toward the development of

efficient catalysts for OCM. These catalysts may be divided into three major groups: alkali and alkaline earth metal compounds, rare earth metals, and other transition-metal compounds. Work on catalysts for OCM has been reviewed [22], and many details can be found therein. The activity and selectivity of catalysts for this reaction are very dependent on the experimental conditions, such as, temperature, space velocity, CH_4/O_2 ratio, and so forth.

Many selectivity and activity determining factors have been identified in the OCM reaction. Selective catalytic materials should generate methyl radicals without their consecutive heterogeneous oxidation. The most challenging property of the selective catalytic materials is their ability to activate methane in the presence of more reactive reaction products (C_2H_4 and C_2H_6), which are the essential CO_x precursors. The above catalyst properties can be partially tuned by appropriate catalyst design taking into account the knowledge from surface science and related kinetic studies. Despite a good knowledge of the fundamentals of the OCM reaction, per-pass yields of C_2 hydrocarbons higher than 30% under conditions close to the anticipated practice have not been achieved. It is not expected that higher values will be achieved in the near future based on present catalyst design only [23]. Catalytic reaction engineering design appears to be helpful for further improvement of the OCM performance. For the reactor design, i.e. fixed-bed, fluidized-bed, countercurrent moving bed and membrane reactors, modeling, simulation and operation, significant knowledge and basic understanding have been accumulated [18]. All process designs, however, suffer from the high costs of separation of the products from unconverted methane and the required gas recycling. As soon as this challenge has been successfully met, the conversion of methane will certainly become economically viable.

1.4.Oxidative Coupling of Methane Process Schemes

Several processes schemes, having in common the OCM reaction, have been suggested, some of them include the use of ethylene as feedstock for the petrochemical industry. Ethylene can be converted to saturated hydrocarbons, oligomers, polymers, and derivatives thereof. Chemical reactions of ethylene with commercial importance are: addition, alkylation, halogenation, hydroformylation, hydration, oligomerization, oxidation and polymerization.

The direct conversion of methane to C_2 hydrocarbons via OCM reaction has attracted academic and industrial interests due to its potential to be an effective method to utilize natural gas for industrial feedstocks. However, the usefulness of this process has been limited so far as it has low methane conversion and/or low hydrocarbons selectivity. An approach to overcome the limitation of OCM process was reported and it consisted of a two-step process. In the first step, methane or natural gas is converted into lower olefins, which is transformed directly into gasoline range hydrocarbons over a zeolite catalyst [24]. It is therefore of great practical interest to convert the diluted ethylene without being separated from the methane streams into a much less volatile product(s), such as gasoline hydrocarbons.

In 1987, the Mobil MTG (Methane To Gasoline) process has been used in New Zealand for gas to gasoline conversion. Researchers at Atlantic Richfield Corporation (ARCO) [25], proposed a non-steady state operation in which the catalyst also acts as the oxidizing agent, thus requiring periodic regeneration using oxygen. Such periodic operation could possibly be carried out in a single fixed-bed or a fluidized-bed catalytic reactor. It is also conceivable that, when applying fluidized-bed operation, oxidative methane coupling and catalyst re-oxidation could be carried out in two different reactors while the catalyst is continuously exchanged between them as in catalytic cracking. Also catalytic conversion of methane to

methanol and formaldehyde as well as to paraffinic, olefinic and aromatic hydrocarbons has been carried out on catalysts containing molybdenum oxide [3], using the OCM reaction as the source of syngas production.

Vereshchagin et al. [26], developed a flow sheet diagram for the conversion process of the LNG of the Krasnoyarsk region, in Russia. Process comprises reactors for oxidative methane coupling (OCM) and ethane dehydrogenation utilizing heat of OCM reaction, products and reagent recycling and block of product separation, which operates at cryogenic temperature and atmospheric pressure. Mass and heat balances for different cases were calculated. It is shown that utilization of LNG as a cooling agent has a beneficial effect on power consumption. Their simulation studies also shown substantial increase of ethylene yield (up to 50%) achieved even with a moderate performance catalyst of OCM. The flowsheet of the process design for OCM combined with ethane dehydrogenation is shown in Figure 1.4.

Figure 1.4: Flow sheet of the LNG process conversion using OCM reaction [26]

In their work they concluded that natural gas treatment process, including helium removal and LNG conversion to ethylene by OCM reaction, is a possible alternative to traditional methods of gas treatment. The main problems that

obstacle its introduction are the OCM reactor design, and selection of the proper materials for OCM reactor and cryogenic equipment.

Hoebnik et al. [27], studied the feasibility of methane coupling as an add-on unit to a naphtha cracker. An existing cold box was used for separation of ethylene and unconverted methane, but arrangements were made for separation of the coupling by-products. The cracker's methane was used as a feedstock. The conclusions was that the concept provided was technically and economically feasible, at spring 1992 prices, only if the catalyst meets the assumed single pass conversion of 30% and selectivity of 80% towards C_2 products. It may use the existing cryogenic separation train of the naphtha cracker for ethylene purification produced via oxidative coupling of methane, and requires only an additional separation section to remove the coupling by-products: carbon dioxide and water. The concept schematic representation is shown in Figure 1.5.
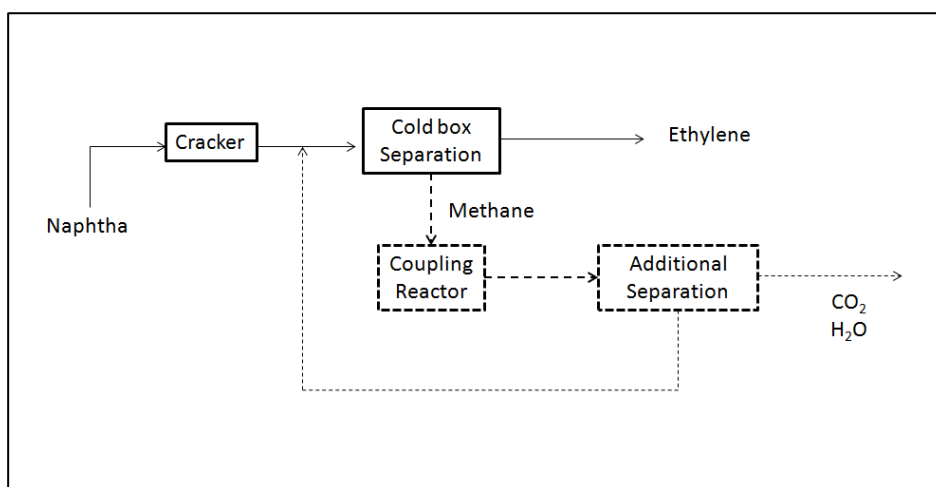
Figure 1.5: OCM reaction as an add-on unit to naphtha cracking [27]

(Full lines, existing equipment; dotted lines, new equipment)

Ren et al. [28], mention that most olefins (e.g., ethylene and propylene) are produced through steam cracking routes; they can also be produced from natural gas (i.e., methane) via methanol and oxidative coupling routes. Their work was the

reviewing of 2008 literature data and then comparing the energy use, CO_2 emissions and production costs of methane-based routes with those of steam cracking routes. They found that methane-based routes use more than twice process energy than state-of-the-art steam cracking routes do (the energy content of products was excluded from the analysis). The methane-based routes can be economically attractive in remote gas-rich regions where natural gas is available at low prices. The development of liquefied natural gas (LNG) may increase the prices of natural gas in these locations. Oxidative coupling routes are currently still immature due to low ethylene yields and other problems. According to the authors, while several possibilities for energy efficiency improvement do exist, none of the natural gas-based routes is likely to become more energy efficient or to lead to less CO_2 emissions than steam cracking routes do.

Finally, Preuß and Baerns [3], suggest a general scheme for the OCM process shown in Figure 1.6.

Figure 1.6: Process scheme for catalytic OCM to Ethylene [3]
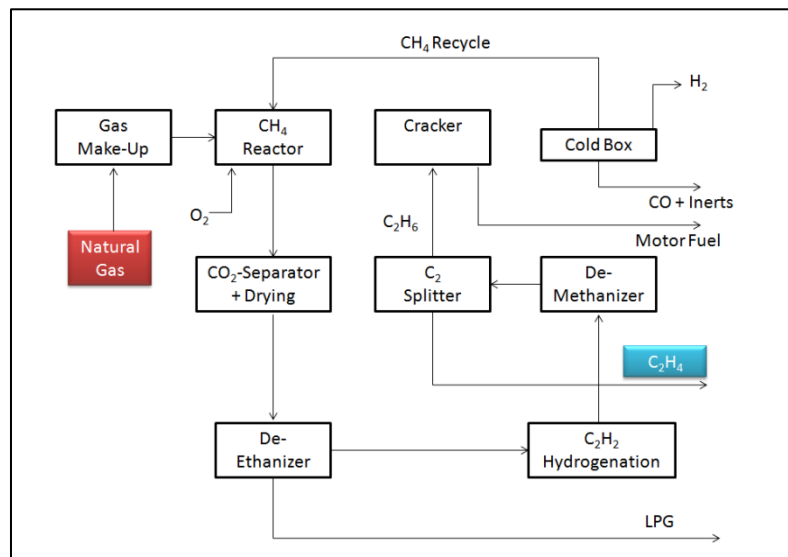
1.4.1. ARCO Process

In 1987 Jones et al. [25], published a paper discussing a series of promoted metal oxide catalyst that transform methane to higher hydrocarbons. This process was done because the need to convert natural gas, located in remote areas of the world, into higher valued and transportable products, specifically olefins with ethylene as the major component. The process is performed oxidatively either in a cycle redox mode or as catalytic reaction of methane and oxygen. Using the last process, Jones and co- workers obtained 25% methane conversion and selectivity values were also 70 – 75% in C_2+ products.

The remote gas field conversion technology applied was the Mobil Methane To Gasoline (MTG) process, the first major advance in commercial alternative fuel production since the development of Fischer-Tropsch (FT) technology, at the time this study was done. A general flowsheet of the ARCO process is presented in Figure 1.7.
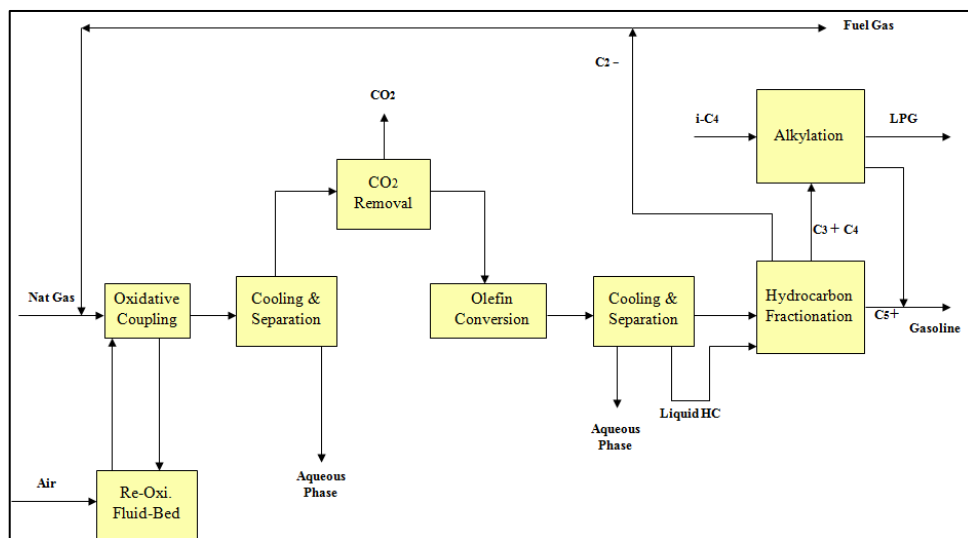
Figure 1.7: General flow diagram for the ARCO process [25]

Jones et al. [25] compared both processes (FT and MTG) and concluded that these processes required steam reforming of methane to produce synthesis gas. In

the case of FT process, the synthesis gas was converted directly to a synthetic crude product while in the MTG process the synthesis gas was converted to methanol, which then reacted to selectively form gasoline or distillate using a zeolite catalyst. Because in both processes the majority of the capital investment was associated with synthesis gas generation, the challenge was to convert methane directly to a liquid fuel at a cost less that Fischer-Tropsch or Methane to Gasoline processes.

Direct methane pyrolisis has been used to produce liquid fuels from methane, with the consequent generation of hydrogen as co-product, using temperatures in the range of 1000 °C to 1190 °C, requiring its combustion and subsequent heat generation. To avoid this endothermicity, oxidative routes to methane was considered.

The continuous oxygen co-feed approach for the methane oxidation to ethylene was done using the catalyst systems that ARCO had developed for the redox methane conversion process. This air or oxygen co-feed requires a higher separation costs. If air and methane are fed into the reactor, unreacted methane and nitrogen must be separated downstream. Alternatively oxygen may be used but this requires air separation. For fuel production, a second step is required.

Olefins oligomerization to gasoline and distillate products can be accomplished over a variety of catalytic systems, according to authors [25]. They selected the ZSM-5 catalyst because it catalyzes the transformation of olefins into gasoline and distillate-range products. With this ARCO process, ethylene is produced as an intermediate product in the catalytic process of methanol to fuels.

As a conclusion, with the ARCO process methane can be converted to higher molecular weight products in a number of increasingly process. Light olefins may be the final products or an intermediate to the final gasoline o distillate products. Since

the oxidative route is not thermodynamically limited, there is still room for much improvement in methane conversion product yields.

1.4.2. Schwittay – Turek Process

Since 1998 the direct conversion of methane to formaldehyde is a long sought goal [29]. Several reviews (Lintz [30], Arena, [31] Michalkiewicz [32] and Lou [33]) have been published about the selective oxidation of methane to formaldehyde and methanol. Formaldehyde is produced industrially from methanol by the following three processes [34]:

(1)   Partial oxidation and dehydrogenation with air in the presence of silver crystals, steam, and excess methanol at 680 – 720 °C (BASF process, methanol conversion = 97 – 98 %).

(2)   Partial oxidation and dehydrogenation with air in the presence of crystalline silver or silver gauze, steam, and excess methanol at 600 – 650 °C (primary conversion of methanol = 77 – 87 %). The conversion is completed by distilling the product and recycling the unreacted methanol.

(3)   Oxidation only with excess air in the presence of a modified Fe-Mo-V oxide catalyst at 250 – 400 °C (methanol conversion= 98 – 99%).

Processes for converting propane, butane, ethylene, propylene, butylene, or ethers (e.g., dimethyl ether) into formaldehyde are not of major industrial significance for economic reasons [34]. Processes that employ partial hydrogenation of CO or oxidation of methane do not compete with methanol conversion processes because of the lower yields of the former processes. However, the utilization of lower alkane resources, particularly CH_4 and C_2H_6, for the production of useful oxygenates is one of the biggest challenges in catalysis research.

In 2002, Schwittay [35], proposed and evaluated economically a process that used the oxidative coupling of methane to formaldehyde production. It is possible to get the direct conversion of methane to formaldehyde but the main disadvantage of one-step conversion process is the very low selectivity with respect to CH_2O at

increasing conversions of methane. This problem can be solved if the products are separated from the reactants in a reactor-separator system; thus subsequent oxidation of the desired product could be avoided and overall ethylene yields of 85% could be achieved [30].

To remove the formaldehyde from the product stream Schwitttay had frozen formaldehyde together with the water vapor. For the separation of ethylene in the oxidative coupling various exchanged zeolites were tested and proven at the temperature ranges between 25 and 250 °C as the most suitable process. For industrial use the problem was the effectiveness of the reactor-separator principle that could both work as well as it does experimentally because of the design size restrictions. When the reaction was the partial methane oxidation, formaldehyde selectivity was 40% at methane conversion of 12%, while in the oxidative coupling of methane reaction the increase in ethylene selectivity was achieved from 43 to 54% with complete oxygen consumption.

Schwittay results were conducted using Aspen Plus simulation program for the implementation of a 359000 t/y plant for methane conversion to formaldehyde and ethylene. After the partial methane oxidation reaction to formaldehyde, the gases are cooled in a gas scrubber and then follow the 49% weight formaldehyde stream distillation obtaining 57000 t/y of CH_2O product. Because of the need to work at low methane conversions the recycled methane to fresh methane ratio is about 50% and therefore the investment volume for heat exchanged to provide the heating and cooling of this high gas flows required makes the process uneconomical. The partial oxidation will only be economically feasible when catalysts are being developed that can achieve a formaldehyde selectivity of 60% even at methane conversions of 10%. Concerning the oxidative coupling of methane reaction to ethylene, 100000 t/y of C_2H_4 was obtained and the amount of zeolite needed for two years continuous operation to ethylene adsorption was considered

uneconomical. However, the method can be carried out economically when the lifetime of the zeolite or the adsorption capacity can be increased for ethylene.

As a conclusion of his work Schwittay mentions that despite not achieved the product increase separation yield in the partial oxidation reaction to formaldehyde, the heterogeneously catalyzed oxidative coupling of methane reaction is economically much more interesting and future work should focus on improving the product adsorption properties of the Ag-zeolites and in the determination of the lifetime of the adsorbent under industrially relevant conditions. A general flowsheet of the Schwittay – Turek process is presented in Figure 1.8.

Figure 1.8: General flow diagram for the Schwittay – Turek process [35]

1.4.3. OXCO Process

At the beginning of the 1990 Australian government coordinated a research program to evaluate the feasibility of using the OCM reaction as a basis of an alternative route to conventional synthesis gas-based processes for producing transport fuel and chemical from natural gas [36]. This new conceptual route was known as the OXCO process, in which a single fluidized bed reactor is used to

combine the methane oxidative coupling step with the pyrolisis of ethane and higher alkane components present in natural gas to provide a method for the total conversion of natural gas to olefins. A conceptual flow diagram of the OXCO process is shown in Figure 1.9.
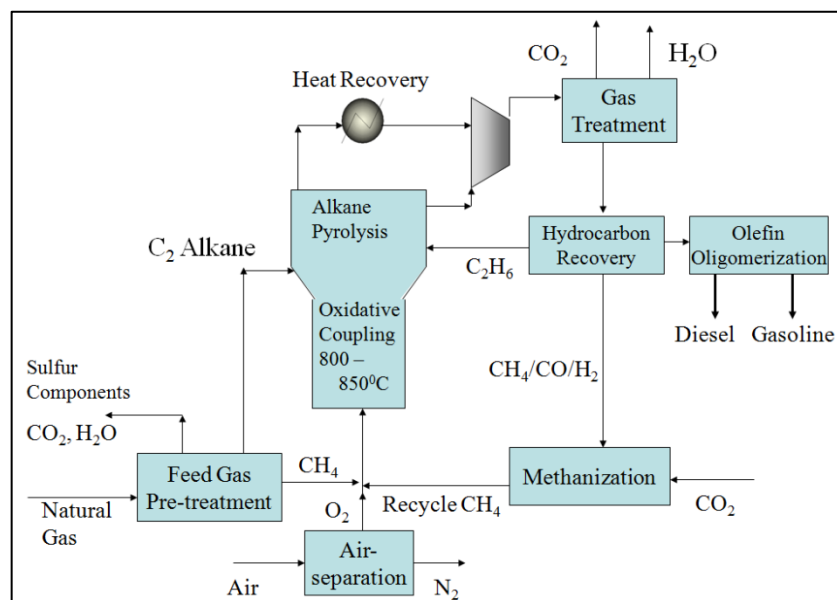
Figure 1.9: The OXCO process concept for natural gas conversion [36]

The topics studied in this research project included catalyst development, process chemistry, reactor development, reaction mechanisms, catalyst characterization, gas phase reactions, ethylene oligomerization and the evaluation of conceptual process economics. The process consists in natural gas pretreatment to remove H_2O, CO_2, sulfur compounds and part or all of the ethane and higher alkanes, the methane coupling reactor, reaction heat recovery, product gas compression and treatment to remove the H_2O and CO_2 formed by the reaction, recovery of the C_2 and higher hydrocarbons by cryogenic technology followed by oligomerization of the olefins to transport fuels. An important feature of the process is the pyrolytic conversion of the higher alkanes (C_2H_4 and higher) to ethylene within a fluidized bed reactor using heat generated by the methane coupling reactions.

The results obtained by Edwards et al. [36], show that ethane pyrolisis was achieved within fluidized bed reactor without affecting the methane coupling performance. They also show that the conversion reactor operates with a per pass conversion of the total carbon input of 29.5% and the overall selectivity of the process to unsaturates is 86%. The product gas, after removal of CO_2 and water, contains 16.8% v/v C_2+ hydrocarbons of which almost 75% are unsaturates. The inclusion of the methanation step allows more that 25% of the CO_x produced by OCM reaction to be converted back to methane for recycle to the reactor.

1.4.4. Suzuki Process

In 1995 Suzuki et al. [37] conducted a study for the conversion of methane via OCM reaction to transportable liquid fuels to utilize remote natural gas effectively. The process developed was characterized as follows:

I.   Application of a circulating fluidized bed with a riser reactor to the OCM process because of its high efficiency of heat removal, temperature controllability and ability to deal with high space velocity reactions.

II.   Applications of a bubbling fluidized bed reactor with an internal heat exchanger for the control of heat generated to oligomerization process.

III. Design of split feed of recycled gas, which is composed of recycled un- converted methane with byproducts, into the reaction process.

IV.   Direct feed of the OCM/pyrolysis reactor effluent to the oligomerization reactor without separation of ethylene from coupling products.

The conceptual block flow diagram of this process is shown in Figure 1.10. Suzuki et al. [37] also conducted an economic comparisons between its process concept and the conventional OCM process, and their evaluation showed that the

optimal performance of the OCM catalyst is 30% methane conversion and 80% C_2+ selectivity under some inverse correlation of conversion and selectivity and their process was more economical then the existing co-feed mode process studied.
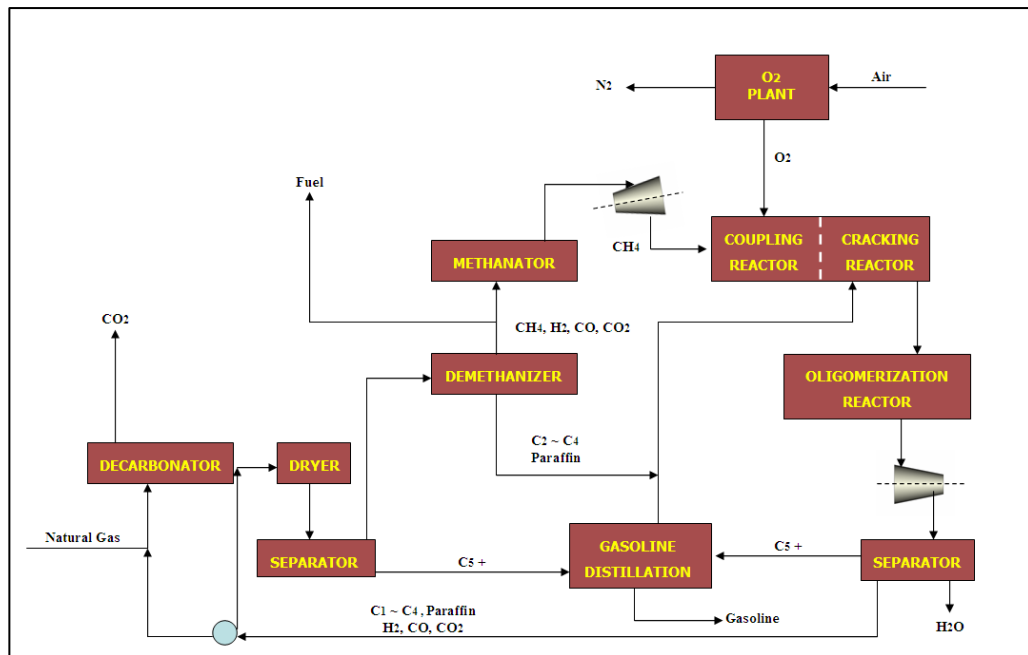
Figure 1.10: Block flow diagram of the Suzuki process [37]

A detailed description of this Suzuki process is found in reference [37]. As a conclusion, in general, the OCM technologies were confirmed to be more economically feasible in the case of installation to deal with a natural gas containing higher hydrocarbons, compared with syngas methods.

1.5. OCM to Olefins and OCM to Gasoline Processes

In 1995 Gradassi and Green [4] published a very detailed study of several natural gas conversion processes from the perspective of a manufacturing entity that has access to substantial low cost natural gas reserves, capital to invest and no allegiance to any particular product. The analysis used the revenues and costs of

conventional methanol technology as a framework to evaluate the economics of the alternative technologies based on the OCM reaction.

The two processes studied concerning the OCM reaction was the oxidative coupling of methane reaction to olefins (OCM-I) and the oxidative coupling of methane to gasoline (OCM-II). Process diagrams for both OCM reactions based are shown in Figures 1.11 and 1.12.
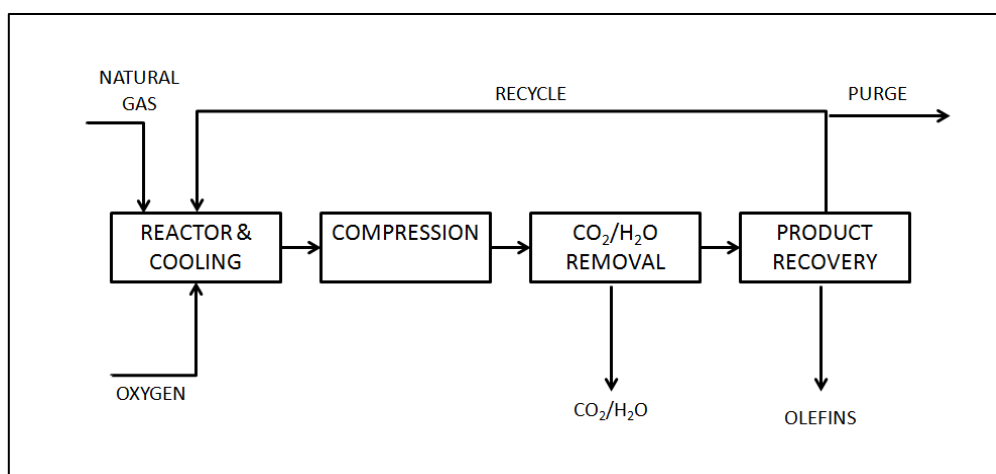
Figure 1.11: Schematic diagram of the OCM to olefins process [4]

The process for OCM-I description consists of a co-feed of a fresh natural gas, a recycle gas stream consisting of mostly unreacted methane and oxygen. The reactor inlet pressure was 4.83 bar. Heat exchange of the feed gas stream with the product effluent raises the feed gas from 21 °C to a reaction temperature of 789 °C and reduces the product gas temperature from 816 °C to about 90 °C. Cooling water was used to reduce this temperature further 38 °C. The temperature of the reactor was maintained below 816 °C by generation of high pressure (103 bar) steam.

The product gas is compressed to 10.3 bar and condensate is removed. The gas stream then passes through an acid gas removal system based on a 30% aqueous mixture of monoethanolamine (MEA) for the removal of CO_2. The gas stream then passes through a refrigeration unit for the removal of additional water

and then finally a molecular-sieve column for the removal of the remaining water vapor and CO_2. A cold-box system is used to recover the C_2+ products, including ethylene, from the product gas stream. Ethylene and propylene are recovered in a typical ethylene plant separation scheme using a deethanizer, a C_2-splitter, a depropanizer and a C_3-splitter. The C_2+ alkanes are used as plant fuel.

The evaluated process had an olefins production of 412000 t/y. Electric power is generated to meet plant requirements using steam turbine generators. High-pressure steam is generated in a gas-fired boiler using fuel gases from the purge gas and from the C_2+ recovery system. This supplements the high-pressure steam from the oxidative coupling reactor. No export power was provided.

In the OCM-II process, (Figure 1.12), natural gas, recycle gas and oxygen are reacted to produce olefins as described above in the OCM-I case. The OCM reactor effluent, which includes light hydrocarbons, carbon oxides and water vapor was partially cooled to 399 °C and was fed at 4.14 bar to the oligomerization reactor where 92% of the olefins was converted to C_5+ liquid hydrocarbons.
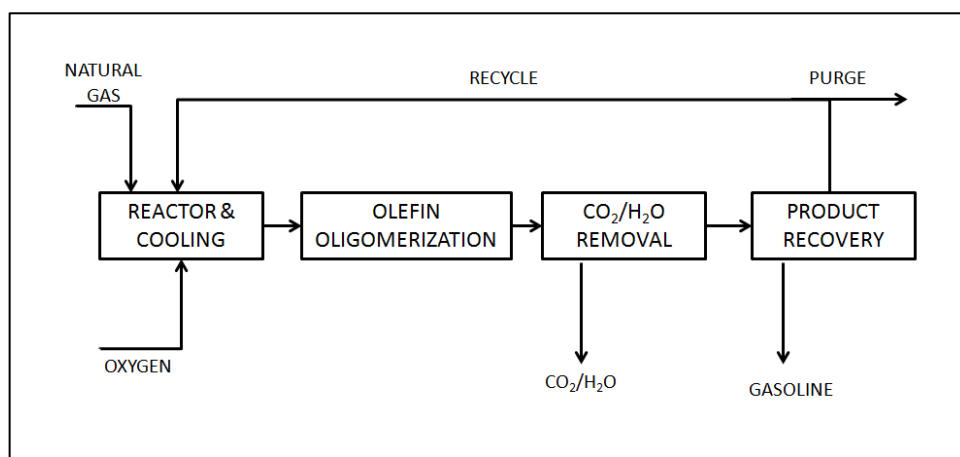
Figure 1.12: Schematic diagram of the OCM to gasoline process [4]

The oligomerization reactor effluent was then cooled to condensate the liquid hydrocarbon product and reaction-produced water. CO_2 was removed from the unreacted gas stream, which was recycled to the OCM reactor. This process produced 212800 t/y of gasoline.

Gradassi and Green research results show the economic analysis results for the two OCM technologies, (OCM-I and OCM-II), and concluded that the payout time for the OCM-I is roughly twice that for the conventional methanol synthesis. This process required the same capital investment, in OCM reactor alone, as the reformer and the methanol converted combined in conventional methanol synthesis. The OCM-II was expected to have an even greater payout time than the OCM-I. The gasoline process suffers the same capital investment penalty as the OCM-I, but it generated an even lower cash margin.

As conclusion they mentioned that with the 1995 market prices, conventional methanol synthesis had a payout time of about 7 years. All other gas conversion processes (OCM-1 and OCM-II), in his review had payout times longer than that of conventional methanol synthesis.

1.6. Purpose of the Research Work

The creation of projects and schemes and the prediction of the financial outcome if the projects were implemented is the activity of chemical engineering design. Design is a creative activity, and as such can be one of the most rewarding and satisfying activities undertaken by an engineer. The design does not exist at the start of the project. The designer begins with a specific objective or customer need in mind and, by developing and evaluating possible designs, arrives at the best way of achieving that objective: a new chemical product or production process.

When considering possible ways of achieving the objective, the designer will be constrained by many factors, which will narrow down the number of possible

designs. There will rarely be just one possible solution to the problem, just one design. Several alternative ways of meeting the objective will normally be possible, even several best designs, depending on the nature of the constraints.

At the beginning of the OCM project I had only a vague notion of available reactor products and only a very superficial simulation of the process. As shown in Figure 1.13, the only simulated sections were reactor outlet compression section, following by a very rudimentary separation of CO_2 and subsequent purification of ethylene produced in the reactor, shown in Figure 1.14.

Figure 1.13: Schematic diagram of the CO_2 removal process

Then it were made simulations of the OCM reaction in order to know exactly the composition of gas leaving the reactor, since it is a fundamental step in the downstream development of the process. An important feature that should be known before starting any proposed design using the OCM reaction is the knowledge of the ethylene production capacity to be obtained, since the first simulations were performed using very low flows, pilot plant flow rate, with which could not have a proper estimation of equipment prices and therefore there are failures in the process costs.

Figure 1.14: Schematic diagram of the Ethylene purification process

After setting the ethylene production capacity in thousands of tons annually, it became necessary to have an oxygen supply source, since the quantities of methane to be used in the reactor require that air will not be introduced because the elimination of nitrogen in the subsequent products separation is a problem.

An attempt to produce results from the OCM simulation process was conducted by Schwittay [35]. His process had as its ultimate objective the production of formaldehyde from the ethylene produced in the same OCM reactor. For the simulation, an average rate of 11.733 kg/s was adopted as the reactant stream of methane. As results of his Aspen$^®$ simulation model a maximum formaldehyde yield of 1.86 kg/s was reached with a use of 8 kg/s of oxygen and reaction temperatures of 600 °C to about 640 °C. The Schwittay process results in a yearly ethylene production of 100300 tons.

The most important difference between the results obtained by Schwittay and those that will be presented in this paper is that the ethylene produced in the OCM reactor is first purified of all its CO_2 content and a light gases stream (CH_4, CO

and H_2) is then removed, resulting in the final purification of ethylene. Subsequently the unreacted CH_4 is used in the production of formaldehyde in a secondary reactor. The proposal of using two reactors, one for the OCM reaction and another for the formaldehyde production, leads to the successful separation of ethylene before the production of formaldehyde without having the problems Schwittay had removing both products simultaneously. Also the amount of CH_4 used will be three times the amount used by Schwittay, because the non-reacted CH_4 from the OCM reaction will be used in the formaldehyde reactor.

This thesis will focus on the techno-economic analysis of several process designs by means of oxidative coupling of methane reaction. Core of this work is the systematic development of new process variants in downstream processes for the oxidative coupling of methane. The aspects of the process and energy integration should be given particular consideration. The specificity of the systematic approach is that not only the operating variables simultaneously, but also the process structures can be improved. Condition for improving is the sensitivity analysis studies of a superstructure that contains all the physically meaningful process, including variants of the best possible process. It has not been taken into consideration processes whose end product are the fuels (gasoline) production from olefins using oligomerization reaction, since the main focus of this work is the production of ethylene, the basic feedstock for the petrochemical industry.

The main tool to be used in the technical and economic analysis and design of several processes using the OCM reaction will be the process simulation and most particularly the Aspen Plus® process simulation software, (version 7.2), program developed by AspenTech Inc. Company and it was specially designed for simulation of oil & gas and petrochemical processes. Economic analysis for each process will be carried out using the Aspen Process Economic Analyzer program, which to date has no rival in the commercial software market for economic evaluation of chemical processes.

Oxidative coupling of methane reaction results will be taken from Jašo experimental results [23], applied to a plug-flow reactor model in Aspen. Knowing that this type of reactor is not the most recommended for this reaction, the intention is to use results for conversion, selectivity and yield that match the experimental data of fluidized bed reactor used in the facilities of the DBTA institute at the Berlin Technical University.

This thesis will consist of a total of seven chapters, covering the following topics:

I.   Oxidative Coupling of Methane, reviews the main approaches which have been proposed for this reaction using the Stansch et al. [38] comprehensive Kinetics of the OCM reaction. This model is suitable for reliable reaction engineering simulations of catalytic reactor performance.

II. Economic Evaluation of Chemical Projects, presents an introduction of the most important economic terms most frequently used in the cost analysis of chemical processes. It will include an example of economic evaluation of a petroleum refining process to better understanding the Aspen Process Economic Analyzer software.

III. Economic Evaluation of Ethylene and Electricity Co-Generation using the OCM reaction, whose purpose is to study the OCM process with a special variant that is the electricity co-generation in addition to the ethylene produced with the OCM reaction.

IV. Techno-Economic Analysis for Ethylene, Formaldehyde and Electricity Co-Generation using the OCM Reaction, the process described herein involves the catalytic processing of methane, via OCM, into ethylene and other by-products and the unreacted methane into formaldehyde production.

V.   Techno-Economic Analysis for Ethylene and Oxygenates Production using the OCM Reaction, describes a feasibility study on the production of methanol and formaldehyde using the non-reacted methane coming from the OCM reaction process right after the separation of the ethylene produced.

Finally, a summary of the most important conclusions and key economic aspects are presented in Chapter 7. Furthermore, some suggestions and an outlook of potentially interesting future processes will be presented.

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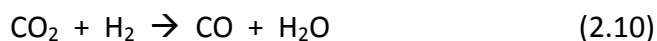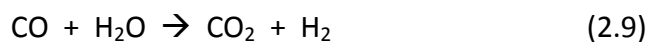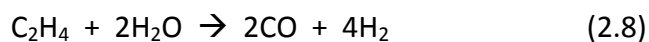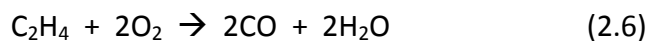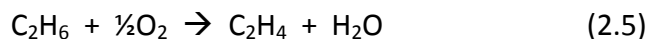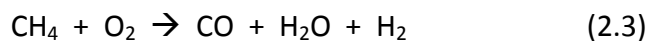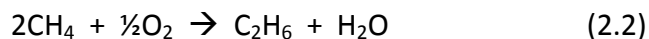
Chapter 2:
Oxidative Coupling of Methane

Since 1993, the catalytic oxidative coupling of methane (OCM) reaction to higher hydrocarbons (C_2+) was investigated with respect to catalyst development, kinetics and mechanism of the reaction and process engineering aspects as well as economics. These studies were supplemented by the design of catalysts for the dehydrogenation of ethane, which is one of the main products of the OCM reaction [1].

It has been shown in various publications over the past 30 years that the OCM is a very promising reaction as an alternative method in the production of ethylene, but two main obstacles that have prevented its industrial application are its relatively low concentration of ethylene in output gases and the enormous amounts of energy required to carry out the reaction. However, further improvement of the catalytic performance, by developing more selective catalysts and by reaction engineering means, is necessary in order to make this process commercially viable. The more promising approach seems to be the improvement of C_2+ selectivity and yield by developing new, alternative reactor designs. Many different reactor concepts were proposed for the oxidative coupling of methane, for instance: counter-current simulated moving bed reactor, solid oxide fuel cell reactor, catalytic dense membrane reactor, fluidized bed reactor, porous membrane rector, and fixed bed reactor. All of these reactor designs mentioned above have their advantages and disadvantages, but only the last three reactor types have the potential to be exploited industrially [2].

Since the pioneering works of Keller and Bhasin [3], Mleczko and Baerns [4], and Ito et al. [5], a huge amount of experimental data on OCM catalysts and their performance have been accumulated. The comprehensive literature search in

databases, e.g. Science Direct (Elsevier), resulted in more than 2700 research articles and reviews on the OCM reaction. In addition, about 140 patents on the OCM reaction have been published in the last 30 years [6]. Despite extensive research has been done on the OCM reaction many fundamental aspects, which determine the choice of catalytic components remains unknown, for instance, distribution between surface-to-gas phase reactions, the participation of non-equilibrium sites in the OCM process, as well as the essential features for an optimal catalyst composition. However, a comprehensive 10-step kinetic model of the oxidative coupling of methane to C_2+ hydrocarbons over a La_2O_3/CaO catalyst was developed by Stansch et al. [7], on the basis of kinetic measurements in a microcatalytic fixed-bed reactor covering a wide range of reaction conditions for the oxidative coupling of methane reaction that can be used for prediction of reactor performances and for various gas-solid contacting modes. The developed model appears to be superior to previous kinetics published, but most important, the wide range of validity and the achieved accuracy allow its application for reaction engineering simulations. The kinetic model is characterized by the following set of stoichiometric equations:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad (2.1)$$

$$2CH_4 + \tfrac{1}{2}O_2 \rightarrow C_2H_6 + H_2O \qquad (2.2)$$

$$CH_4 + O_2 \rightarrow CO + H_2O + H_2 \qquad (2.3)$$

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2 \qquad (2.4)$$

$$C_2H_6 + \tfrac{1}{2}O_2 \rightarrow C_2H_4 + H_2O \qquad (2.5)$$

$$C_2H_4 + 2O_2 \rightarrow 2CO + 2H_2O \qquad (2.6)$$

$$C_2H_6 \rightarrow C_2H_4 + H_2 \qquad (2.7)$$

$$C_2H_4 + 2H_2O \rightarrow 2CO + 4H_2 \qquad (2.8)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (2.9)$$

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad (2.10)$$
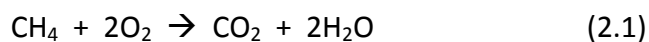
The estimated rates for the above reactions can be given in Eqs. (2.11 – 2.16). Moreover, the kinetic parameters used in the reaction scheme and the conditions suitable for use of Eqs. (2.1 – 2.16) are presented in Table 2.1.

$$r_j = \frac{k_{o,j}\, e^{-Ea/RT}\, P_C{}^{m_j}\, P_{O2}{}^{n_j}}{\left[1+\left(K_{j_{CO2}}\, e^{-\Delta Had,CO_{2,j}/RT}\right) P_{O2}\right]^n}; \quad j = 1, 3-6 \tag{2.11}$$

$$r_2 = \frac{k_{o,2}\, e^{-Ea_2{}^2/RT}\left(K_{o_{O2}}\, e^{-\Delta Had,O2/RTP_{O2}}\right)^{n2} P_{CH4}}{\left[1+\left(K_{o_{O2}}\, e^{-\Delta Had,O2/RTP_{O2}}\right)^n + K_{j_{CO2}}\, e^{-\Delta Had,O2/RTP_{O2}}\right]^2} \tag{2.12}$$

$$r_7 = k_{o,7}\, e^{-Ea_7/RT}\, P_{C2H6} \tag{2.13}$$

$$r_8 = k_{o,8}\, e^{-Ea_8/RT}\, P_{C2H4}{}^{m_8}\, P_{H2O}{}^{n_8} \tag{2.14}$$

$$r_9 = k_{o,9}\, e^{-Ea_9/RT}\, P_{CO}{}^{m_9}\, P_{H2O}{}^{n_9} \tag{2.15}$$

$$r_{10} = k_{o,10}\, e^{-Ea_{10}/RT}\, P_{CO2}{}^{m_{10}}\, P_{H2}{}^{n_{10}} \tag{2.16}$$

Table 2.1: Kinetic parameters (Stansch et al. [7])

Reaction number (k)	$k_{o,j}$ gmol*gcat.$^{-1}$*s^{-1}*Pa$^{-(m+n)}$	Ea_j kJ/mol	K_j, CO_2 Pa^{-1}	ΔH_{ad}, CO_2 kJ/mol	K O_2 Pa^{-1}	ΔH_{ad}, O_2 kJ/mol	m_j	n_j
1	0,20 x 10^{-5}	48	0,25 x 10^{-12}	-175	---	---	0,24	0,76
2	23,20	182	0,83 x 10^{-13}	-186	0,23x10^{-11}	-124	1,00	0,40
3	0,52 x 10^{-6}	68	0,36 x 10^{-13}	-187	---	---	0,57	0,85
4	0,11 x 10^{-3}	104	0,40 x 10^{-12}	-168	---	---	1,00	0,55
5	0,17	157	0,45 x 10^{-12}	-166	---	---	0,95	0,37
6	0,06	166	0,16 x 10^{-12}	-211	---	---	1,00	0,96
7	1,20 x 10^{7}	226	---	---	---	---	---	---
8	9,30 x 10^{3}	300	---	---	---	---	0,97	0,00
9	0,19 x 10^{-3}	173	---	---	---	---	1,00	1,00
10	0,26 x 10^{-1}	220	---	---	---	---	1,00	1,00

2.1 OCM Process description

For the OCM reaction process two important parameters have to be decided before conducting any kind of simulation work: 1) the ethylene production in terms of annual production rate and 2) the reactor performance temperature. The optimal temperature profile along a fixed bed plug flow reactor is determined over La_2O_3/CaO as the catalyst to maximize the ethylene production [8]. Experimental results achieved with the fluidized bed reactor located in the TU-Berlin pilot plant have shown that the optimum reaction temperature is 820 ° C. (Jašo [10]).

The modeled process uses 1174 t/d of fresh methane, which undergoes by catalytic processing via OCM to ethylene and other by-products, and the non-reacted methane can go to either recycled or as raw material for synthesis gas production. Laboratory data, [10], were used to size the reactor while data from Aspen model were used to size the rest of the process equipment. In Figure 2.1 is shown the process flow diagram for the original OCM process, studied in this chapter.
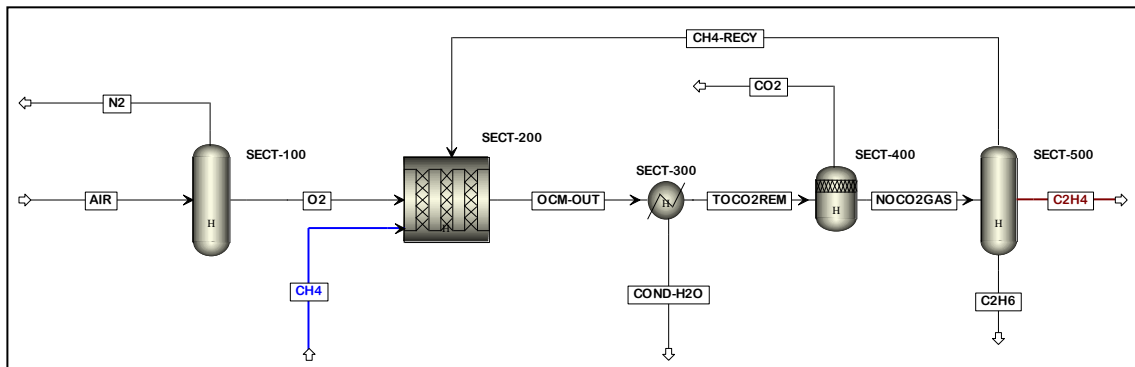

Figure 2.1: General flow diagram for the oxidative coupling of methane process

The simulations were performed using an Aspen hierarchy blocks to provide a hierarchical structure model to complex simulations. For the OCM process it has been included the following process areas: air separation unit (Section 100), OCM

reaction (Section 200), gas compression (Section 300), amine treatment for CO_2 removal (Section 400), and ethylene separation (Section 500).

2.1.1 Air Separation Unit (ASU)

Oxygen was first extracted from the atmosphere by a chemical process. This was superseded in the 1920s by the cryogenic process involving low temperature liquefaction and distillation of air. Over the years, the sizes of the oxygen plants have grown from 100 tons per day (TPD) to almost 4,000 TPD. The cryogenic air separation process is by far the most widely used. The choice of oxygen production technologies depends on several factors: the volume required, the purity required, the customer location, and the oxygen usage pattern. For the large tonnage oxygen customers (over roughly 300 TPD), a cryogenic plant is usually more economic. A commercial-scale OCM plant would require thousands of tons of oxygen each day and cryogenic distillation is the only commercially available technology today to produce such large quantities of O_2 economically and at high purity [31]. Cryogenic ASU is considered to be a mature technology, which is the only technology currently available for large capacity plants. Oxygen is separated from air cryogenically at a pressure of approximately 6 bars and very low temperatures (about -177 °C). Electricity or steam produced in later steps can be used for the performance of the compressor drivers in the air separation unit. The reason which requires the separation of oxygen from air, to provide pure oxygen to the OCM reaction instead of using air directly into the reactor, is because the non-reacted methane will be recycled, after being purified from its heavy products, together with the H_2 and CO formed as co-products in the reactor. If these gases are recycled together with the N_2, these impurities in the feed will affect the reactor design and make their size much larger, which adversely affects the final equipment costs [9]. Besides the reason mentioned above, the molar ratio of methane to oxygen (99% purity) should be controlled at about 2:1 in order to lower the risk of explosion and to reach desired selectivity to ethylene in the OCM reactor. The equipment and model design

and construction of air separation plant can be found at Linde's web page. Figure 2.2 shows a schematic of this Linde Column. (http://www.linde-Engineering.com/en/process_plants/air_separation_plants/index.html).
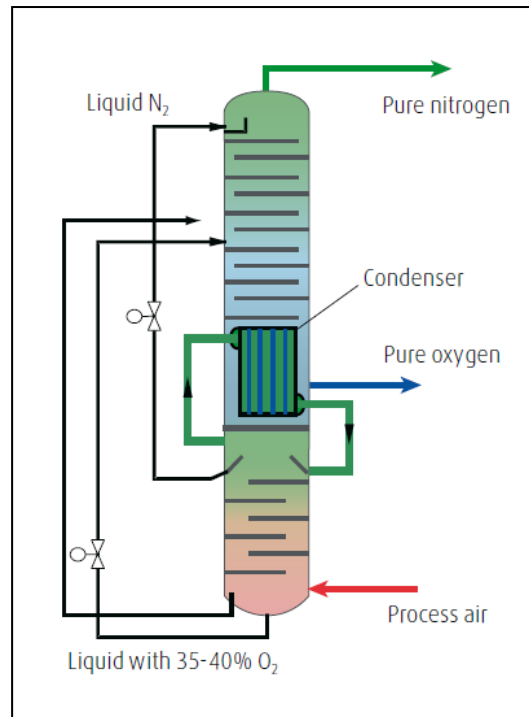
Figure 2.2: Linde´s double-column rectification system [31]

The air separation unit collects air and recovers oxygen by cryogenic distillation. Air is first compressed to 6.4 bars using three stages compressor, with water removed via interstage coolers operating at 85 °C. The dehydrated air is sent to the cryogenic distillation unit, which is assumed to have the following separation conditions: Oxygen is recovered at 1.1 bar and 15 °C with the fractional recoveries of O_2 and Ar being 0.999 and 500 ppm, respectively; N_2 is recovered at 1.1 bar and 15 °C with the fractional recoveries of O_2, N_2 and Ar being 0.043, 0.947, and 0.01, respectively. In Aspen Plus®, this is modeled by a specification block for simplicity. The nitrogen stream at atmospheric pressure is able to be used as purge gas inside the OCM plant and then vented to the atmosphere. From 18000 t/d of fresh air this ASU can deliver 3491 t/d of O_2 and 14509 t/d of N_2, both gases at the conditions explained before.

Figure 2.3 shows a schematic of this Air Separation Unit, section 100 of the OCM process.
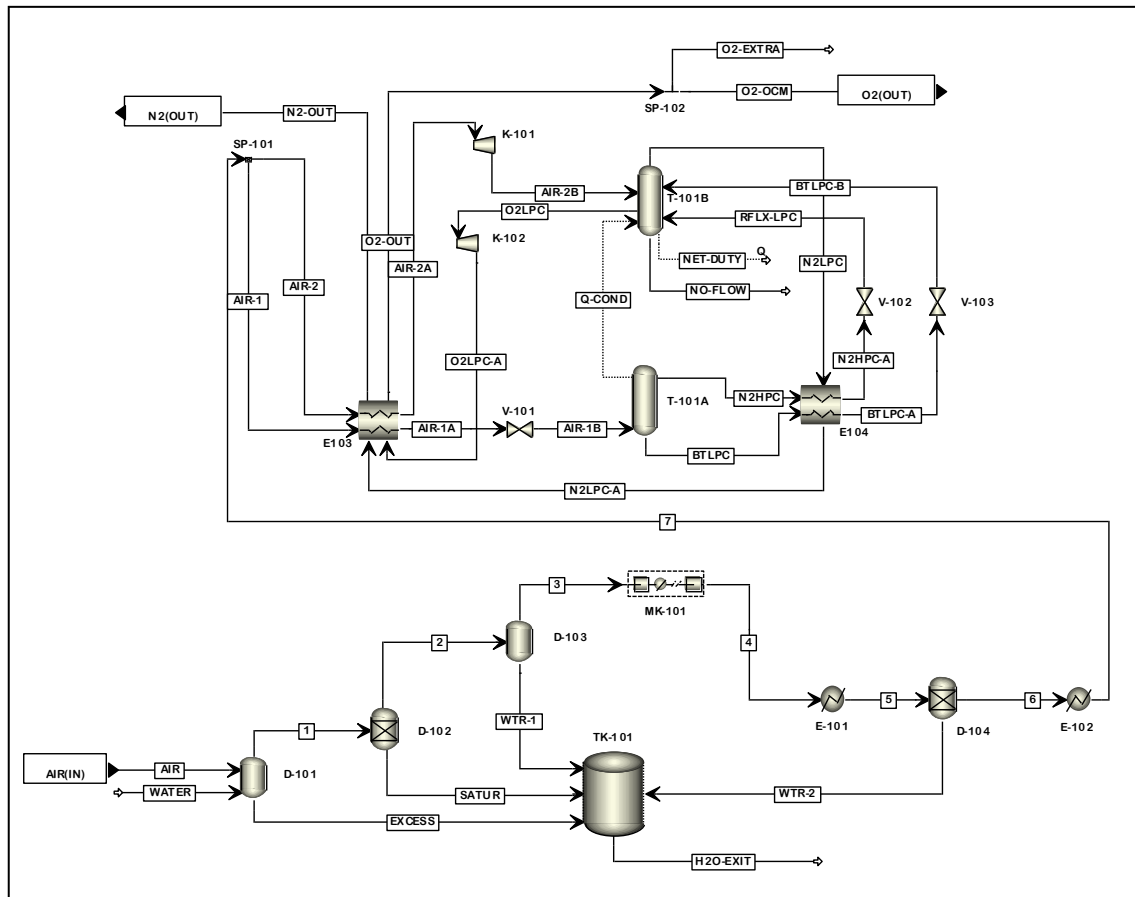
Figure 2.3: Diagram of the Air Separation Unit section

2.1.2 OCM Reactor

The OCM reaction is widely accepted to proceed in combinations of heterogeneous and homogeneous reactions. The reaction scheme, proposed by Stansch et al. [7] which consists of a ten-step network of reactions, is used. The operational range for the OCM 10 reaction steps have been presented as follows [7]:

- Temperature operational range: 850 – 1100 K

- Reactor pressure range: 0.1 – 0.41 MPa

- CH_4/O_2 molar ratio: 2 – 25

From previous experiments [1], it was found that an optimum temperature exists for a high C_2+ selectivity. For a CH_4/O_2 ratio of 10 and a total pressure of 4.1 bar it was found to be at about 1070 K. At this temperature a C_2+ selectivity of 48 % is observed at total oxygen conversion. An optimum temperature exists for a high C_2+ selectivity, depending on which catalyst we are working [8].

A common oxidative coupling reactor design has either a fluidized bed or an oxygen permeable membrane reactor. The simulation of these reactions was made using the plug-flow reactor block in Aspen. In the reactor, methane (CH_4) and oxygen react over a catalyst to form water and a methyl radical (-CH_3). This reaction is called partial oxidation of methane. The methyl radicals combine to form higher alkenes, mostly ethane (C_2H_6), which dehydrogenates into ethylene (C_2H_4). The function of the catalysts is to control the activity of oxygen ions so that reactions can be kept on the desired path. Complete oxidation (rapid formation of CO_2 before the radical's link up to form ethane and ethylene) is an undesired reaction. The catalysts used are mostly oxides of alkali, alkaline earth and other rare earth metals [6]. Hydrogen and steam are sometimes added to reduce coking on catalysts. After one pass, nearly 45.3% of methane conversion is achieved; results in selectivity to C_2^+ are 42% and at the same time the per-pass ethylene yield on a molar basis of methane is about 20% due to special reaction conditions [10]. The total oxygen feed by mass is completely consumed. Ideally, 100% is desired since oxygen is difficult to separate and can cause undesired combustion or even explosion. The ratio of methane to oxygen should be controlled at about 2:1 in order to lower the risk of explosion and to reach desired selectivity to ethylene [10]. With this design parameters conversion, selectivity and the yield increased with temperature and the maximum value of yield was obtained at 1093 K. The reactor was simulated using the commercial

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software Aspen Plus® version 7.2, as mention above, using the rigorous plug flow reactor model with rate-controlled reactions based on Stansch kinetics [7].

The reactor dimensions are:

- Length: 3 m
- Diameter: 0.5 m
- # tubes: 2000

$V = \frac{1}{4}\pi L D^2$ = 0.589 m^3

Because the kinetic equations introduced in the Aspen Plus program are calculated by taking into consideration the reactor volume and not the nature of the catalyst, these dimensions are those that have achieved the values of conversion, selectivity and yield reported in this study. Additional information is needed to model the reactor using a catalyst:

- Bed voidage = 0.3
- Particle density of 3.6 g/cm^3.

In the Aspen plug flow reactor model, called *RPlug*, the composition changes along its length. The basic describing equations involve the integration of appropriate composition and rate terms along the reactor length. An overall energy balance is also performed. *RPlug* uses an integral method to solve mass, energy, and component attribute conservation equations for each differential element of reactor length. These equations have the form (for each component and for enthalpy):

$$Accumulation = Input - Output + Generation \qquad (2.17)$$

This Aspen model integrates these variables while keeping the integration error below a specified tolerance. The integration error is applied to scaled variables to keep all error relative to the magnitude of the variable. *RPlug* model uses a variable-

step-size Gear algorithm during this integration to solve the differential form of the conservation equations. Each equation is solved for in each element using a trial-and-error method. The Newton Convergence method is used to correct each wrong guess to a new value. Integration convergence tolerance determines how tightly these equations are solved. Tight (small) tolerances result in small steps, long run times, and increased model accuracy. An Aspen simulation result shows good agreement with experimental reactor model used by Jašo, [10], in his study of OCM reactions. These values are shown in Table 2.2 and Figure 2.4 illustrates the reactor section for the OCM reaction process.

Table 2.2: OCM Reaction Results

Variable Studied	Jašo Experiment	Salerno Simulation
Catalyst	$Mn/NaWO_4/SiO_2$	---
Temperature (°C)	825.0	820.0
Conversion (%)	45.00	45.26
Selectivity (%)	50.00	42.15
Yield (C_2+) (%)	19.60	19.08
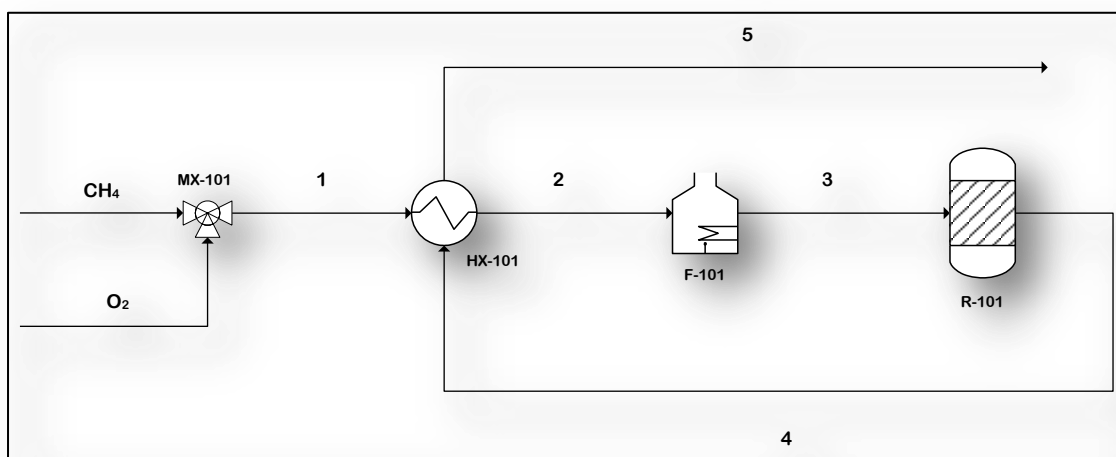
Figure 2.4: Diagram of the OCM reaction section

2.1.3 Cooling and Gas Compression

To immediately stop the reaction and prevent degradation of ethylene formed, and thus prevent the production of secondary reactions that reduce the value of the OCM gas, it is necessary to cool the reactor output gases. This is done using a quench tower to cool down the gases. The quench tower was modeled as an equilibrium packed tower, with 10 stages and 6.5 m diameter.
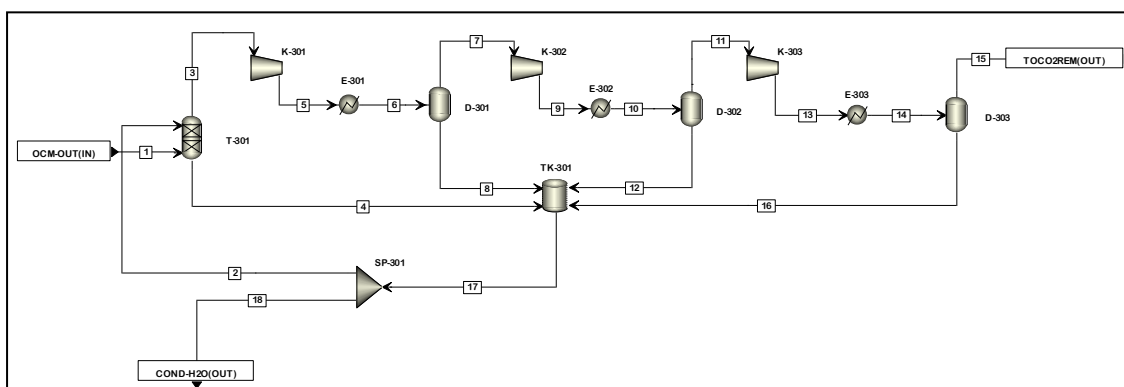
Figure 2.5: Diagram of the gas compression section

Tower internals are Sulzer Mellapack-plus structured packing 252Y and the section packing height is 5 m. The cooled gases coming from the quench tower, (T-301), at 79 °C saturated with water are compressed in a multi-stage compressor up to 10.1 bars, where near the 98.4% of the water in the OCM gases are removed by condensation and later cooled down to 40 °C. The compression is carried out by 3 stages compressor with inter-stage coolers that lower the OCM gas temperature to 90 °C using a mixture of C_2H_4-CH_4 as refrigerant. Figure 2.5 shows the schematic of this process.

2.1.4 Amine Treatment

The cooled gases at 40 °C and 10.09 bars are introduced into the bottom stages of a series of three (3) consecutive absorber columns, (T-401, T-402 and T-403), using Monoethanolamine (MEA) 15% wt at 40 °C as absorbent solution. The maximum strength of the chemical solvent (MEA) is limited to 30% wt due to corrosion restrictions. The design characteristics of the base case absorber and stripper are summarized in Table 2.3. The MEA solvent is then regenerated in a two (2) parallel stripping columns, (T-404 and T-405), thereby releasing a steam diluted CO_2 product. Amine scrubbing applied to CO_2 capture has been studied by several groups [11-14]. The simulation model consists of an absorber and a stripper using rate-based calculation. The operation data from a pilot plant at TU-Berlin were used to specify feed conditions and unit operation block specifications in the model. Thermo-physical property models and reaction kinetic models are based on the works of Aspen Technology [15].

Table 2.3: Design Characteristics of the Absorbers and the Strippers

	Absorber T-401	Absorber T-402	Absorber T-403	Strippers (T-404 & T-405)
Column Diameter (m)	5.3	4.3	3.6	6.5
Packing Height (m)	4.75	4.75	2.70	10.45
Structured Packing Type	Sulzer MellapackPlus	Sulzer MellapackPlus	Sulzer MellapackPlus	Sulzer MellapackPlus
Average HETP (m)	0.1227	0.1404	0.3000	0.1969
Packing Liquid Holdup (m^3)	0.5578	0.3172	0.2164	1.2066
Column Pressure drop (kPa)	0.3524	0.4537	0.3807	1.2029
Condenser Duty (kW)	---	---	---	-37046.8
Reboiler Duty (kW)	---	---	---	67699.2
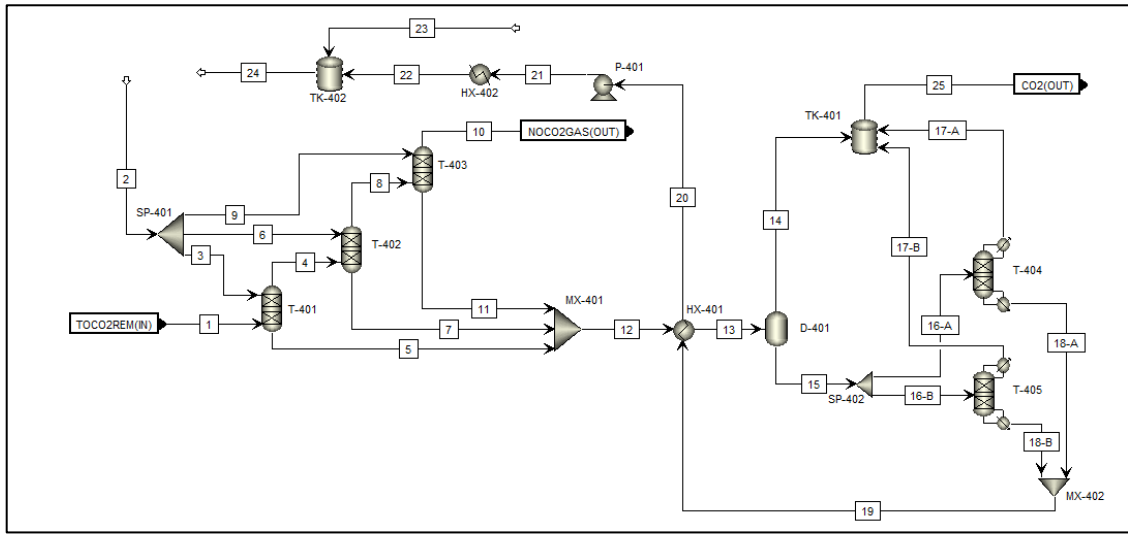
Figure 2.6: Diagram of the CO$_2$ removal treatment process

The Aspen Rate-Based MEA model provides a rate-based rigorous simulation of the process. Key features of this rigorous simulation include electrolyte thermodynamics and solution chemistry, reaction kinetics for the liquid phase reactions, rigorous transport property modeling, rate-based multi-stage simulation with Aspen Rate-Based Distillation which incorporates heat and mass transfer correlations accounting for columns specifics and hydraulics. The model is meant to be used as a guide for modeling the CO$_2$ capture process with MEA. Equilibrium and transport property models and model parameters have been validated against experimental data from open literature [16-17]. Figure 2.6 shows the diagram for this amine treatment process.

2.1.5 Ethylene Separation

After removing all CO$_2$ produced in the reactor, gas stream needs to be further released of all its water content and goes to the separation section of the plant. First the CO$_2$ free OCM gases are compressed to 35.129 bars in order to avoid hydrate formation when the columns are operated at very low temperatures [18]. This pressure also allows easy separation of C$_2$H$_4$/C$_2$H$_6$ as shown in Figure 2.7.

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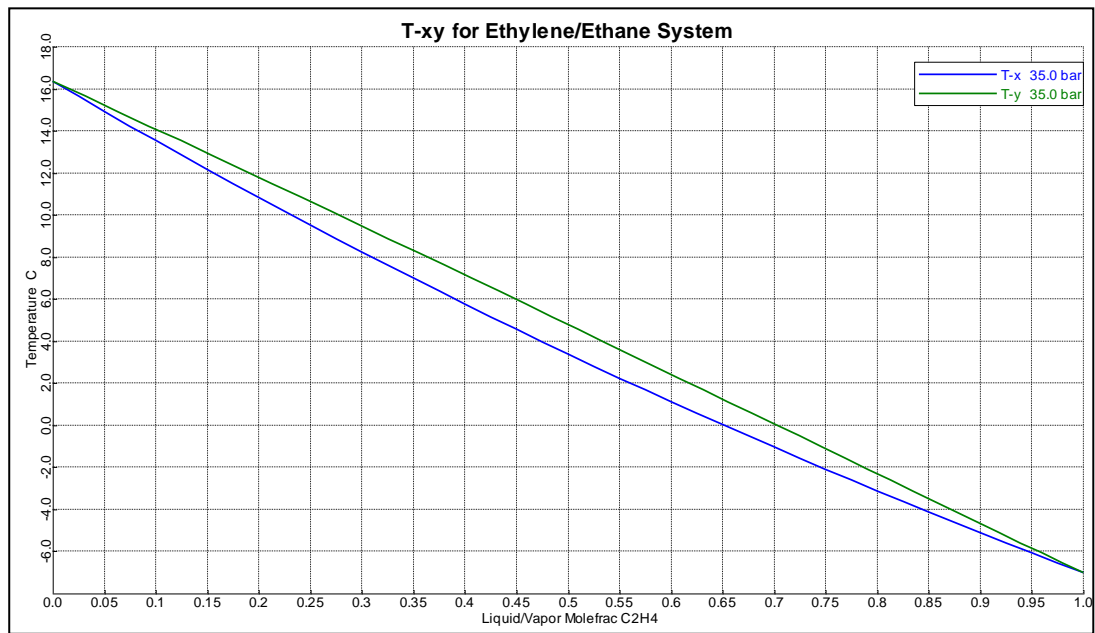
Figure 2.7: Two phase equilibrium temperature for the C_2H_4/C_2H_6 system

Schematic of this separation section of the OCM process is shown in Figure 2.8.
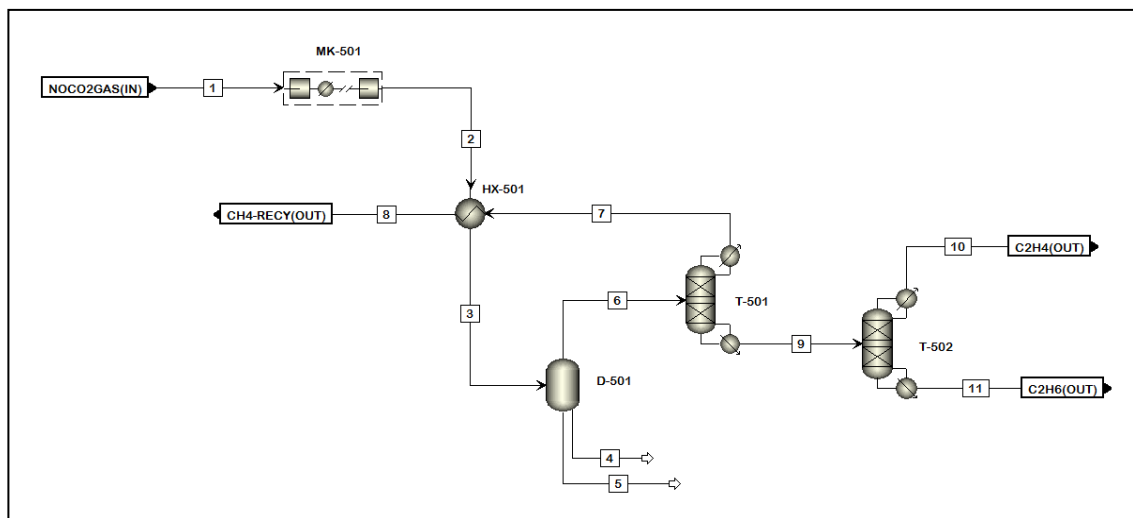
Figure 2.8: Diagram of the ethylene separation process

The compression system consists of a multistage compressor, (MK-501), with inter-stage cooling which decrease gas temperature to 90 °C. After pressurization the final step for water removal is lowering the gas temperature to -40 °C, using the gas-gas heat exchanger HX-501, and then the water separation occurs in the flash drum D-

501. Water free gases go then to its final separation in the two cryogenic distillation columns. The first column (T-501) is the demethanizer and the CH_4, CO and H_2 is separated from the ethylene-ethane stream. The bottom stream consists of ethane and ethylene that is separated in the deethanizer (T-502). Columns details are given in Table 2.4.

In order to compare the ethylene production performance of this OCM process the C_2H_4 produced in the OCM reactor is equivalent to a 408.84 t/d and with this design, the pure ethylene final production rate is 403.2 t/d with 99.8% molar purity. This value is equivalent to an annual production of 131315 tons, which means that for every ton of methane that enters the reactor 0.155 ton of ethylene is produced. Ethylene loses from reactor production to final purification is 5.64 t/d.

Table 2.4: Columns design results

	Column T-501	Column T-502
No. Stages	36	74
Column Diameter (m)	5.5	3.4
Structured Packing Type	Sulzer MellapackPlus	Sulzer MellapackPlus
Packing Section Height (m)	10.00	10.65
Top Stage Temperature (°C)	-106.9	-8.5
Top Stage Pressure (bar)	35.0	33.8
Bottom Stage Temperature (°C)	-5.9	14.8
Condenser Duty (kW)	-7556.93	-10369.49
Reboiler Duty (kW)	3235.22	11420.34

2.2 Energy savings for ethylene separation: Feed-Splitting Concept

Separation of ethylene from light gas mixture is one of the most energy intensive separations in petrochemical processes, which uses distillation columns up to 100 m tall and containing over 100 trays, but it is also energy-intensive due to the similar volatilities of ethane and ethylene and very large reflux ratios and also due to the need for sub-ambient temperatures. Traditional cryogenic distillation is both effective and reliable, and remains the dominant technology used to separate ethylene from ethane; however, many alternative separations have been investigated, including extractive distillation, chemical and physical sorption, and membrane-based separations [19]. Copper (I) and Silver (I) form electron donor/acceptor complexes with olefins, and several chemical systems have been designed using these transition metals as selective separation agents [20,21]. Short reviews of each of these technologies are shown below [22]:

a) <u>Extractive Distillation</u>. On the basis of results from computer simulations, the study concludes that extractive distillation offers no advantage over traditional distillation for the hypothetical solvents studied. Solvents could be found which can be economically utilized for the olefin/paraffin separation.

b) <u>Physical Adsorption</u>. The use of molecular sieves to perform olefin/paraffin separations has been investigated by numerous researchers. An economic comparison indicated that the energy costs were lower, but capital costs were higher, than a comparable distillation process.

c) <u>Chemical Adsorption</u>. The bases for chemisorptions of an olefin by a metal complex, usually copper and silver ions, are the core of this technology. Regeneration is accomplished by pressure swing. For large plant production in a commercial scale, the use of silver ions are simply unaffordable and a very expensive solution.

d) <u>Physical & Chemical Absorption</u>. This technology uses Silver- or Copper-based absorption processes and offer potential for olefin recovery. A combination of pressure reduction and thermal swing is used to regenerate the complexing agent. Significant feed pretreatment is required to remove feed contaminants, such as H_2S and CO_2, which will interfere with the complex formation or destroy the complexing agent.

e) <u>Membrane Separation</u>. The use of metal-based facilitated transport membranes has been studied for a variety of olefin/paraffin separations. This technology has the inconvenience of not accounting for the decrease in membrane productivity.

All technologies mentioned above have negatively impacted their acceptance to be applied in the natural gas and petrochemical industry. The unpredictable nature of the separations unit feedstock impacts the use of new olefin/paraffin technologies. Technologies, such as metal-based absorption, which are susceptible to deactivation by feed contaminants may not be acceptable for applications where tight control of the feed composition is not possible. The addition of feed pretreatment steps negatively impacts the process economics and may make the new technology impractical.

An absorption process with aqueous $AgNO_3$ solvent has been employed instead of conventional ''cold- box'' technology because of costs. The $AgNO_3$ process was developed in the 1990´s as a membrane absorption concept, but was commercialized with a conventional absorption column. However in this application hydrogen in the feed gas may cause precipitation of silver, and more development may be required to overcome this problem. An adsorption process might be an alternative, but with current adsorbents, separation factors between ethylene and other gases are not high enough to achieve the deep removal of ethylene and

relatively high ethylene purity aimed at in this application. Polymer membranes are commercially available for ethylene recovery from various purge streams that occur in polyethylene plants and development is continuing with membranes for ethylene/ethane separation. However it is doubtful whether polymer membranes will ever have a high enough selectivity to go beyond bulk removal applications [19, 20]. To date, none of these approaches has proven to be a practical alternative to cryodistillation.

The data shown in Table 2.4 present high energy values used in the T-502 column for the separation of ethylene. For this reason a new proposal has been done to reduce the amount of energy required by the condenser in the ethylene-ethane column by partially pre-cooling the feed(s) by the distillate, using a scheme similar to that employed for warm columns. In distillation columns it is essential to minimize the expensive energy requirements of the refrigeration cycle that produces the tower reflux. Typically, more than half of the process heat distributed to plant operations ends up in the reboilers of distillation columns. By this, high-level energy is fed at the base of the column and about the same amount of energy is released at the top, unfortunately at a much lower temperature level. The difference between the two Gibbs energies can be seen as the necessary energy investment to reverse the mixing entropy and to separate the components of a given feed by a distillation process [23]. To find a solution to this problem some researchers have proposed alternatives focused on the feed-splitting concept [24].

In the conventional distillation operation for ethylene-ethane separation, as typified in Figure 2.9, low-temperature distillation column has been the preferred technology for several decades. However, this binary separation process consumes about 36 percent of the refrigeration energy required in, for example, an ethylene plant [25]. The C_2 splitter is commonly operated at high-pressure, utilizing closed-cycle propylene refrigeration, which is incorporated with the refrigeration systems serving other parts of the plant. The desired objectives for any ethylene separation

process are to obtain a high-purity ethylene product combined with a high percentage recovery of the ethylene. The conventional distillation technology can accomplish both of these objectives. The main goal of this study is to reduce the amount of energy required by the reboiler in the ethylene-ethane column by partially pre-cooling the feed(s) by the distillate, using a scheme similar to that employed for warm columns.
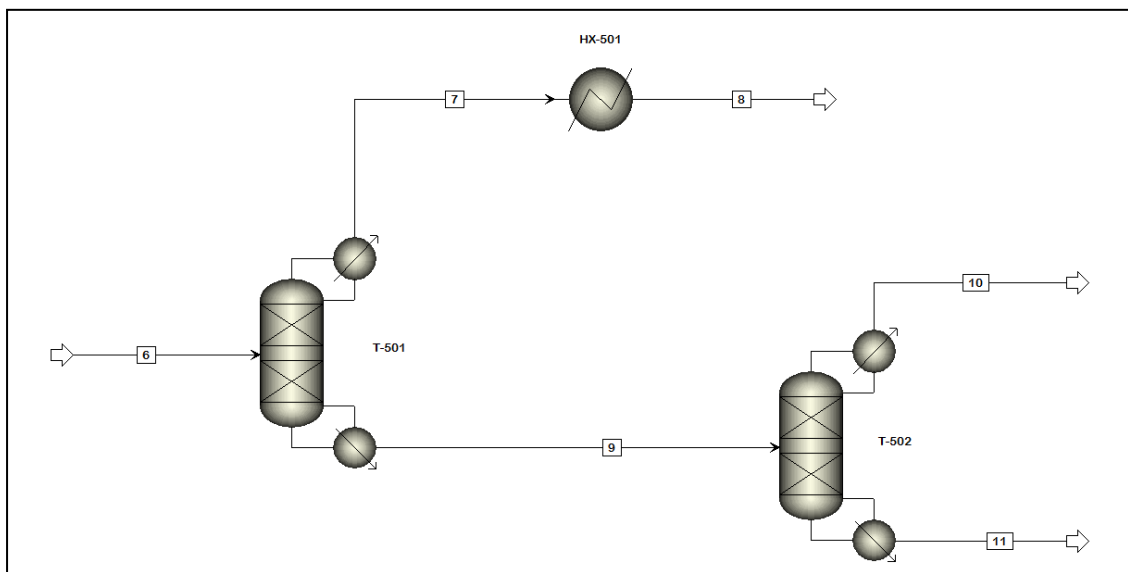
Figure 2.9: Conventional ethylene separation system

The heat requirement Q of a single rectification column can be minimized best by effective heat exchange between the warm products and the cold feed, and also by efficient insulation of the column. Furthermore, the operational reflux ratio R should be kept as small as possible; optimum ratios are in the range of $R = 1.05 - 1.1 \, R_{min}$ [26]. Soave [24] has shown that in a cold tower, if the enthalpy of the feed is decreased by pre-cooling with the distillate, the final result is a decrease in the condenser and reboiler duties; his study was applied to a demethanizer column of a "cold box" of an ethylene plant. In the present work the feed-splitting principle to an ethylene-ethane distillation tower is applied, using the steady-state Aspen Plus® simulation tool for the calculation and study of this ethylene column.

2.2.1 Simulation models

The first simulation model has the same schematic shown in Figure 2.9. The data on the feed to the demethanizer column are reported in Table 2.5. Starting point is the outlet stream of the flash drum D-501, from the ethylene separation section of the OCM process, in which all the CO_2 and H_2O contents of are removed, introduced in a demethanizer tower to remove all of its CH_4 content, along with H_2 and CO, before entering to the ethylene-ethane fractionating column. Both columns were modeled using rate-based calculations. With this approach, mass and heat transfer between the phases flowing one to the other is assumed, based on the two-film theory (AspenONE Process Engineering webinar, 2008). With this program the standard specifications for the rating mode are reflux ratio and distillate flow rate, among other choices. This Aspen Plus® column model, named *RadFrac* in its rate-based calculation type, offer considerable flexibility in user specifications [27]. For the columns internals Sulzer MellapakPlus 752Y structured packing shows better performance in case of circulating the flow rate rather than random packing [28], and also this type of packaging is suggested by the Sulzer Company for petrochemical processes [29] and was used in the simulation. Three alternative solutions of feed configurations are studied, and each one has to guarantee a distillate with at least 98% weight of ethylene.

To be consistent in the base case comparison with the alternatives to be studied, all three ethylene-ethane column topologies shown later are run with the same tray section (72 theoretical stages) and at the same operating pressure (33.8 bars). Just the feed location varies from case to case. In order to reduce the condenser and reboiler duty different solutions of feed configuration to the ethylene-ethane column were proposed for improving its performance with the feed-splitting technique.

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Table 2.5: Demethanizer column feed

Property	Value	Flow rate (kg/hr)	
T (°C)	-50.000	H_2	2929.519
P (bar)	35.100	CO	5232.119
F (kg/hr)	85413.164	CH_4	59160.501
		C_2H_4	17005.404
		C_2H_6	1066.089
		CO_2	19.496
		H_2O	0.036

2.2.1.1 Alternative 1

In this alternative (Figure 2.10) the feed is first split into two phases. The vapor phase is pre-cooled with the cool stream from the condenser, and a warmer distillate is obtained. The liquid phase is fed directly to the column. For both phases, liquid and vapor, feed tray position in the column was chosen carefully based on a sensitivity analysis to get the maximum mass fraction recovery of C_2H_4 at the top of the column. The feed temperature to the ethylene-ethane column decreased, the minimum reflux ratio and the condenser duty also decreases.
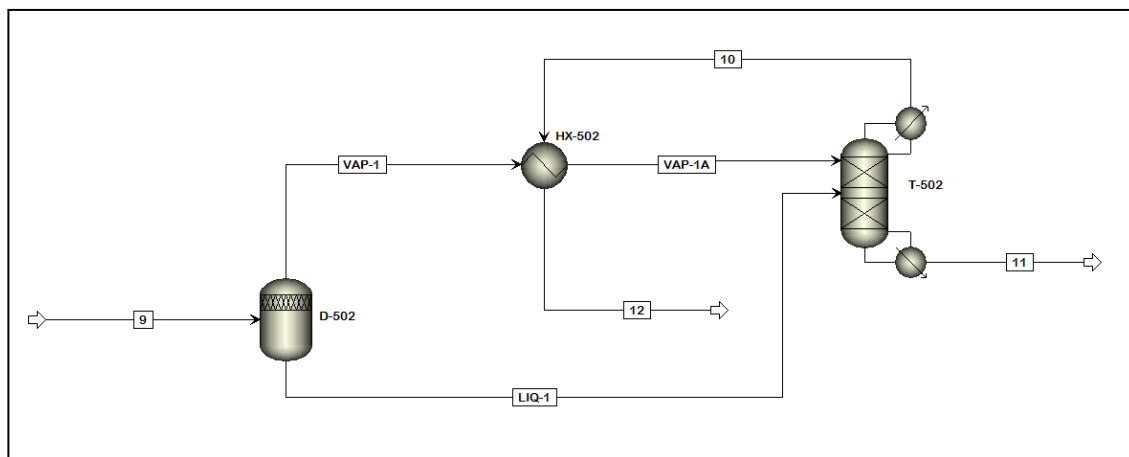
Figure 2.10: Alternative 1 for the ethylene-ethane column

2.2.1.2   Alternative 2

In this alternative, shown in Figure 2.11, part of the feed to the ethylene-ethane column is flashed, at constant pressure lowering its temperature, and consequently vaporizing certain amount of the stream. The vapor phase goes to the heat exchanger, decreasing its temperature a little more, and then is adiabatically flashed again to generate a second liquid stream which feeds the column T-502. Again, as in alternative 1, a sensitivity analysis was performed to choose all the feeds streams trays to the column based on the minimum condenser and reboiler duties.
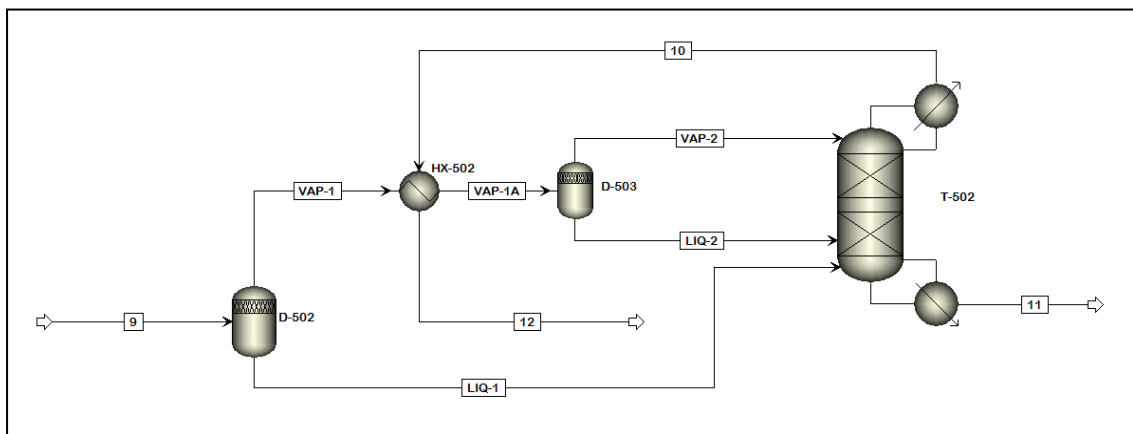
Figure 2.11: Alternative 2 for the ethylene-ethane column

2.2.1.3 Alternative 3

In the last alternative (Figure 2.12) only a fraction of the vapor phase is pre-cooled. This fraction has to be determined by sensitivity analysis, making sure to maintain the quality specifications of the desired ethylene product at the top of this column.
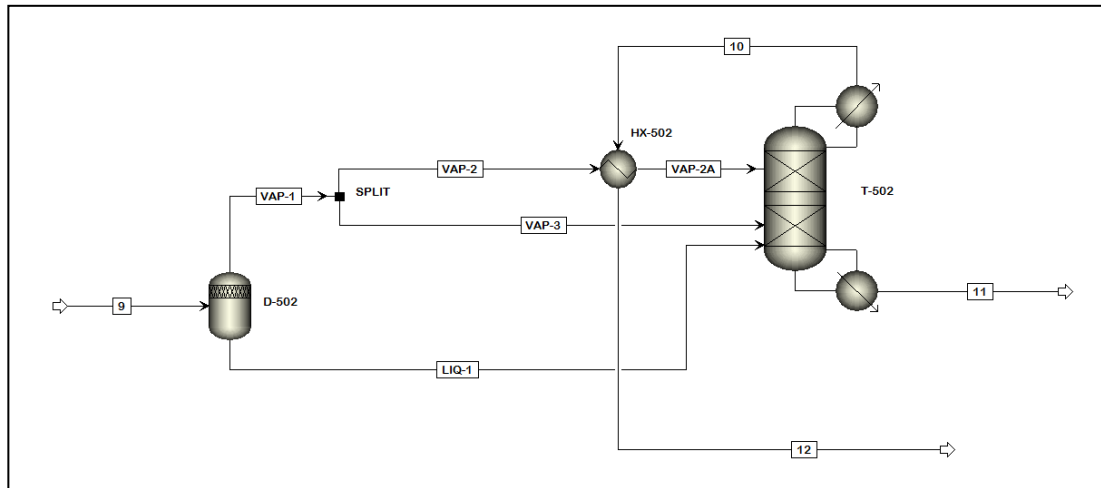
Figure 2.12: Alternative 3 for the Ethylene-Ethane Column

In all three cases the liquid phase obtained from the first flash is fed directly to the column, taking into account that this phase has a flow rate that is too low for good heat-exchange performance with the distillate. Also with these three studied configurations it was necessary to find the best feed trays. This can be done by changing the position of each feed stream one at a time. For all the simulations the hot/cold outlet temperature approach, in the pre-cooler (HX-502), was also kept constant. Also the flash drum D-502 conditions were kept constant in all three cases studied.

2.2.2 Results and Discussions

To properly evaluate the simulation results the comparisons were made with the conventional separation ethylene-ethane column (T-502 from Figure 2.9). In the Table 2.6 is shown the duty values for condenser, reboiler, and flow rate of ethylene

at the top of this column. Table 2.7 shows the ethylene recovery results for all the four cases studied. Comparing the conventional and the alternative 1 case, there is a substantial decrease in the condenser and reboiler duties, around 25% for condenser and 26.5% for reboiler respectively; while at the same time the C_2H_4 product slightly decreases just 0.076%.

Table 2.6: Ethylene-Ethane Column Results

Case Studied	Heat Duty (kW)		Ethylene Flow (kg/h)
	Condenser	Reboiler	Stream 10
Conventional	-10371.53	11422.25	16785.61
Alternative 1	-7779.55	8390.19	16772.77
Alternative 2	-7671.37	8280.34	16774.51
Alternative 3	-8693.52	8592.75	16786.52

Further improvements, alternative 2, lead to a small decrease in condenser duty (108 kW less) and practically the same decrease in the reboiler duty (around 110 kW less), simultaneously maintaining the same amount of ethylene at the top of the tower. Alternative 3 raises again the condenser and reboiler duties, keeping the ethylene recovery at the same amount that in the conventional case.

Table 2.7: Ethylene Recovery Results

Case Studied	Ethylene Flow (kg/h)		Recovery
	Total		
	Column Feed	Top	(mass %)
Conventional	16801.14	16785.61	99.91
Alternative 1	16801.14	16772.77	99.83
Alternative 2	16801.14	16774.51	99.84
Alternative 3	16801.14	16786.52	99.91

In order to verify the feasibility of implementing the proposed solutions an economic study of the costs associated with each of the alternatives studied was performed. The low ethylene concentrations in the product stream lead to high separation cost. Cryogenic distillation has been considered for separation, operating

around -110 °C and pressures of 35 bars. This implies a large temperature difference between oxidative coupling and separation [29, 30].

Distillation columns to separate H_2, CH_4, C_2H_4 and C_2H_6 are the most expensive and intensive units in ethylene plants, because the distillation requires high energy consumption, increased refrigeration capacity and a large number of stages, all of which increase both the capital and production costs.

Figure 2.13 shows the results of the costs associated with implementing each one of the alternatives studied in this work and compared with the classic separation of ethylene, the base case (conventional separation).
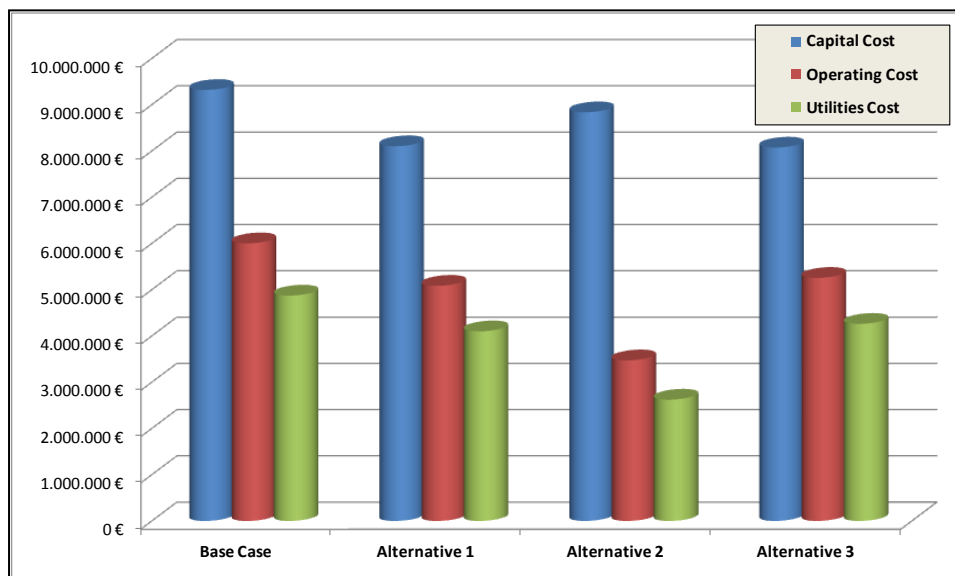
Figure 2.13: Economic analysis results

Capital and operating cost for the base case are the highest of all cases studied and also utilities cost. These three values decrease steadily with the application of the feed-splitting technique, alternatives 1 and 2, until they begin to increase with the implementation of alternative 3. The increase in the value for the capital cost in the alternative 2 can be explained because the increment in the equipment cost (adding the flash drum D-503). When applying the feed-splitting concept to the ethylene-

ethane column (T-502), condenser and reboiler duty decreases under the same operating conditions (pressure, number of theoretical stages of the column, internals type, feed flow rate and composition); as a result, operating and utilities cost also decreases. It can be observed that the condenser values decreases with each improved alternative, until a further splitting of the vapor phase can't be reached.
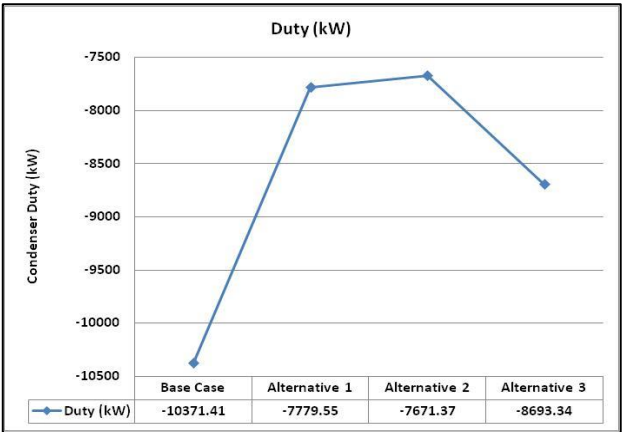
Figure 2.14: Condenser duty results for tower T-502
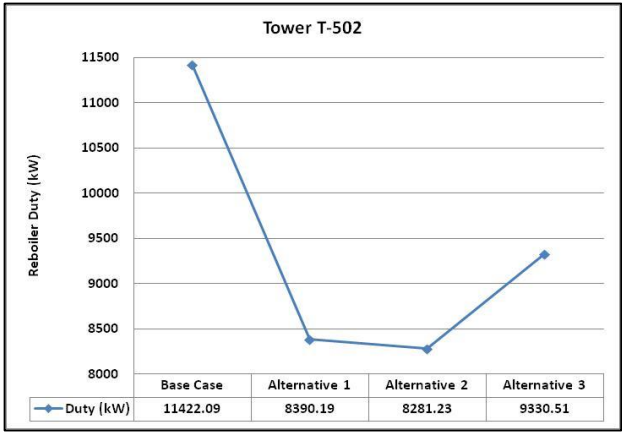
Figure 2.15: Reboiler duty results for tower T-502

Comparing the results shown in Table 2.6 we can see a slight improvement in the flow rate of ethylene product at the top of the column T-502, therefore, alternative 2 shows the best performance in case operating cost thus obtaining both the

recovery and the desired purity of the ethylene product. Further ethylene recovery can be achieved, with implementation of alternative 3, but with higher operational and utilities cost.
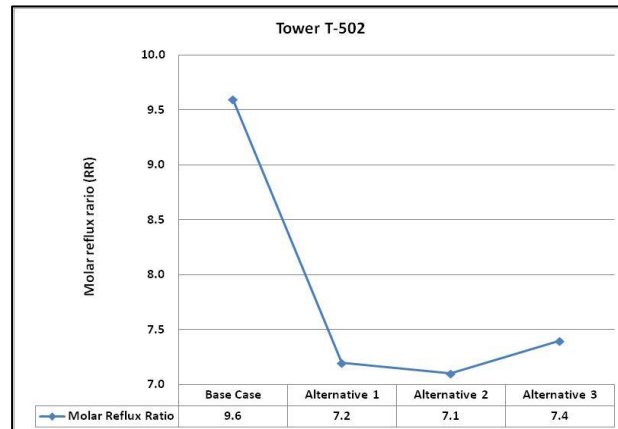
Figure 2.16: Reflux ratio results for tower T-502

For each alternative studied in this work Figures 2.12, 2.13 and 2.14 shows the impact on reducing the heat of the condenser, reboiler and the reflux ratio.

2.2.3 Conclusions

The goal of significantly reducing the heat duty required by the condenser has been achieved by 26% and simultaneously has been reduced the amount of heat duty required by the reboiler (27.5%).

If the flow to the HX-502 heat exchanger is not divided, there will be an increase of the ethylene recovery at the top of the T-502 tower.

With this feed-splitting concept 99.8% of the initially ethylene can be recovered. Considering the data reported in Table 2.4, the advantages of applying the feed-splitting concept in a pilot plant is highly profitable, in order to save as much energy as possible and reduce the expenses, in 5 million €/year (almost 26%), in the

amount of refrigerant used in the condenser thus achieving optimize resources, both energetic and financial.

The sensitivity analysis and the corresponding simulations results show the efficiency of the presented approach. It is possible to further lower the energy consumption by looking for the best location of the feed trays and also reducing the reflux ratio.

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Chapter 3:
Economic Evaluation of Chemical Projects

Methane conversion processes are capital intensive. The relative economics of different process schemes is therefore expected to be more affected by differences in total capital cost than in feedstock cost and other operating costs. Numerous process schemes have been proposed for converting methane to liquid hydrocarbon fuels. Economic evaluation studies generally conclude that none except the best of these schemes are attractive at oil prices below 20 US$/Bbl [1]. With actual oil prices over 100 US$/Bbl any process that uses methane as a raw material needs to be evaluated in economic terms and not only in its technical feasibility.

Most chemical engineering design projects are carried out to provide information from which estimates of capital and operating costs can be made. Chemical plants are built to make a profit, and an estimate of the investment required and the cost of production is needed before the profitability of a project can be assessed. Cost estimation is a specialized subject and a profession in its own right, but the design engineer must be able to make rough cost estimates to decide between project alternatives and optimize the design [2].

Process economics is required to evaluate design options, carry out process optimization and evaluate overall project profitability [3]. Two simple criteria can be used:

a) economic potential

b) total annual cost

These criteria can be used at various stages in the design without a complete picture of the process. The dominant operating cost is usually raw materials. However,

other significant operating costs involve catalysts and chemicals consumed other than raw materials, utility costs, labor costs and maintenance. To understand the scope of proper economic evaluation is necessary to know the terms that are used in the analysis of costs of any project. That's why this chapter is devoted to reviewing the terms most frequently used in the cost analysis of a chemical process. The following concepts are taken from Towler and Sinnott [2]:

Fixed Capital Investment: The fixed capital investment is the total cost of designing, constructing, and installing a plant and the associated modifications needed to prepare the plant site. The fixed capital investment is made up of:

a)   The inside battery limits (ISBL) investment, the cost of the plant itself. The ISBL plant cost includes the cost of procuring and installing all the process equipment that makes up the new plant.

b)   The modifications and improvements that must be made to the site infrastructure, known as offsite or offsite battery limit investment (OSBL). OSBL investment includes the costs of the additions that must be made to the site infrastructure to accommodate adding a new plant or increasing the capacity of an existing plant. Offsite investments often involve interactions with utility companies such as electricity or water suppliers. For typical petrochemical projects, offsite costs are usually between 20% and 50% of ISBL cost, and 40% is usually used as an initial estimate if no details of the site are known.

c)   Engineering and construction costs. The engineering costs, sometimes referred to as home office costs or contractor charges, include the costs of detailed design and other engineering services required to carry out the project. A rule of thumb for engineering costs is 30% of ISBL plus OSBL cost for smaller projects and 10% of ISBL plus OSBL cost for larger projects.

d)   Contingency charges. Contingency charges are extra costs added into the project budget to allow for variation from the cost estimate. A minimum contingency charge of 10% of ISBL plus OSBL cost should be used on all projects.

Working Capital: Working capital is the additional money needed, above what it cost to build the plant, to start the plant up and run it until it starts earning income. Working capital can vary from as low as 5% of the fixed capital for a simple, single product process, with little or no finished product storage, to as high as 30% for a process producing a diverse range of product grades for a sophisticated market, such as synthetic fibers. A typical figure for petrochemical plants is 15% of the fixed capital (ISBL plus OSBL cost).

Variable Costs of Production: Variable costs of production are costs that are proportional to the plant output or operation rate. Variable costs can usually be reduced by more efficient design or operation of the plant.

Fixed Costs of Production: Fixed production costs are costs that are incurred regardless of the plant operation rate or output. If the plant cuts back its production, these costs are not reduced. Fixed costs should never be neglected, even in the earliest stages of design, as they can have a significant impact on project economics.

Revenues: The revenues for a project are the incomes earned from sales of main products and byproducts. The production rate of main product is usually specified in the design basis and is determined based on predictions of overall market growth. Determine the type of products we want to recover, purify and sell is usually more difficult than find out the main product. Some byproducts are produced by the main reaction stoichiometry and are unavoidable unless new chemistry can be found. These stoichiometric byproducts must usually be sold for whatever price they can get; otherwise, waste disposal costs will be excessive. Other byproducts are produced from feed impurities or by nonselective reactions. The decision to recover, purify, and sell; recycle or otherwise attenuate; or dispose of them as wastes is an important design optimization problem.

Margins: The sum of product and byproduct revenues minus raw material costs is known as the gross margin. This concept is very useful because raw materials costs are almost always responsible for the value of production costs, typically 80% to 90% of the total production costs. Prices of raw materials and commodities are generally very difficult to predict, due to daily price fluctuations that they suffer in the stock market where are traded worldwide. However, profit margins are less susceptible to alterations as producers move these prices to their customers. For commodities such as bulk petrochemicals and fuels margins are typically very low, less than 10% of revenues.

Profits: The gross profit is defined as the main product revenues minus the cash cost of production (CCOP). This CCOP is the cost of making products, not including any return on the equity capital invested. The CCOP is the sum of the fixed and variable production costs. Gross profit includes all the other variable costs in addition to raw materials, and also includes fixed costs and byproduct revenues.

The profit made by the plant is usually subject to taxation. Different tax codes apply in different countries and locations, and the taxable income may not be the full gross profit. The net profit (or cash flow after tax) is the amount left after taxes are paid:

$$\text{Net profit } = \text{ gross profit } - \text{ taxes} \qquad (3.1)$$

Depreciation: The value of a plant and equipment decreases as it gets older because it gradually wears out and because it turns obsolete. Also the process becomes less efficient and there are new technologies that surpass in many ways a part or the entire production process, such as improvements in control strategies and automation of some plant sections.

Since 1986 in the United States there have been changes in the tax law that specifies the use of two depreciation methods [4]:

a) Straight-Line: this method is the simplest and allows for a uniform amount to be deducted from revenues each year and is used most commonly. In this method, the Salvage Value is subtracted from the Total Project Cost. This result is then divided by the Economic Life of Project, so that the project is depreciated evenly over its economic life.

b) Modified Accelerated Cost Recovery System (MACRS): this method is a combination of the declining balance and the straight-line methods of calculating the depreciation. The MACRS approach assumes that operations begin during the second half of the first period and stop during the first half of the last period. Therefore, as a result of the two half periods (one at the beginning and one at the end of the operating cycle), it takes 6 periods to depreciate a project which has an Economic Life of 5 periods. The depreciation rate for the first period, D1, is 2/N, where N is the Economic Life of Project. However, the half-life convention reduces this factor to 1/N. For the second period the depreciation rate, D2, is D1 (1-1/ N). For the third period the depreciation rate, D3, is D1 (1-1/N-D2). This process (multiplying the factor by the Total Project Cost continues until the Straight Line Method produces a higher value for the depreciation. When the Straight Line Method produces a higher value, this higher value is used for the remaining depreciation calculations.

3.1   Computer Tools for Cost Estimation

It is difficult for engineers outside of Engineering, Procurement and Construction (EPC) sector to collect recent cost data from a large set of real projects and maintain accurate and up-to-date cost correlations. Instead, the most common method for making preliminary estimates in industry is to use commercial cost-estimating software. Several companies around the world use commercial software

to predict costs and make economic analysis process. The discussion in this chapter will focus on Aspen Process Economic Analyzer software, as this is probably the most widely used program and is the one with which the author is most familiar. This software is made available as part of the standard Aspen/Hysys academic license and so is available in any university that licenses Aspen Technology products. It is also available in most chemical companies, among them are: Linde Group, Fluor, Petrobras, PDVSA, ConocoPhillips, BASF, Wacker Chemie AG ([1]), Shell and many others related to the petrochemical and natural gas industry.

The Aspen Economic Evaluation product family enables companies to rapidly and confidently evaluate capital investment projects early in the design process, to understand the economic implications of engineering decisions, and to effectively manage the project. The Aspen Economic Evaluation product family combines the industry's most comprehensive costing with rigorous engineering and construction models to generate highly accurate cost estimates. Companies deploying these solutions are able to reduce capital and operating costs, increase engineering efficiency and quality, and accelerate time-to-market with faster payback [5]. Aspen Process Economic Analyzer is designed to automate the preparation of detailed designs, estimates, investment analysis and schedules from minimum scope definition, whether from process simulation results or sized equipment lists. It lets you evaluate the financial viability of process design concepts in minutes, so that you can get early, detailed answers to the important questions of "How much?", "How long?" and, most importantly, "Why?".

The Aspen Process Economic Analyzer cost-estimating tools are simple to use and give quick, defensible estimates without requiring a lot of design data. Design information can be uploaded from any of the major flowsheet simulation programs, or else entered manually in the Aspen Process Economic Analyzer program. The program allows the design to be updated as more information on design details

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[1] Personal conversation with Frederic Gobin, Bussiness Consulting Director AspenTech Europe SA/NV.

becomes available so that a more accurate estimate can be developed. Costs can be estimated for a whole plant or for one piece of equipment at a time. Over 250 types of equipment are included, and they can be designed in a broad range of materials, including United States, United Kingdom, German, and Japanese standard alloys. The Aspen Process Economic Analyzer software uses a combination of mathematical models and expert systems to develop cost estimates. Costs are based on the materials and labor required (following the practice used for detailed estimates) rather than installation factors. If design parameters are not specified by the user, then they are calculated or set to default values by the program. The user should always review the design details carefully to make sure that the default values make sense for the application. If any values are not acceptable, they can be manually adjusted and a more realistic estimate can be generated. The technology does not rely on capacity-factored curves for equipment pricing, nor does it rely on factors to estimate installation quantities and installed cost from bare equipment. It follows a unique approach where equipment, with associated plant bulks, is represented by comprehensive design-based installation models. Project teams are able to reach faster, more accurate decisions based on consistent technical and economic information. Academic authors usually do not have access to sufficient high quality cost data to be able to make reliable correlations, and most of the academic correlations predict lower costs than would be obtained using Aspen Process Economic Analyzer program or other detailed estimating methods. These correlations are adequate for the purposes of university design projects but should not be used in real projects. It is for this reason that one should use the results obtained with commercial software, in its latest version, in order to obtain better accuracy calculating plant cost estimations.

3.2   Oil Refinery Economic Evaluation Example

In order to explain the calculation procedure for the Aspen Process Economic Analyzer program, a typical refinery process was selected. This was done because, as explained in Chapter 1, several OCM processes schemes uses oligomerization reaction to transform ethylene to fuels (Suzuki and OXCO) or hydrocarbons to gasoline (ARCO and Mobil), and thus it can be performed more efficiently comparisons of these processes that are intended for the production of fuels using the ethylene from the OCM reaction.

When liquid transportation fuels are the desired product, the methane conversion routes need to be evaluated against the conventional fuel manufacturing route, for example, petroleum refining. It is now well known that in this year 2012 crude oil costs and taxes are still bigger influences than refinery production and product exports in gasoline price increases. Medium-sized refinery complexes with production capacities of the order of 100,000 barrels per day (Bbl/d) require some US\$ 500×10^6 - 1000×10^6 investment [1]. Using the Nelson-Farrar cost indexes these costs in 2011 Euros are equivalent to 783×10^6 - 1566×10^6 €. The 1996 Lang and Tijm economic study [1], was based on 20% capital charge that corresponds to a capital cost in the range of 3-6 \$/Bbl of product, a modest amount compared to the feedstock cost of 17-22 \$/Bbl of product which was typical of that year. This cost was based on crude oil prices in the range of 15-20 \$/Bbl (year 1996) and a conversion efficiency of some 90% carbon. Methane conversion plants show a much higher capital cost than feedstock cost alone, however. At natural gas cost of 0.5 \$/GJ (year 1996) and conversion efficiency of 80% carbon, the feedstock cost of gas conversion plants amounts to approximately 4 \$/Bbl of product whereas the required capital cost of some processes has been reported to exceed this by large [6].

As with many commodity chemical processes, petroleum refineries have increased in scale considerably since the first ones were built in the early 20th century. Economies of scale have played a large part in defining the current make-up of petroleum refineries worldwide. Due in part to the expansion of distribution facilities, environmental regulations, and the removal of price controls in 1981, many of the very small scale (less than 10,000 barrels per day (BPD)) refineries have shut down since 1980. The total number of refineries has decreased from over 300 in 1980 to 144 in 2004 [7].

This chapter describes a feasibility study on the steady-state simulation of pre-flash, atmospheric and vacuum distillation unit columns in a typical crude oil refinery and it was performed using AspenTech simulation software. Steady-state simulation results obtained by Aspen plus were used to get the economic evaluation of the process. All the concepts of economic analysis of chemical processes explained earlier in this chapter were used in the displayed results of economic analysis.

3.2.1 Brief Process Description

The first step of any petroleum refinery is to feed crude oil into a distillation column to obtain the rough product cuts that will be further refined and blended downstream. Most initial distillation is done at atmospheric conditions. When feeding a heavy crude slate, bottoms from atmospheric distillation units are sometimes sent to a vacuum crude tower for further component separation. After this process comes the alkylation [8].

Alkylation. This process consists of the reaction of isobutane with a mixed light olefinic (usually C_3 and C_4) stream to produce a high octane gasoline blending component. The resulting product is usually blended to make premium, 90 to 93 octane, gasoline. This reaction occurs at cold temperatures and low pressures, using stirred sulfuric acid as a reaction catalyst.

Aromatics. In general, aromatics units tend to be pair with more complex refineries that have both reforming capacity and a strong market for aromatics

products (benzene, toluene, and xylenes). Large refineries that are paired with olefins plants also usually possess some sort of aromatics processing capacity. Raw feed from refinery reformers or heavy sections of olefins plants are sent to aromatics processing units for extraction. This is usually a physical conversion, which consists of solvents, zeolite adsorption, and distillation.

Fluidized Catalytic Cracking. A standard process in many refineries is the upgrading of gas oil to gasoline. FCC units have been present in refineries for over 50 years, and are considered a very mature technology. In this process, a fluidized catalyst reacts with an inlet gas oil stream at high pressure to produce a predominantly unsaturated product stream suitable for gasoline blending. The catalyst is separated from exit gases in a cyclone, regenerated in a separate reactor, and then reintroduced into the process reactor.

Hydrocracking. In this process, gas oil or distillate is converted to lighter, higher octane blending components in the presence of hydrogen. Unlike an FCC unit, the process occurs over a fixed bed at high pressure. Because of the presence of hydrogen in the reactor, the product produced is saturated, with different blending properties than FCC product.

Naphtha Reforming. Many straight-run pipe-still naphtha or condensates from natural gas liquid processing have low octane values due to the presence of paraffinic hydrocarbons. In order to increase the octane value and make the naphtha streams more suitable for blending, reformers are used. Reforming reactions usually occur at high temperatures over fixed-bed platinum catalysts. The product reformate is a branched, unsaturated hydrocarbon stream. Hydrogen is also produced in this reaction.

Desulphurization. Unless the crude slate is very sweet, most refinery gasoline and on-road distillate products require desulphurization to meet product specifications. This is a mature technology, using hydrogen and a fixed-bed catalyst to remove sulfur from the product stream.

3.2.2 Modeling Petroleum Processes

Petroleum refining processes are highly complex and integrated. They have unique characteristics that set them apart from other chemical processes, including:

• Process feedstock, which consist of complex and wide-boiling mixtures of hydrocarbons, whose exact compositions are unknown.

• Highly-coupled and heat-integrated fractionation units, used to separate feedstock into a variety of products with different specifications.

• Open steam and cooling water for stripping and heat recovery, giving rise to the presence of two liquid phases throughout the refining process.

• Degree of separation specified in terms of distillation temperatures, gaps, overlaps, and other properties.

• Product specifications given in terms of stream properties such as flash point, pour point, sulfur content, metal contents, and octane number.

The process consists of the following steps:

1. The process feed (MIXCRUDE), consisting of a blend of two crude oils (OIL-1 and OIL-2), goes to the pre-flash furnace.

2. The pre-flash tower (PREFLASH) removes light gases and some naphtha from the partially vaporized feed.

3. Pre-flash bottoms (CDU-FEED) are further processed in the crude distillation unit (CDU). The CDU consists of a crude unit furnace and an atmospheric tower. First, the crude unit furnace partially vaporizes the bottoms from the pre-flash. Then the atmospheric tower separates the pre-flash bottoms into five cuts:

Heavy Naphtha (HNAPHTHA)

Kerosene (KEROSENE)

Diesel (DIESEL)

Atmospheric gas oil (AGO)

Reduced crude (RED-CRD)

4. Reduced crude goes to the vacuum distillation unit (VDU) for further fractionation under vacuum conditions. The VDU consists of a vacuum unit furnace and vacuum tower. The vacuum tower produces the following additional cuts:

Overhead (OFF-GAS)

Light vacuum gas oil (LVGO)

Heavy vacuum gas oil (HVGO)

Asphaltic residue (RESIDUE)

Figure 3.1 shows the process flowsheet for this simulation. The process feed, consisting of Venezuelan oil blend [8], goes first to the pre-flash furnace where it is partially vaporized. The partially vaporized feed then enters the pre-flash tower. Steam feeds to the bottom of the tower. The tower produces wide naphtha cut as a distillate product. The tower has 10 theoretical stages, no reboiler, and a partial condenser. The condenser operates at 170 °F and 39.7 psia, with a pressure drop of 2 psi. The tower pressure drop is 3 psi. The tower is stripped with open steam in the bottom. The steam stream is at 400 °F and 60 psia, and has a flow rate of 5000 lb/hr. The furnace operates at a pressure of 50 psia and a temperature of 450 °F. The distillate rate is estimated at 27750 Bbl/day. Its value is manipulated to produce wide naphtha cut with an ASTM 95% temperature of 375 °F.

The topped crude from the pre-flash tower goes first to the crude furnace, then to the atmospheric tower. The tower has:

• A total condenser.

• Three coupled side strippers.
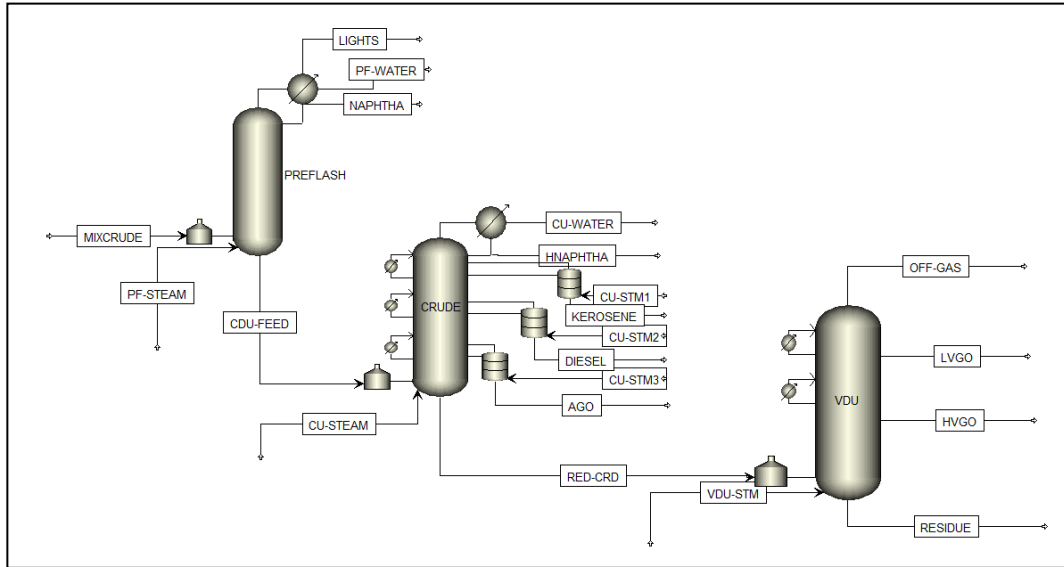
• Two pumparound circuits.

Figure 3.1: Crude Fractionation Train Schematics

The furnace operates at a pressure of 24.18 psia and provides an overflash of 3% in the tower. The furnace outlet enters the atmospheric tower on stage 22 of the main fractionator. The main fractionator is modeled with 25 equilibrium stages. The heavy naphtha product flow is estimated at 24000 Bbl/day, and is manipulated to achieve an ASTM 95% temperature of 375 °F. The condenser operates at 15.7 psia with a pressure drop of 5 psi. The tower pressure drop is 4 psi. The main fractionator has 2 pumparound circuits.

Finally the last equipment is the simulation of the vacuum tower. The vacuum tower has no condenser or reboiler. Stripping steam is fed to the bottom of the tower in stream VDU-STM at 400 °F, 60 psia, and 20000 lb/hr. The furnace operates at a pressure of 2.03 psia, and provides an overflash of 0.6%. The overflash is bypassed to the tower furnace. The tower has two pumparound circuits. The duty for the first pumparound is adjusted so that the top of the tower is at 150 °F. The tower has six equilibrium stages. The light vacuum gas oil is taken out from stage 2 as a total draw. The flow was estimated to be 12000 Bbl/day. The second pumparound provides all the necessary reflux for the lower section of the tower. The heavy vacuum gas oil is withdrawn from stage 4 at 25000 Bbl/day.

3.2.3 Economic Model and Design Assumptions

As mentioned above, the economic analysis of the oil refining process described was carried out using the software Aspen Process Economic Analyzer. This software includes an economics module that lets you perform interactive economic scenarios. It develops key economic measures, including payout time, interest rate of return, net present value, and income and expenses on changing any economic premise. It performs economic analyses over the time line of a project, from the strategic planning phase through engineering, procurement and construction of the process facility, into start-up and throughout the production life of the process facility. With this, one can study the impact of cyclic changes in market conditions and identify economic threats and opportunities upon changing costs of feedstock, products and/or utilities for each period in the life of a project.

Total installed equipment cost (TIC) and indirect plant expenses have been set as a fraction of purchased equipment cost. Installation costs include charges for equipment installation, instrumentation, piping, electrical connections, building, warehouse and site development. Indirect expenses include costs for engineering and supervision, construction expenses, legal and contractor fees. Contingency cost is estimated as 18% of the total direct and indirect plant costs. The total direct and indirect costs along with the contingency give an estimate of the fixed capital investment (FCI) required for the project. Working capital accounts for the startup costs and is estimated as 15% of FCI. The FCI and working capital constitute the total capital investment (TCI) in the project. The prices for feedstock, raw materials and by-products have been derived from market data (West Texas Intermediate oil price reports) and conservative estimates based on assumptions. It is assumed that utilities required for the plant are purchased and the wastewater treatment is carried out for a fixed price at an external facility. Labor costs are estimated based on general assumptions for employee hours required per day for the number of operating steps. Overhead expenses are accounted as a fraction of labor costs and maintenance costs are calculated as a fraction of the total purchased equipment

cost. Insurance and legal fees are calculated as a fraction of installed equipment costs. These costs comprise the operating costs for the process. The discounted cash flow analysis is based on certain assumptions and takes into account cash flows over the entire plant life. In the discounted cash flow analysis the project investment is spent over three years following the assumptions stated below. The total operating costs are incurred every year and also include credit from sale of the following refinery products: LPG, Naphtha, Kerosene, Diesel and Gasoil.

Estimated product prices are linked to a West Texas Intermediate (WTI) crude price, [9], therefore, for economic evaluation purposes the following equations for the refinery products at the plant gate are summarized in table 3.1.

Table 3.1: Refinery products price calculation formulas [9]

Refinery Product	Price Calculation Equation
LPG	$[(WTI - 3.87) * 0.85] - 2.40$
Naphtha	$(WTI - 4.71) * 0.95$
Kerosene	$(WTI + 3.53) * 0.95$
Diesel	$[(WTI + 2.94) + 4.0] * 0.95$
Gasoil	$(WTI - 7.74) * 0.95$

As WTI crude prices are quoted in U.S. $ per barrel, it is necessary to perform the conversion of this price in € / liter, calculating the value of the Euro at 1.32328 U.S. dollars.

The plant depreciation costs are recovered in the first eleven years of operation following Modifies Accelerated Cost Recovery System method (MACRS). The difference between these annual costs and the annual sales of the refinery products give the net revenue in the respective year. Income tax is incurred at the rate of 34% on the taxable income derived after covering the losses forwarded from

the previous operating year. Deducting the income tax from the net revenue gives us the annual cash income for each operating year. These revenue streams from the operating years and the investment costs are discounted to the 2009 year of reference following a 10% internal rate of return. The sum of these costs and revenues in the year of reference give us the net present value (NPV) of the project. The following items are some of the major assumptions critical to the analysis [4]:

- The process has been modeled to utilize 185000 Bbl/day of Venezuelan crude oil which is assumed to be produced on-site in several oil field locations.
- The plant operates on a continuous basis for 8000 hours every year.
- The oil price will be associated with the WTI crude oil prices.
- The plant is 100% equity financed and the lifetime is assumed to be 20 years.
- The construction period is assumed to be 3 years, with 32% of the capital investment spent in 1st year, 60% in year 2 and 8% in year 3.
- The start-up time is assumed to be 15 weeks during which period the revenues have been assumed to be 50% of normal capacity.
- The income tax rate is 34% and the plant is depreciated following the US Internal Revenue Service (IRS) Modified Accelerated Cost Recovery System (MACRS).
- The Internal Rate of Return (IRR) for this project is set at 10%.
- All the costs and prices are updated to 2012 dollar value using appropriate indices.

3.2.4 Economic Evaluation Results

The capital expenses for the crude oil refinery products are presented in Table 3.2 and it shows the project summary for the capital costs. Equipment costs, taken from Aspen Process Economic Analyzer results, are typically only 20% to 40% of the total installed costs, with the reminder based on factors [4].

Table 3.2: Refinery capital expenses results

Economic Parameter	Price (Millions EUR)
Total Installed Equipment Costs	17.41
Total Direct and Indirect Costs	27.64
Contingency	4.22
Fixed Capital Investment	27.64
Working Capital	5.02
Total Capital Investment	31.84

Table 3.3 shows a comparison of results calculated using the factors shown in the literature and the same results calculated by the simulator. The formulas used in calculating the economic parameters are shown in Table 3.4.

As shown in Table 3.3, the values prepared using the formulas are more conservative than those generated by the simulation program for the total direct and indirect cost; however, the software predicted results are similar to the ones obtained applying the equations of such traditional economic analysis of chemical processes.

Table 3.3: Economic parameters results comparison

Economic Parameter	Price Calculation Results (using formulas)	Aspen Process Economic Analyzer Results
Total Installed Equipment Cost	17,405,500 €	17,405,500 €
Total Direct and Indirect Costs	23,427,803 €	27,644,300 €
Contingency	4,217,005 €	4,216,930 €
Fixed Capital Investment	27,644,808 €	27,644,300 €
Working Capital	4,146,721 €	5,015,450 €
Total Capital Investment	31,791,529 €	31,844,100 €

Table 3.4: Economic parameters calculation formulas

Economic Parameter	Price Calculation Equation
Total **I**nstalled **E**quipment **C**ost (TIEC)	$Aspen\ Software\ Results$
Total **D**irect and **I**ndirect **C**osts (TDIC)	$TDIC = TIEC * 1.346$
Contingency (C)	$C = TDIC * 0.18$
Fixed **C**apital **I**nvestment (FCI)	$FCI = TDIC + C$
Working **C**apital (WC)	$WC = FCI * 0.15$
Total **C**apital **I**nvestment (TCI)	$TCI = FCI + WC$

Table 3.5 shows the investment analysis result for the production of the refinery products.

Table 3.5: Investment analysis results

Project Results Summary	Price (€)
Total Project Capital Cost	31,844,100
Total Operating Cost	4,121,760,000
Total Raw Materials Cost	3,716,410,000
Total Utilities Cost	30,306,800
Total Product Sales	3,836,250,000
Desired Rate of Return	10 %
Payout Period	17.1672 years
Profitability Index	1.01193

Capital Cost: indicates, by period, the amount of initial, non-variable costs associated with the project.

Operating Cost: the total expenditure on the following items necessary to keep the facility operating: Raw Materials, Operating Labor Cost, Maintenance Cost, Utilities, Operating Charges, Plant Overhead, Subtotal Operating Cost, and General and Administrative costs incurred during production.

Payout Period: the expected number of years required to recover the original investment in the project. This value indicates the length of time that the facility needs to operate in order to recover the initial capital investment (fixed capital investment plus working capital).

Profitability Index: shows the relative profitability of any project; it shows the present value of the benefits relative to the present value of the costs. For each period, this number is computed by dividing the Present Value of the Cumulative Cash Inflows by the Present Value of the Cumulative Cash Outflows. If the profitability index is greater than one, then the project appears to be profitable. If this index is less than one, then the project appears not to be profitable. If this number equals zero then the project incurs no losses or gains (break-even point) [5].

The volatility of the market for oil trades, mainly because the political situation of the producing countries makes the prices always changing. For this reason the refinery products cost were attached to the West Texas Intermediate (WTI) oil prices to compensate the market fluctuation. Figure 3.2 shows the cash flows for the refinery process project for the 20 years period.
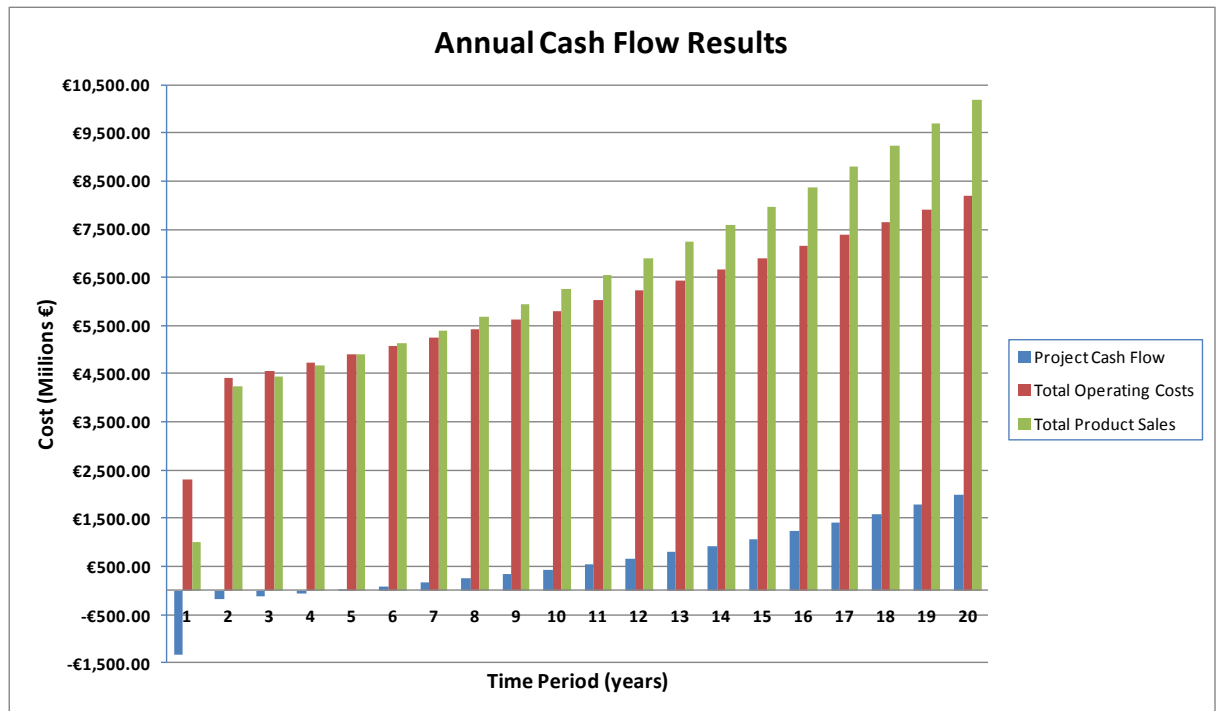

Figure 3.2: Cash flow for refining process

As shown in Figure 3.2, the project's cash flow is negative until the beginning of the 5th period. Then it grows continuously to a value of about 1750 million Euros at the end of the useful life of the project. The operating costs, as well as the total product sales, grow constantly in each period, and the former are only lower than the total product sales from the 6th period. For this reason, although the payout period is 17 years, Profitability Index of greater than 1, indicating that the project is profitable.

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Chapter 4:
Economic Evaluation of Ethylene and Electricity Co-Generation using the OCM Reaction

The purpose of this chapter is to study the OCM reaction with a special variant that is the co-generation of electricity in addition to ethylene produced in the OCM reactor, using a scheme process suggested by Swanenberg [1].

Light olefins (e.g., ethylene and propylene) are the most important basic petrochemicals, which are used to produce plastics, fibers and other chemicals. While most olefins are currently produced through steam cracking routes, they can also possibly be produced from natural gas (i.e., methane) via oxidative coupling routes. Methane-based routes can be economically attractive in remote, gas-rich regions where natural gas is available at low prices [2]. Since the pioneering work in the early 1980s, OCM has attracted much attention from both academia and industry. The number of publications and patents reached a peak between years 1988 to 1992 and being the subject of much academic and industrial interest, so far no pilot plants have been built for the entirely OCM reaction process.

Several schemes have been proposed in which the OCM process is integrated with processes involving endothermic reactions, e.g. cracking of ethane to ethylene [3] or steam reforming of methane to syngas [4]. Alternatively, the heat of the OCM reaction can be used to generate electricity. This concept was studied by Swanenberg, whose report [1] was the starting point for the current work. Swanenberg considered two options: the first was essentially an ethylene plant with electricity as co-product; the second was essentially an electric power plant with ethylene as co-product. The process scheme of the first option is shown in Figure

4.1. OCM produces ethylene, water, CO_2 and heat. Heat is used for electricity co-generation and CO_2 can be separated and be sold if a market exists. The main features are as follows:
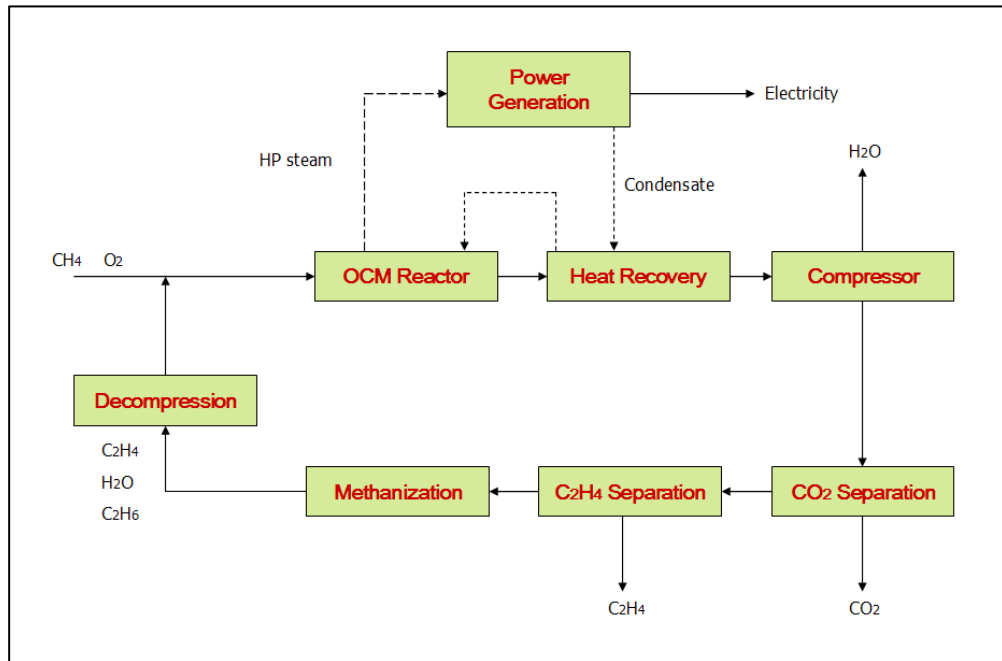

Figure 4.1: Oxidative coupling of methane to ethylene and electricity

Production of methane and oxygen: First, methane is separated from natural gas and is purified. Oxygen is separated from air cryogenically at a pressure of approximately 6 bars and very low temperatures (about -185 °C). Electricity or steam produced in later steps can be used for air separation. The mass ratio of methane to oxygen (99% purity) should be controlled at about 2.5:1 in order to lower the risk of explosion and to reach desired selectivity to ethylene.

Oxidative coupling of methane: Oxidative coupling of methane, as mentioned in Chapter 1, is a promising route for the conversion of natural gas to ethylene that can be used for the production of petrochemicals or fuel. The reaction takes place in the presence of catalysts at temperatures from 650 to 850 °C. This is an exothermic process and in addition to being

more energy efficient, it will increase the use of natural gas as a source of ethylene, the basic building block in polymers.

Compression, separation and heat recovery (petrochemicals production): The gaseous streams leaving the reactor, containing the ethylene produced together with the other gases of the OCM reaction, are compressed and water is condensed; then, the gases pass through an acid gas removal system, generally with a conventional solvent absorption process using aqueous solution of monoethanolamine (MEA) where CO_2 is removed. Additional water is condensed in a refrigeration unit and then completely removed along with CO_2.

Methanization process (methane production): In the methanization section, CO, CO_2 and H_2 are converted to methane, which is recycled as feedstock to increase the total yield. This is an optional reactor step in which the CO and H_2 present in the recycle stream are converted to CH_4 and H_2O. Methanization will improve the yield of C_2H_4 [1]. If it is not applied, the CO and H_2 are probably oxidized to CO_2 and H_2O in the OCM reactor. It is possible, [5], to carry out the catalytically reacting carbon dioxide (CO_2) with renewably-generated hydrogen (H_2) to produce methane (CH_4) according to the Sabatier reaction: $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$. From the remaining stream, ethylene/ethane is separated through C_2 separation unit.

Heat recovery: Using cold water is possible to cool the gas products exiting the OCM reaction and also producing High Pressure (HP), Intermediate Pressure (IP) and Low Pressure (LP) steam for using as source for power generation.

Power generation: The HP, IP and LP steam are used to produce electricity in a conventional expansion/condensing cycle.

Figure 4.2 shows a generic OCM route diagram with integrated electricity co-generation and air separation for oxygen production.
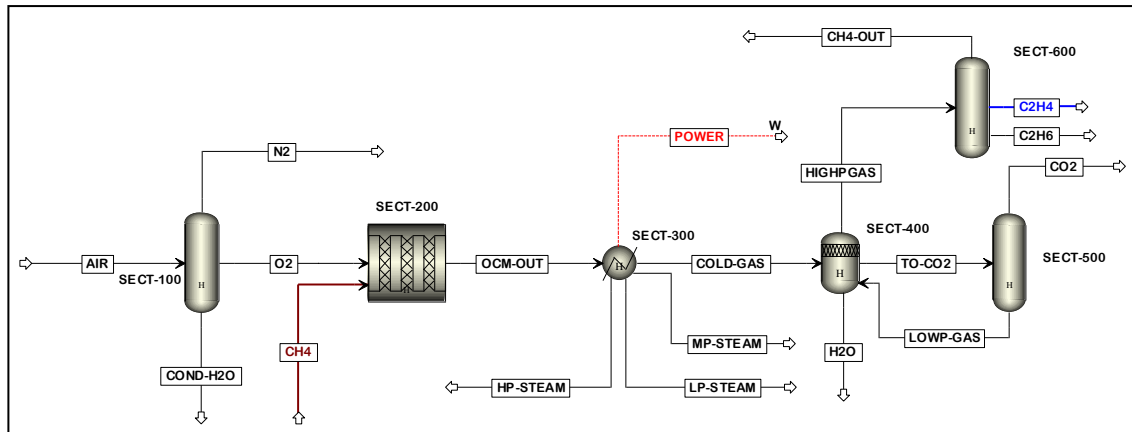

Figure 4.2: OCM schematic to produce ethylene and electricity

4.1 Modeling and improvement of utility systems

To analyze a utility system it is first necessary to develop a simulation model, which can be done using commercially available software. According to Varbanov et al. [6], the simulation model should allow part-load performance of the steam system components. It should provide a simulation of the complete material and energy balance around the steam system, and be capable of predicting the fuel, power generation, water requirements, etc. for any condition of the steam system.

The model must take into consideration operating constraints around the system, for example with respect to steam flows from steam generation devices and steam flows through steam turbines. Once such a simulation model has been developed, it can be subjected to optimization. The important degrees of freedom in utility systems are [7]:

a. Multiple steam generation devices. Each steam generation device within the utility system can use a different fuel or a different combination of fuels, and usually has its own efficiency that varies

with the steam load. The firing in the gas turbine combustor and supplementary firing are two independent degrees of freedom. Steam can also be generated from waste heat within a process. However, such in-process steam generation will be assumed here to be fixed according to the operation of the process.

b. <u>Multiple steam turbines</u>. Generally, steam turbines have different efficiencies, depending on their size, design, age and maintenance. For a given turbine, the efficiency varies with load. Hence, if there are two or more steam paths through the utility system via different steam turbines connecting two steam headers, this introduces additional degrees of freedom for internal flow distribution.

c. <u>Letdown stations</u>. Steam can be transferred between headers via letdown stations rather than steam turbines. Usually, large letdown flows indicate a missed opportunity for power generation. However, in some instances, letdown station flows can be exploited to bypass constraints in the steam turbine flows at one level in order to exploit the letdown flow at a lower level for power generation. Also, if the letdown station involves de-superheating by injection of Boiler Feed Water (BFW), the temperature al the exit of de-superheating is an additional degree of freedom.

d. <u>Condensing turbines</u>. Condensing steam turbines provide utility systems with additional degrees of freedom, generating extra power, but rejecting heat to atmosphere.

e. <u>Vents</u>. As with condensing steam turbines, venting steam from low-pressure headers also provides additional degrees of freedom to increase power generation. While this might seem a waste of steam,

if there is a significant price differential between the price of power and heat, it can be economic. Again, heat is rejected to the atmosphere.

An improved model for existing utility systems can be used to make continuous and discrete decisions. Discrete decisions relate to the operational status (on/off) of the devices. For example, it might be possible to switch between a steam turbine and an electric motor on a particular drive.

The energy balances of the system elements include nonlinear terms that result in a nonlinear optimization, with the potential to bring all of the associated problems of local optima. Fortunately, this difficulty can be overcome by fixing both the temperature and the pressure of the steam mains during the optimization to produce a linear optimization model, which is straightforward to solve. This is followed by a rigorous simulation after each optimization step. The linear optimization is repeated, followed again by rigorous simulation, and so on, until convergence is achieved. This procedure usually requires no more than four or five iterations to reach convergence.

4.2 Utilities cost calculation example

Knowing the procedures to be performed to meet the needs of utilities in the process, the next step is to analyze the costs of steam generation and refrigerant, since these two utilities are the most commonly used in distillation columns.

Steam is the most widely used heat source on most chemical plants. The generation process employs boiler feed water at high pressure that is preheated and fed to boilers where high-pressure steam is raised and superheated above the dew point to allow for heat losses in the piping [8]. Very high pressure steam is generated in utility stream boilers. This is expanded in steam turbines to provide

steam at high, medium and low pressure. The final exhaust steam from the steam turbines is condensed against cooling water. The steam turbine generates power. It may be that this power generation needs to be supplemented by the import of power from an outside power station. It might also be the case that excess power is generated on the site and exported [9].

For large chemical plants steam is often required at several different pressure levels; however, it is often generated at the highest level and then let down to the lower pressure levels through turbines. These turbines produce electricity used in the plant. Because there are losses of steam in the system due to leaks and sometimes process users not returning condensate, there is a need to add makeup water [10].

Boiler feed water preheat can be accomplished using process waste heat or convective section heating in the boiler plant. High-pressure (HP) steam is typically at about 40 bar, corresponding to a condensing temperature of 250 °C. Some of the HP steam is used for process heating at high temperatures. The remainder of the HP steam is expanded either through steam turbines known as back-pressure turbines or through let-down valves to form medium-pressure (MP) steam. The pressure of the MP steam is typically about 20 bar, corresponding to a condensing temperature of 212 °C. Medium-pressure steam is used for intermediate temperature heating or expanded to form low-pressure (LP) steam, typically at about 3 bar, condensing at 134 °C. Some of the LP steam may be used for process heating if there are low temperature heat requirements. Low-pressure (or MP or HP) steam can also be expanded in condensing turbines to generate shaft work for process drives or electricity production. Unless steam is purchased from a third party according to some contract price, steam does not have a direct cost. It is simply an intermediary between the primary costs (e.g., fuel) and the end users [7]. The price of HP steam can be estimated from the cost of boiler feed water treatment, the price of fuel, and the boiler efficiency.

As an example, in this work it has been used simulation program Aspen Process Economic Analyzer to calculate the production costs of HP-Steam for this process. The schematics of this process for predicting steam costs are shown in Figure 4.3 and the calculations results are:

Total Operating Cost: 8.023.240 €/year

Operating Hours per year: 8000

HP-Steam Produced: 228000.00 kg/hr

HP-Steam Cost = 8023240 € / 8000 hr = 1002.905 €/hr

$$HP - Steam\ Cost = \frac{1002.905\ €/hr}{228000.00\ kg/hr} = 0.0043987\ €/kg$$
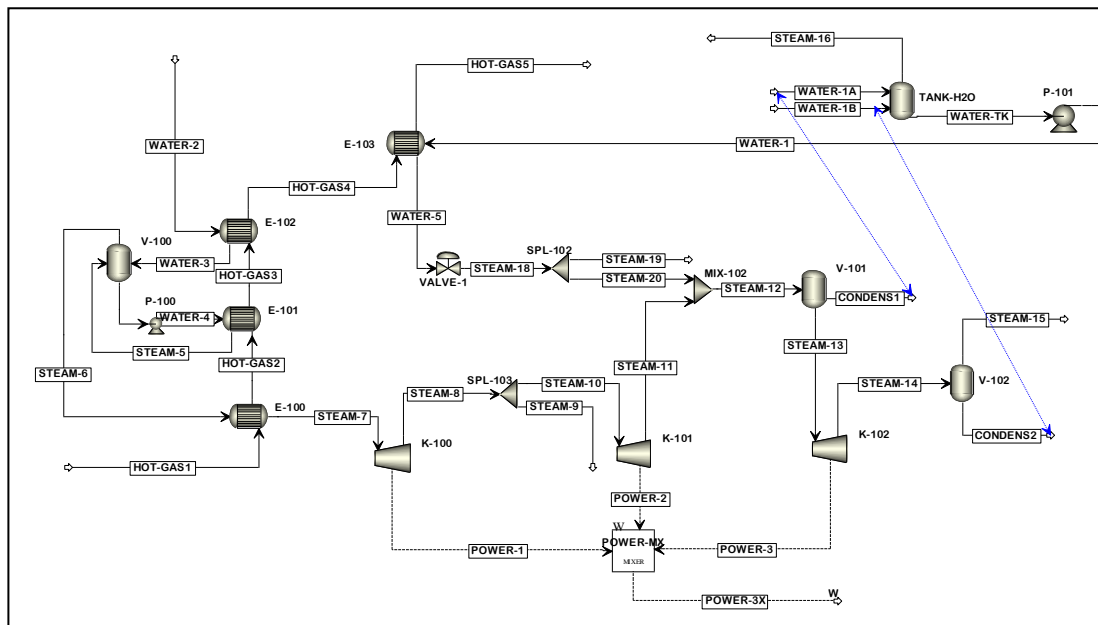
Figure 4.3: Steam & power generation process

4.3 Process Description

The Co-generation process has common sections with the OCM process previously described in Chapter 2 (Figure 2.1). Section 100 (Air Separation Unit), 200 (OCM Reactor), 400 (CO_2 Removal) and 500 (C_2H_4 Purification) presents the same schematics shown in Figures 2.2, 2.4 and 2.6, respectively, and have already been explained in Chapter 2. The improvement done to the conventional OCM process was based in the introduction of a co-generation process unit in which the heat recovered from the reactor was used to produce steam and consequently electricity. Bañuelos [11] conducted a research based on the schematics shown in Figure 4.2 and concluded that the consideration of the co-generation concept has been applied to the process in other studies previously evaluated with not so promising results. The main reason for this poor outcome was due primarily the final destination of electricity production, which was given for sale and not for the own process consumption, as it was considered in her work. Therefore, the electricity as a product did not showed a profitable future owing to the poor amount produced in comparison with the big energy retailers.

Using the OCM process, with a gas mixture temperature of around 500 °C coming from the OCM reactor section 200 (Figure 4.2), the heat recovered was used to produce steam from high, medium and low quality through a number of heat exchangers with an output temperature over 180 °C. The total amount of power generated was around 90000 kW, same that was used for the own plant consumption, since the power requirements of the compressor in sections 100 and 400 of the co-generation process consumes about 89000 kW. This assumption was applied among several scenarios for the economic analysis. It is important to mention that the equipment used in the power generation due to their size and their capacity can be easily found in the market. Therefore, the availability would not be a problem, as shown in Figure 4.4, that displays the turbine SST-500 model from Siemens, and it has the required capacity [12]. In Figure 4.5 is shown the

power and steam generation schematic and the explanation of this process is as follows:

Hot gases coming from OCM reactor section 200 (Fig. 4.2), are at 486 °C and such conditions allow its utilization for generating the steam required, using cooling water, to produce electricity with a turbine.
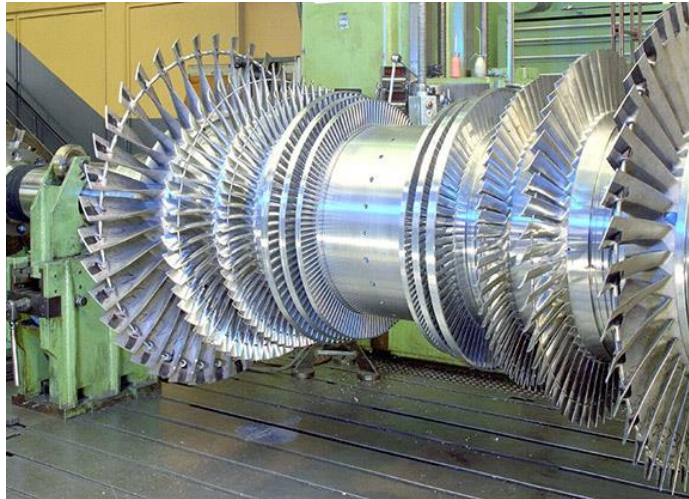

Figure 4.4: Siemens Steam Turbine model SST-500 [12]

This process employs 6 heat exchangers in series (HX-301 to HX-306) that are cooling the process gas from the 486 °C to 102 °C. The cold water required are represented in streams WATER-1 and WATER 2 with mass flowrate and conditions as follows, respectively: 540713 kg/h at 60 °C and 10.5 bar and 456000 kg/h at 180 °C and 35 bar. This water is processed in this section to generate three (3) steam streams: a) stream STEAM-3 at 294 °C and 34 bar; b) stream STEAM-6 at 241 °C and 20 bar; c) stream STEAM-9 at 178 °C and 9.5 bar. All these three streams enter into the turbines K-301, K-302 and K-303, respectively, generating a total production of 90321 kW of electricity. The exhaust steam of each turbines exits at conditions shown in table 3.1, and can still be used as heating source in other sections of the plant, before it condenses and be collected to be recycled at the cooling towers outside battery limits. The process gas leaving the last train of exchangers (stream

9), goes to the next plant section, to be compressed in two steps, in order to get the necessary pressure to be treated at the MEA absorption columns in section 500.
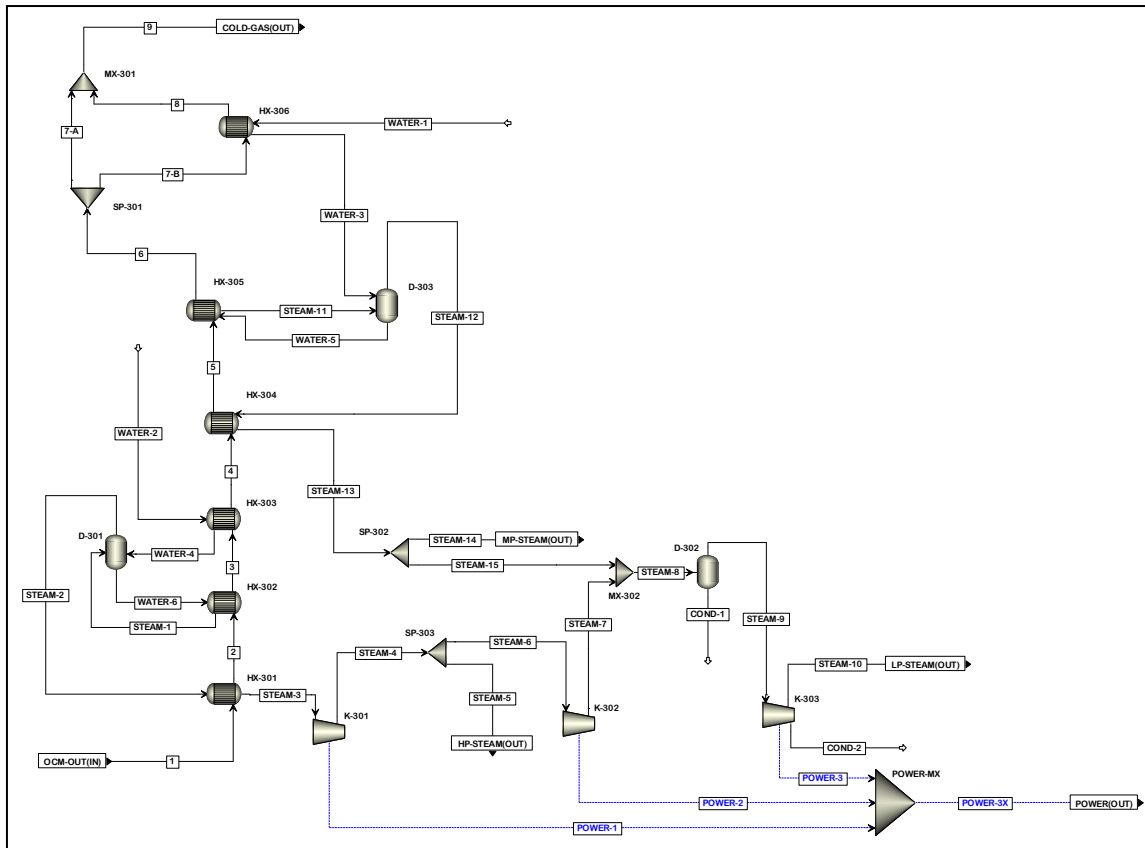
Figure 4.5: Power and steam generation schematic

Table 4.1: Steam production conditions

Stream	Product	Temperature (°C)	Pressure (bar)	Sat. Temp (°C)
STEAM-5	HP Steam	241.0	20.00	212.417
STEAM-14	MP Steam	180.0	9.50	177.699
STEAM-10	LP Steam	100.0	1.01	99.911

Sections 500 and 600 of the process shown in Figure 4.2 are identical to sections 400 (CO_2 removal) and 500 (C_2H_4 purification) shown in Figure 2.1 and have already been explained in full detail in Chapter 2.

4.4 Economic Analysis Results

As mentioned above, the economic analysis of this chapter has already been investigated by Bañuelos [11], and her economic analysis was based on the study of operating conditions applied at different plant locations, including: Germany, China, Middle East, Russia and Venezuela. Parts of her conclusions are the following:

1) The most profitable scenarios are located in the Middle-East region with a payout in the OCM conventional plant scenario around 6 years. However, the good expectative of this location, has to consider the new coming additions of ethylene that will affect the market due to the competition.

2) In China, still with the advantages in the labor force cost neither the scenarios are feasible, mainly due to the cost of the utilities and the methane itself.

3) According to the analysis results the two more profitable scenarios are Venezuela and Middle-East. In either Venezuela or Middle-East the economic analysis gives an acceptable payout period. Nevertheless, the Middle-East location represents a very risky investment due to the coming new ethylene plants projects, which are planned to startup in 2010. Therefore, the most safe and profitable location is Venezuela in which the ethylene market is brand new.

4) The electricity that comes from the co-generation part of the plant has to be used in the process itself and not as a product sales, as was done in previous studies [1].

5) As a key for the success of the OCM process in the market is the methane price. Therefore the importance in the plant location in order to get better feedstock prices and as consequence better margins.

6) Not because one location is not profitable as ethylene producer, doesn't mean that it couldn't be a good market as it is in the China case. The constant growing from this market makes difficult to afford its own demand caused the importation of ethylene.

In Table 4.2 is show part of her economic analysis results for the profitable scenarios and countries of the co-generation process.

After reviewing and updating the results it has been decided to update the economic analysis study and adapt it to a single geographic region where it could give acceptable economic values for the OCM process with electricity co-generation. The region chosen was Venezuela, because it has the lowest prices of the raw material necessary for the OCM process, natural gas, and also has the highest potential production of South America.

Table 4.2: Financial factors results for Co-generation process [11]

Country	IRR (%)	NPV (€)	Pay Out (years)	Profitability Index
Russia	23.39	64.14×10^6	12.81	1.14
Venezuela	24.46	61.37×10^6	12.97	1.18
Middle East	30.10	169.4×10^6	8.17	1.16

IRR: Internal Rate of Return
NPV: Net Present Value

The capital expenses for the co-generation process are presented in Table 4.3 and it shows the project summary for the capital costs. As explained in Chapter 3, the Aspen Process Economic Analyzer software was used to perform this study. Table 4.4 shows the investment analysis result for the co-generation process using the OCM reaction and Figure 4.6 shows the annual cash flow results of this process.

Table 4.3: Co-generation capital expenses results

Economic Parameter	Price (Millions EUR)
Total Installed Equipment Costs	172.15
Total Direct and Indirect Costs	238.72
Contingency	42.97
Fixed Capital Investment	272.84
Working Capital	44.38
Total Capital Investment	295.85

Starting the analysis of the economic results obtained and shown in Table 4.3, we see that the results appear to show the profitability of the co-generation. However, a review of the results shown in Table 4.4 indicates that the values of operating costs and utilities are very close to the total project costs, although the price of the raw material is more than acceptable. Payout period is too high, more than 15 years; therefore, as shown in the same table, profitability index is less than one, which proves then that the project appears not to be profitable.

Finally, revenue from the sale of ethylene, the main product of co-generation process, shown in Figure 3.6, shows a steady growth of revenue cash flow from the 3rd year of the project and have been calculated based on a price of ethylene in the market of 1135 €/metric ton for a plant with a production capacity of 250000 metric tons per year.

Table 4.4: Investment analysis results

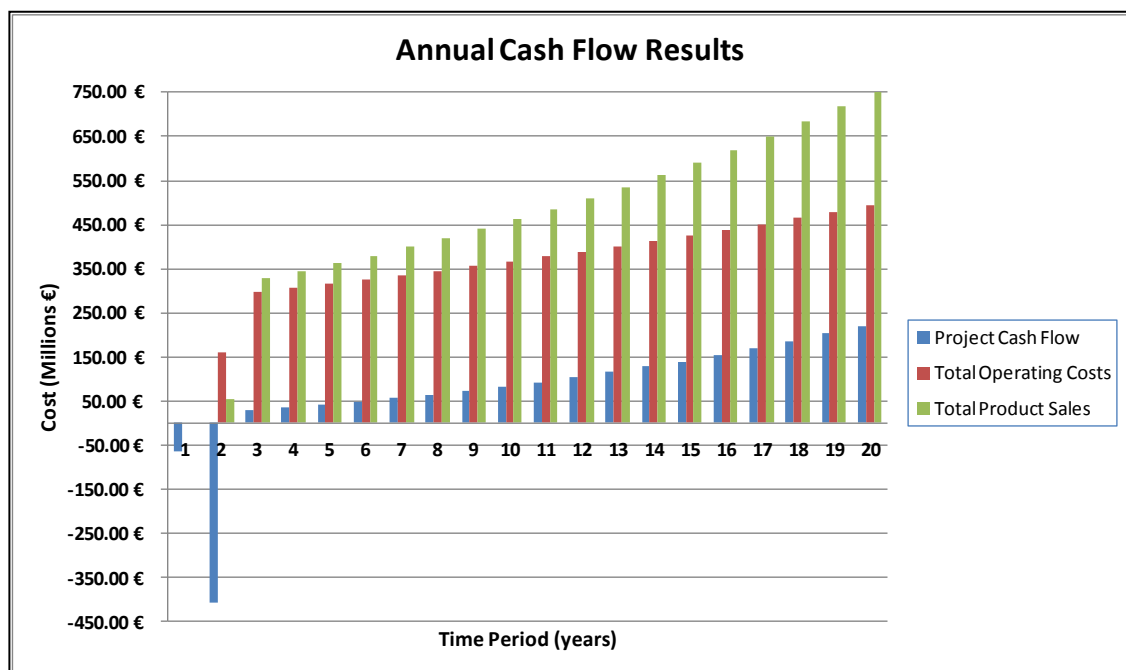| Project Results Summary	Price (€)
Total Project Capital Cost	295,847,000
Total Operating Cost	272,837,000
Total Raw Materials Cost	83,765
Total Utilities Cost	242,331,000
Total Product Sales	283,750,000
Desired Rate of Return	10 %
Payout Period	15.1636 years
Profitability Index	Less than 1

Figure 4.6: Cash flow for co-generation process

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Chapter 5:

Techno-Economic Analysis for Ethylene, Formaldehyde and Electricity Co-Generation using the OCM Reaction

The large amount of research interest focused during last decades on the catalytic partial oxidation of methane to oxygenates using the Methane Partial Oxidation (MPO) reaction, has allowed ascertaining the extended use of natural gas, the predominant component of which is methane, as a highly abundant and low-cost carbon source. Although progress toward obtaining a yield that would make a process industrially viable has been very low, the study on the partial oxidation of methane to C_1 oxygenates, such as formaldehyde and methanol, over heterogeneous catalysts at atmospheric pressure, has gained increasing attention in recent years as an alternative to the costly, energy-intensive steam reforming method of production in the current chemical industry.

Hydrocarbon fuels are presently the world's primary source of energy. To harness their chemical potential, current technology relies almost exclusively on combustion. However, the resulting emissions pose serious threats to the environment, including global warming, ozone depletion, and photochemical smog. As a result, it has become apparent that improvements must be made in the ability to utilize the energy of hydrocarbon fuels. In response to tough emissions regulations and the environmental hazards associated with gasoline and diesel fuel emissions, many automobile manufacturers are actively pursuing lighter hydrocarbon alternative fuels, including natural gas, which is composed of approximately 80% methane. In other applications, for example, home heating, gas

turbines, and electrical power turbines, natural gas is already being utilized extensively, making methane a vitally important fuel for the future [1].

Natural gas consists mainly of methane with varying proportions of ethane, propane, nitrogen and impurities such as CO_2, H_2S or trace metals. This gas, after necessary treatment to remove the undesirable components, is principally used as fuel for heating and power generation in locations far from reservoirs, with only 7% going to the production of chemicals such as methanol and ammonia [2]. Methane is currently being used for home and industrial heating and for the generation of electrical power. In many aspects is an ideal fuel because of the existence of distribution systems in most populated centers, its ease of purification and the fact that is has the largest heat of combustion compared to the amount of CO_2 formed, among all hydrocarbons. On the other hand, methane is an under-utilized resource for chemicals and liquid fuels. Known resources of natural gas are enormous and rival those of liquid petroleum. Because methane is a very stable compound with a bond energy = 411 kJ/mol its chemical conversion processes require extreme reaction conditions [3]. Consequently, most of the processes had not had commercial success, except for the steam reforming process to produce syngas [4]. Large resources of natural gas have made methane and also the NGL components (ethane and propane) important raw materials for the chemical industry. In many cases, however, the development of the discovered gas fields has been obstructed by the demand for large investment in transportation facilities (e.g., gas pipelines) and other related infrastructures, which are expensive and may not be available for all consumption points. These transportation and environmental problems (re-injection into oil wells, flaring or venting) and the increasing oil price have led to world-wide efforts for directly converting methane into easy transportable value added products, such as ethylene (feedstock for petrochemicals), aromatics (ethyl benzene) and liquid hydrocarbon fuels (methanol). To promote the exploitation of such gas fields, natural gas conversion technology to transport fuel or petrochemical feed stocks has been studied for several decades. These methods, which are well-

known indirect methane conversion technologies, however, also require large investment in facilities and are expensive to operate. Consequently, even the existing methods retain significant obstacles in the development of natural gas fields, in particular marginal fields. Thus, to exploit natural gas resources more widely, new methods have been developed that converts natural gas into liquid fuel more efficiently and economically than the conventional methods. With this in mind, development of a new process that converts methane into liquid fuel (e.g., gasoline) directly, rather than through synthetic gas, has been carried out [5].

Indirect routes for methane conversion are based on partial oxidation and the most used reaction is the highly energy consuming steam reforming to produce synthesis gas (CO and H_2). The synthesis gas is converted either to liquid fuels through Fischer-Tropsch or to methanol and subsequently to olefins or gasoline. These two or three steps processes require high investments in production plants. Considerable efforts have been made for many years to develop direct conversion reactions producing partially oxidized compounds (mainly methanol) and products derived from oxidative coupling of methane (ethane and ethylene). Light olefins (e.g., ethylene and propylene) are the most important basic petrochemicals, which are used to produce plastics, fibers and other chemicals. Most of them are produced by steam cracking. As the current global capacity for light olefin production has exceeded 150 million tons, steam cracking is now the most energy consuming process in the chemical industry, accounted for about 20% of the final energy use (including burnt fuels and electricity only; excluding the energy content of chemicals) in the global chemical industry while 200 million tons of CO_2 is about 30% of the total CO_2 emissions from the global chemical industry (mostly due to combustion of fossil fuels) [6]. With this energetic picture in mind, several alternatives have being proposed for the production of ethylene from methane, since more than 80% of natural gas on the mass basis is methane, through the so-called C_1 routes. This chapter describes a feasibility study on the production of ethylene, electricity and formaldehyde using the oxidative coupling of methane

(OCM) reaction. The feasibility was evaluated in terms of energy savings, CO_2-emission reductions and costs, compared to the separate production of ethylene and formaldehyde with conventional technology. The process described herein involves the catalytic processing of methane, via OCM, into ethylene and other by-products and the non-reacted methane into formaldehyde.

5.1 Methodology

Aspen Plus® process simulation software (version 7.2) was used to model and study several process designs to determine the best conditions for using the non-reacted methane streams taken from various points in the process. The results from Aspen Plus model were exported to Aspen Process Economic Analyzer which was used to create an engineering economic model. The model has been constructed to update all cost values accordingly based on relevant indexes. Results from the process model simulations were used in an economic analysis to size process equipment and develop an estimate of capital costs (developed from a variety of sources) and operating costs. Capital costs were taken from prices of several unit operations that employ well-known technology that can be purchased as modular packages (i.e., amine treatment, on-site O_2 supply) used the overall cost for the package unit when available. Costs for common equipment items (e.g., tanks, pumps) were estimated using the Aspen Process Economic Analyzer costing software. Other more specific unit operations (OCM reactor, air cooled heat exchangers, etc.) used cost estimates from other studies and/or from vendor quotes. The installed capital costs were developed using general plant-wide factors including items such as cost contributions for equipment installation, instrumentation and controls, piping, electrical systems, buildings, and yard improvements. Overhead and contingency factors were used with the installed equipment costs to determine a total plant investment cost. This cost and plant operating expenses were used in a discounted cash flow analysis to determine the cost of ethylene and formaldehyde production with a specific discount rate, referred here as the minimum ethylene selling price that was the primary value used to

compare alternate designs during process synthesis. This analysis has been carried out with 2010 Euro value as a point of reference.

5.2 Process background

Several reviews [7, 8] have been published about the selective oxidation of methane to formaldehyde. In 1999 Linz et al. [9] made a research work consisting on the one-step conversion of methane to formaldehyde, obtaining high selectivities with respect to formaldehyde only at very low conversions of methane. However, by separating the products from the reaction stream after differential conversions, decompositions and oxidation of the product was prevented. Repeating recycling of the remaining reaction stream resulted in high yields of formaldehyde.

Additionally Schwittay [7], conducted a more detailed study on the production of formaldehyde from methane in which he noted the need for the use of methane in remote areas of natural gas production. He points out that the challenge for the future is the use of methane on petrochemical plants, since it comes as a by-product of the oil production industry. On the other hand, in the future will be prohibited more often the flaring or venting the methane to the atmosphere for environmental reasons and therefore, natural gas researchers are looking for the easiest possible method for converting methane into valuable products. Such procedures could be the ethylene partial oxidation of methane to formaldehyde or the oxidative coupling of methane. In both cases, the products are less stable than the reactant, so that the selectivity decrease with increasing conversion of methane and high yields are not available. It was therefore suggested to separate the low conversions with high selectivity to formaldehyde or ethylene formed from the reactant stream and recycles the unreacted methane.

The purpose of this chapter is to present the process engineering and economic evaluation of this concept. To this end, the reaction kinetics is determined at selected catalysts [8], and also the separation and purification of the desired

products, in this case, formaldehyde. The schematic of his process is shown in Figure 5.1. [7].
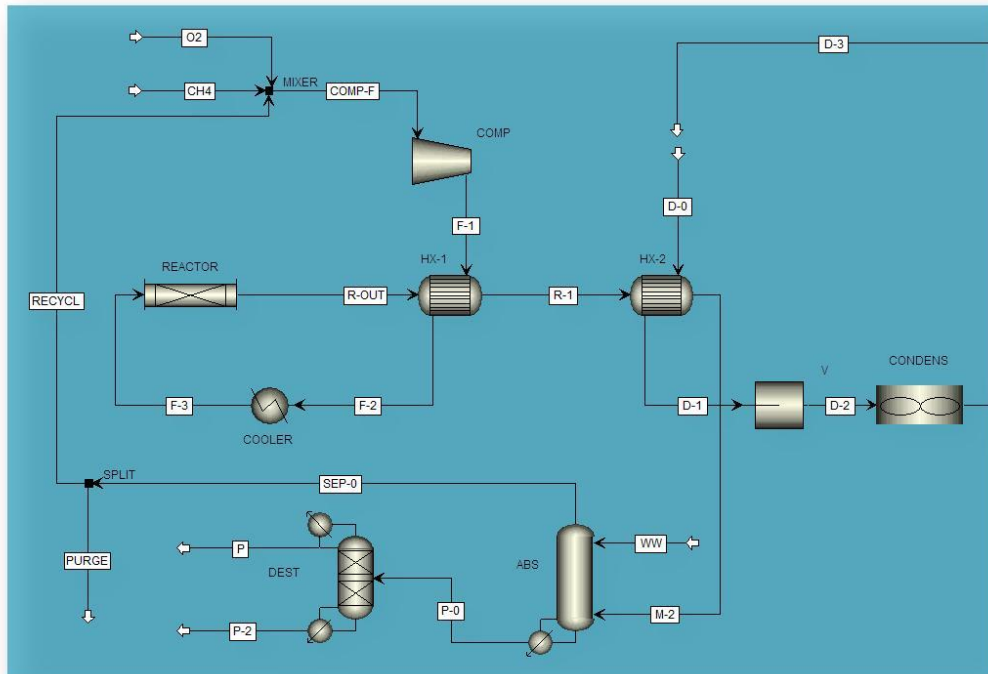
Figure 5.1: Oxidative coupling of methane to ethylene, formaldehyde and electricity

5.3 Process Description

The explanation of the OCM process has already been done in detail in previous chapters. Due to the complex oxidation and heterogeneous catalytic reaction, the process suffers from low selectivity and yield of ethylene and ethane. However, there is still research going on to improve the selectivity and yield of C_2 products towards an economical industrialization. Even with these values, interest in catalytic OCM has already gone through the stage of intensive studies in reactor analysis and improvement [10]; this implies that an optimum ratio of conversion/selectivity exist, in order to achieve the highest possible yield of C_2 hydrocarbons [11]. It has turned out that, it is difficult to obtain satisfactory results with a single pass of the reagents through the catalyst. An alternative, which allows a considerable improvement, is the reaction of formaldehyde synthesis from the re-circulation of unreacted methane after selective adsorptive separation of the

products. The modeled process uses 2175 t/d of methane, which undergoes by catalytic processing via OCM to ethylene and other by-products, and the non-reacted methane goes catalytically into formaldehyde. Laboratory data [11], were used to size the OCM reactor while data from Aspen simulation model were used to size the rest of the process equipment. In Figure 5.2 is shown the process flow diagram for the alternative formaldehyde production process, studied in this work.
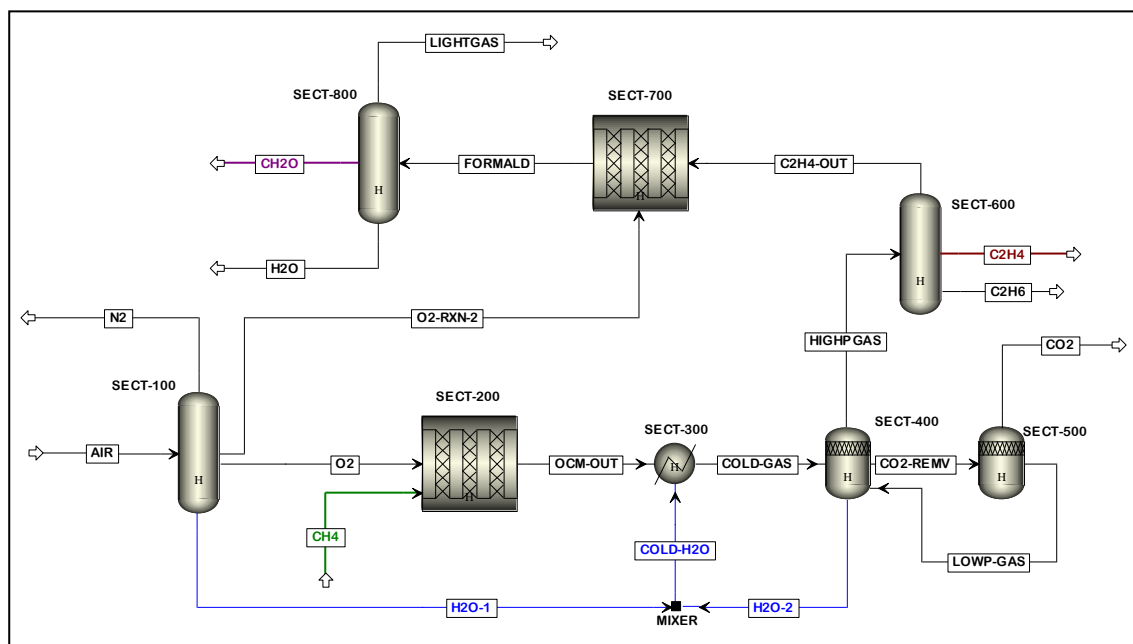
Figure 5.2: General flow diagram for the proposed process

The simulations were performed using an Aspen hierarchy blocks to provide a hierarchical structure model to complex simulations. From the OCM process it has been included, in this formaldehyde production alternative, the following process areas: Air separation unit (Section 100), OCM reaction (Section 200), Gas compression (Section 400), CO_2 removal (Section 500), and Ethylene separation (Section 600). The modified process includes the Heat recovery with power generation (Section 300), Formaldehyde reaction (Section 700) and Formaldehyde separation (Section 800).

The reason for which it is necessary to provide pure oxygen to the OCM reaction, instead of using air, is because the non-reacted methane will be recycled, after being purified from its heavy products, together with the H_2 and CO formed from the OCM reaction. If these gases are recycled together with the N_2, these impurities in the feed will affect the reactor design and make their size much larger, which would influence the equipment costs [12]. In addition to the above reason, the molar ratio of methane to oxygen (99% purity) should be controlled at about 1.7:1 in order to lower the risk of explosion and to reach desired selectivity to ethylene in the OCM reactor.

5.3.1 OCM Reaction

The OCM reaction is widely accepted to proceed in combinations of heterogeneous and homogeneous reactions. The reaction scheme, proposed by Stansch et al. [13] which consists of a ten-step network of reactions, is used and has been explained in details in Chapter 2.

5.3.2 Heat Recovery and Steam & Power Generation

In order to immediately stop the reaction and thereby prevent degradation of ethylene formed, it is necessary to cool the reactor output gases to prevent secondary reactions that reduce the value of the OCM gas.

In the original OCM process this is done using a quench tower to cool down the gases. For this proposed process (ethylene and formaldehyde with power generation), using the condensed water provided from the air separation unit and the compression sections is possible to cool the reactor gas products by means of Heat Recovery Steam Generator (HRSG) to take advantage of the higher temperature of the flue gas. The flue gas exits the HRSG section at temperatures above the water dew point at this operation conditions (T = 75 °C and P = 1.15 bar). The heat released by the OCM hot gases is used to generate MP steam, that is utilized as source for power generation, and then is further expanded in the gas

turbine, concept that was subsequently studied [14], producing 15.9 MW of electricity in a conventional expansion turbine. The Figure 5.3 shows the schematic of this process.

Figure 5.3: Diagram of the HRSG process

This section is very similar to Section 300 of the co-generation process for electricity production explained in Chapter 4. Here it uses 4 heat exchangers in series (HX-301 to HX-304) that are cooling the process gas from the 485 °C to 68 °C. The cold water required are represented in streams H2O-1 and H2O-CON1 with mass flowrate and conditions as follows, respectively: 155043 kg/h at 20 °C and 12 bar and 99106 kg/h at 32 °C and 1.01 bar. This water is processed in this section to generate one (1) steam stream, STEAM-3, at 314 °C and 9.5 bar. After entering into the turbine K-301, a drawn vapor stream is produced with the following conditions: 196 °C and 2.5 bar. The total electricity produced is 15911 kW. The exhaust steam, STEAM-4, can still be used as heating source in other sections of the plant, before it condenses and be collected to be recycled at the cooling towers outside battery limits. The process gas leaving the last train of exchangers (stream 6), goes to the

next plant section, to be compressed in two steps, in order to get the necessary pressure to be treated at the MEA absorption columns in section 500.

5.3.3 Gas Compression and Amine Treatment

The cooled gases coming from the HRSG section are compressed in a multi-stage compressor up to 35 bar, where the 99.4% of the water in the OCM gases are removed by condensation and later cooled down to 40 °C using a closed loop refrigeration process with ammonia. First the cooled gases at 68 °C and 1.11 bar are introduced in the first compression stage and immediately after cooled are fed into the bottom stages of a series of absorber columns that uses monoethanolamine (MEA) as absorbent solution. The MEA solvent is then regenerated in a distillation column thereby releasing a high purity CO_2 product. Amine scrubbing applied to CO_2 capture has been studied by several groups [15 – 18]. The model consists of an absorber and a stripper using rate-based calculation. The operation data from a pilot plant at TU-Berlin were used to specify feed conditions and unit operation block specifications in the model. Thermo-physical property models and reaction kinetic models are based on the works of Aspen Technology [19]. Equilibrium and transport property models and model parameters have been validated against experimental data from open literature [20 – 21]. Figure 5.4 shows the diagram for this amine treatment process.

5.3.4 Ethylene Separation

After removing all CO_2 produced in the reactor, the gas is further released of all its water content and goes to the separation section of the plant. This section consists of two cryogenic distillation columns: the C-601 demethanizer column and the C-602 deethanizer column. Figure 5.5 shows the alternative employed for the ethylene-ethane separation system.
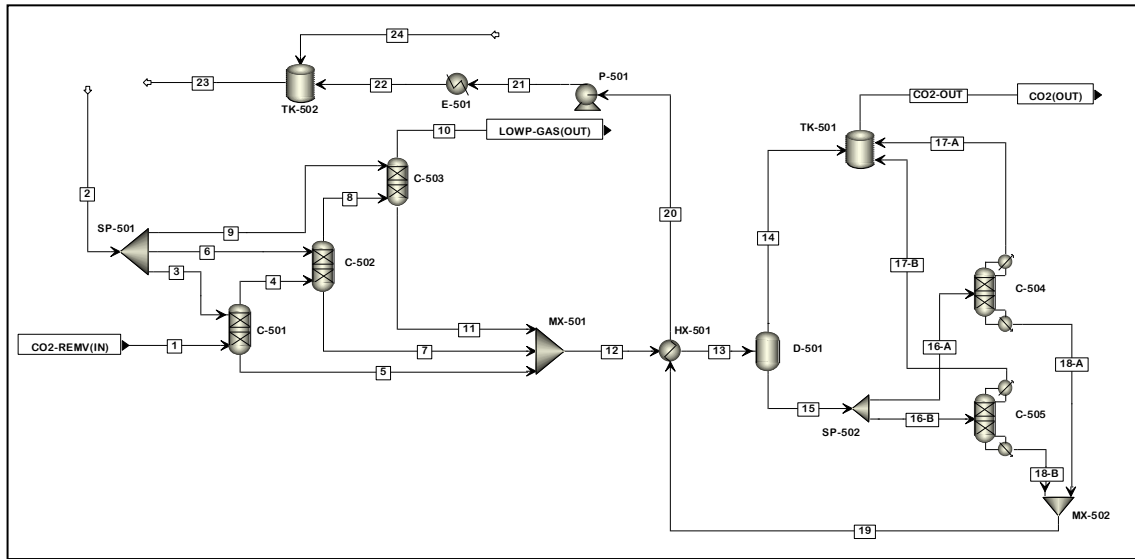
Figure 5.4: Diagram of the amine treatment process

In the C-601 column the unconsumed methane is separated from the product stream. The product stream consists of ethane and ethylene that is separated in the C-602 deethanizer column.
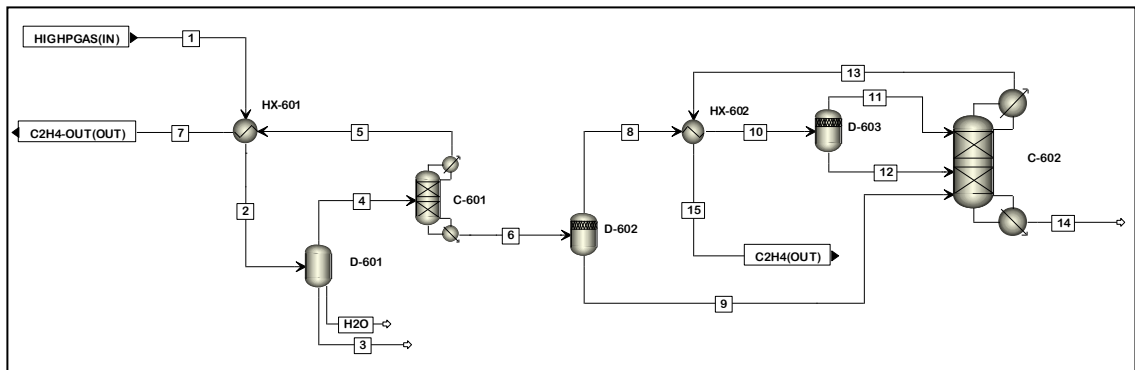
Figure 5.5: Diagram of the alternative ethylene separation process

In this ethylene separation section the feed-splitting principle to an ethylene-ethane distillation tower is applied, using the steady-state Aspen Plus® simulation tool for the calculation and study of this ethylene column. This concept was fully explained in Chapter 2. With this feed-splitting concept 98% of the initially ethylene

can be recovered. The heat requirement Q of a single rectification column can be minimized best by effective heat exchange between the warm products and the cold feed, and also by efficient insulation of the column. In a previous work, [22], it has been shown that in a cold tower, if the enthalpy of the feed is decreased by pre-cooling with the distillate, the final result is a decrease in the condenser and reboiler duties.

5.3.5 Formaldehyde Reaction and Separation

Finally, the top product from the demethanizer column (non-reacted methane, CO, H_2) is used as a raw material for the formaldehyde reaction. This one-step conversion of methane to formaldehyde has been studied since 1999 by Lintz et al. [9]. Although it is commonly recognized that a one-step process will not necessarily be more energy-efficient than the traditional process via synthesis gas, a simple one-step process may be economical for remote sites where until now spare natural gas is vented or flared. Yang et al. [8], have demonstrated the feasibility of production of formaldehyde from methane. They used a conventional fixed-bed reactor and a hybrid packed-bed membrane reactor to investigate the selective oxidation of methane to formaldehyde over a Mo-Co-B-O/SiO_2 catalyst at atmospheric pressure and in the reaction temperature range of $883 - 963$ K. This reactor uses the selective oxidation of methane yielded essentially formaldehyde, CO, CO_2, and H_2O, which takes into account chemical kinetics obtained from the fixed-bed reactor experiment. Using additional oxygen as the oxidant to fulfill the reaction conditions, the CH_4/O_2 molar ratio was about 7.5/1. Oxygen was supplied to produce the annual amount of 24.3 x 10^6 kg pure formaldehyde (35% CH_4 conversion, CH_2O selectivity of 10.7%). The reaction scheme, proposed by Yang et al. [8], which consists of a four-step network of reactions, is used.

The reaction steps have been presented as follows:

$$CH_4 + O_2 \rightarrow CH_2O + H_2O \qquad\qquad (5.3\text{-}1)$$

$$CH_2O + \tfrac{1}{2}O_2 \rightarrow CO + H_2O \qquad\qquad (5.3\text{-}2)$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad\qquad (5.3\text{-}3)$$

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2 \qquad\qquad (5.3\text{-}4)$$
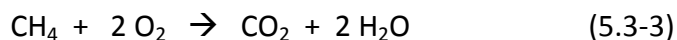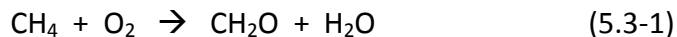
The detailed reaction kinetics for this methane to formaldehyde reaction was also taken from Yang et al. [8]. All formaldehyde produced in this reactor has been purified using a distillation column getting a liquid CH_2O product with 99.65% mass purity. The remaining non-reacted methane is sent to a tank and because the selectivity to carbon dioxide still increased slowly with methane conversion, CO_2 may not only be produced mainly from complete methane oxidation (reaction 5.3-3) but also from the oxidation of CO (reaction 5.3-4).

5.4   Economic Model and Design Assumptions

The intention of this part of the project was to evaluate the economics of the OCM reaction in an industrial scale. The most important aspect was to work out the comparative economics and to identify crucial costs on this basis rather than estimating the absolute costs. In order to achieve this goal the sensitivity of the economics to the OCM process location and raw material costs was studied. A discount cash flow analysis is used to assess the process economics which are modeled using the Aspen Process Economic Analyzer. The purchased equipment cost (PEC) was estimated using data from the same Aspen software mentioned before. Total installed equipment cost (TIC) and indirect plant expenses have been set as a fraction of purchased equipment cost. Installation costs include charges for equipment installation, instrumentation, piping, electrical connections, building, warehouse and site development. Indirect expenses include costs for engineering and supervision, construction expenses, legal and contractor fees. Contingency cost is estimated as 18% of the total direct and indirect plant costs.

The total direct and indirect costs along with the contingency give an estimate of the fixed capital investment (FCI) required for the project. Working capital accounts for the startup costs and is estimated as 15% of FCI. The FCI and working capital constitute the total capital investment (TCI) in the project. The prices for feedstock, raw materials and by-products have been derived from market data (e.g. ICIS chemical and oil price reports) and conservative estimates based on assumptions. It is assumed that utilities required for the plant are purchased and the wastewater treatment is carried out for a fixed price at an external facility. Labor costs are estimated based on general assumptions for employee hours required per day for the number of operating steps. Overhead expenses are accounted as a fraction of labor costs and maintenance costs are calculated as a fraction of the total purchased equipment cost. Insurance and legal fees are calculated as a fraction of installed equipment costs. These costs comprise the operating costs for the process. The total purchase cost of catalyst is incurred at every 10-year intervals in the discounted cash flow analysis. This price was taken from the EVONIK Industries web page [23], using its *Catalyst Cost Calculation Tool*, which helps to better understand the economic considerations associated with the use of precious metal catalysts.

The discounted cash flow analysis is based on certain assumptions and takes into account cash flows over the entire plant life. In the discounted cash flow analysis the project investment is spent over three years following the assumptions stated below. The total operating costs are incurred every year and also include credit from sales of co-products (electricity and formaldehyde). The plant depreciation costs are recovered in the first nine years of operation following Modifies Accelerated Cost Recovery system method (MACRS). The annual sales of ethylene follow the selling price in €/1000 kg and annual plant output from the process. The difference between these annual costs and the annual sales of ethylene give the net revenue in the respective year. Income tax is incurred at the rate between 15% - 39%, depending on plant location, on the taxable income derived after covering the losses forwarded from the previous operating year.

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Deducting the income tax from the net revenue gives us the annual cash income for each operating year. These revenue streams from the operating years and the investment costs are discounted to the 2010 year of reference following a 10% internal rate of return. The sum of these costs and revenues in the year of reference give us the net present value (NPV) of the project. In the current analysis the selling price of ethylene is iterated at a set internal rate of return to gain a net project value of zero. This ethylene price at zero net present value is the Minimum Ethylene Selling Price (MSP). The following items are some of the major assumptions critical to the analysis: [24]

- The process has been modeled to utilize 2.8 x 10^6 m^3 of methane per day (at 25 °C and 1.2 bar) which is assumed to be produced on-site in remote gas field locations.
- The detailed reaction kinetics for both, formaldehyde and OCM reaction from methane reaction are taken from Yang et al. [8] and Stansch et al. [13] respectively. The reactor size is estimated using residence time and catalyst bulk density.
- The plant operates on a continuous basis for 8000 hours every year.
- The methane price is assumed to be different, depending on plant location, between 15.88 and 210.0 €/1000 m^3. The oxygen price (for the formaldehyde production) also depends on the location and it is in the range between 17 and 19 €/1000 kg.
- The plant is 100% equity financed and the lifetime is assumed to be 20 years.
- The construction period is assumed to be 3 years, with 32% of the capital investment spent in 1st year, 60% in year 2 and 8% in year 3.
- The start-up time is assumed to be 5 months during which period the revenues have been assumed to be 50% of normal capacity.
- The income tax rate depends on plant location and it is in the range between 15% - 34% and the plant is depreciated following the IRS Modified accelerated Cost Recovery System (MACRS).

- The catalyst has a savage value at the end of lifetime, which is recovered.

- The Internal Rate of Return (IRR) for this project is set at 10%.

- All the costs and prices are updated to 2010 Euro value using appropriate indexes (1 € = 1.32032 US$)

5.5   Results and Discussions

5.5.1   Process analysis

The steady state flow rates of raw materials, products and by-products streams are summarized in Table 5.1. Both simulated processes (original OCM and alternative OCM proposed) consume a 2175 t/d pure methane as feed-stock, resulting in a production of 356 t/d of 99.5% purity ethylene (original OCM) and 321 t/d of same purity ethylene (alternative OCM proposed). The difference in ethylene production in both processes can be explained because the alternative process goes through more equipment before their final separation in the distillation columns. The CH_4/O_2 molar feed ratio in the OCM reactor for the original and alternative OCM process is 1.7; as a result in both processes a gas phase by-product stream composed by H_2O, C_2H_6, CO_2, CO and H_2 is obtained. Although this is a by-products stream with low economic value, the flow of CO and H_2 are sufficiently attractive to try to separate it from the mixture and used it as synthesis gas in a, for example, methanol synthesis reactor. The non-reacted methane in both process are 22% wt. of the reactor outlet stream, and can be allow to be recycled to the OCM reactor (original OCM process). In the alternative OCM process this non-reacted methane is then re-designed to use this CH_4 stream, after ethylene purification, to be the raw material for the formaldehyde process. The CO_2-enriched stream obtained after the amine process section together with the CO_2 and H_2O formed as by-products of both, formaldehyde and OCM reaction, can be used for the methanation of carbon dioxide reaction by hydrogen reduction [25], and then recycled back to the OCM reactor. Electricity can be generated with the MP steam, in a

conventional expansion/condensing cycle, using an industrial Siemens steam turbine, model SST-500, that operates with steam up to 30 bars and 400 °C (see Figure 4.4).

Table 5.1: Mass flow rates of key components of OCM and proposed alternative process

	Original OCM Process	Alternative OCM Proposed
Raw Materials	(metric ton/day)	
Methane	2175.4	2175.4
Oxygen	2560.7	3993.4
Products		
Ethylene production	356.4	320.9
Formaldehyde production	---	73.0
Electricity generated (kW)	---	15911
Ethylene purity (mass %)	99.6	99.4
By-products		
H_2O	1401.1	2180.4
C_2H_6	19.6	19.6
CO_2	1732.1	2762.8
CO	100.4	15.9
H_2	69.7	69.7
Non-reacted CH_4	1051.2	683.3

All these improvements in the process can result in a more favorable economic analysis. In the case of the OCM process the nitrogen obtained from the air separation unit, which is at 95% wt. purity, can be sold for many applications in a wide variety of areas including its use as purge-gas in the reactors when carrying out the catalyst regeneration and as feedstock for ammonia plants used in the production of nitrogen fertilizers.

5.5.2 Economic Analysis

Before starting the economic study of the OCM process a preliminary analysis of possible plant locations should be developed. Natural Gas (methane) is a commodity which price varies strongly from one region to

another. Moreover, not only the price of raw materials is affected by the location of the plant but also the costs associated with the production, namely: steam, refrigeration, electricity, fuel, wages, etc., affecting strongly the profitability of a petrochemical project. Table 5.2 shows the operating costs of different regions. Due to low natural gas prices in Venezuela, which has the highest production potential in South America, this geographical location has been chosen to perform the economic analysis of this project.

Table 5.2: Cost, taxation and pricing for different regions

	China	Germany	Middle East	Russia	Venezuela	
Operation Costs						Units
Operator	2.75	10.33	7.55	6.94	2.47	€/Op/hr
Supervisor	3.51	13.43	9.75	8.97	3.71	€/Sup/hr
Electricity	0.0807	0.147	0.0246	0.034	0.07212	€/kWh
Fuel	13	12.4	1.97	4.11	13.683	€/MWh
Utilities						
Steam (HP)	14.4	22.891	2.29	4.9	15.22	€/Ton
Steam (MP)	14.3	20.84	2.63	4.6	9.46	€/ton
Refrigerant	3.19	5.95	1.09	2.28	1.46	€/Ton
Raw Materials						
Oxygen	17 - 19	18 - 19	17 - 18.64	17 - 18.74	17.1 - 18.69	€/Ton
Methane	144.3	210.5	21.4	97.4	13.78	€/Mm^3
Products						
Ethylene	1054	840	840	1054	1025.2	€/Ton
Electricity	0.0807	0.147	0.0246	0.034	0.032	€/kWh
Formaldehyde	643	643	643	643	643	€/Ton
Tax Rate	25%	29.8%	20 - 85%	20%	15 - 34%	Percent

The capital expenses for the production of ethylene from OCM reaction for both processes are summarized in Table 5.3. The common sections to both processes are: Air Separation Unit, OCM Reaction, Gas Compression, CO_2 Removal and Ethylene Separation. The differences in capital costs results show that the alternative procedure is around 24% more expensive; however in the C_2H_4

separation section has a higher equipment costs for the original OCM process because it uses a compressor to raise the process gas pressure to 35 bar, which is not needed in the alternative process, that employs the feed-splitting technique, so that the savings in equipment investment represents around 25% using this technique. As expected, the alternative process requires an excess of 40.3 million Euros in total capital investment due to the formaldehyde production and separation sections.

Table 5.3: Capital expenses for the production of ethylene using OCM reaction

Process Section	Price (Million EUR)	
	Original OCM Process	**Alternative OCM Proposed**
1. Air separation Unit	32.53	32.53
2. OCM Reactor	21.89	21.89
3. Heat Recovery	---	3.83
4. Gas Compression	16.56	14.37
5. CO_2 Removal	7.98	10.21
6. C_2H_4 Separation	7.37	5.53
7. Formaldehyde Reaction	---	13.59
8. CH_2O Separation	---	5.18
Total Installed Equipment Cost	86.33	107.13
Total Direct and Indirect Costs	123.12	152.78
Contingency	22.16	27.50
Fixed Capital Investment	145.28	180.28
Working Capital	21.79	27.04
Total Capital Investment	167.07	207.32

The operating expenses are included in Table 5.4. The cost of the utilities (refrigeration, cooling water, steam) are the major contributor to the operating expenses that accounts for the 71.4% of the total operating costs for the original OCM process and 73.8% for the alternative OCM proposed.

The other costs represent general and administrative costs incurred during production such as administrative salaries/expenses, Research & Development, product distribution and sales costs. The by-product sales in the original OCM

include a small fraction of the nitrogen produced in the air separation unit, while the alternative process includes the formaldehyde production. Due to the generation of electricity in the heat recovery section, the net total expenses are lower in this alternative OCM proposed process.

Table 5.4: Operating expenses for the production of ethylene using OCM reaction

Operating Expenses	Original OCM Process (millions EUR/year)	Alternative OCM Proposed (millions EUR/year)
Methane feed	12.83	12.83
Utility costs	80.79	98.06
Labor costs	0.17	0.19
Overhead and maintenance	2.39	2.98
Others	16.96	18.75
Total expenses before credit	113.14	132.81
By-product credit	88.77	95.71
Net total expenses	24.37	37.10

Table 5.5 shows the final results for the discount cash flow analysis for both processes. Economic analyses of both alternatives are based on a total annual production of 135840 metric tons. The C_2H_4 production and yield difference for both processes is around 10%. This difference is because the alternative process requires more equipment for the CO_2 separation from the light gases (H_2, CO, CH_4), before the final separation of the ethylene produced, resulting in product losses at the secondary streams of this equipment. On the other hand, there is a 24% difference in the minimum selling price of ethylene for both processes due to the difference in capital investment costs.

The catalyst cost (LaO/CaO for the OCM reaction and MoO_3/SiO_2 for the formaldehyde reaction) represents 48% of the total capital investment over the entire plant life. About 48 metric ton of catalyst priced at 2080 EUR/kg is needed to maintain continuous production during the project lifetime.

Table 5.5: Results of discounted cash flow analysis

Operating Expenses	Process Case	
	Original OCM	Alternative OCM
Annual CH_4 input (metric ton/year)	725133	725133
Annual C_2H_4 production (metric ton/year)	118733	113300
Product yield (kg C_2H_4/metric ton CH_4 feed)	163.83	147.84
Total capital investment (million EUR)	167.07	207.32
Catalyst cost (million EUR)	70.80	89.80
Minimum product selling price (EUR/kg)	1.23	1.53
Minimum product selling price (EUR/m^3)	1.55	1.93

The minimum selling price represents the minimum price at which there is some profit. The volatility of the market for oil and natural gas trades, mainly because the political situations of the producing countries, the prices are always changing. For this reason, the value for the C_2H_4 is higher (around 24%) in case of OCM alternative proposed process because of the total capital investment and this value is around 1.98 times higher than the actual market price for ethylene. However selling by-products compensates this high ethylene sales cost for this process. Finally, the payout period, the expected number of years required to recover the original investment in the project, is 8 years. This value indicates the length of time that the facility needs to operate in order to recover the initial capital investment (total capital cost plus working capital). For a project of 20 years, these results clearly show that it is possible investment in the ethylene processing technology using the scheme suggested here. Figure 5.6 shows the cash flows for each project for the 20 years period.

Cash Flow Results

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Original OCM	-33.4	-185.5	51.8	57.1	62.9	69.0	75.6	82.6	90.2	98.2	106.8	115.9	125.7	136.0	146.5	158.3	170.8	184.1	198.2	213.1
Alternative Process	-37.1	-249.9	48.4	53.9	59.8	66.1	72.9	80.1	87.9	96.2	105.1	114.6	124.7	135.5	146.3	158.6	171.7	185.5	200.3	215.9
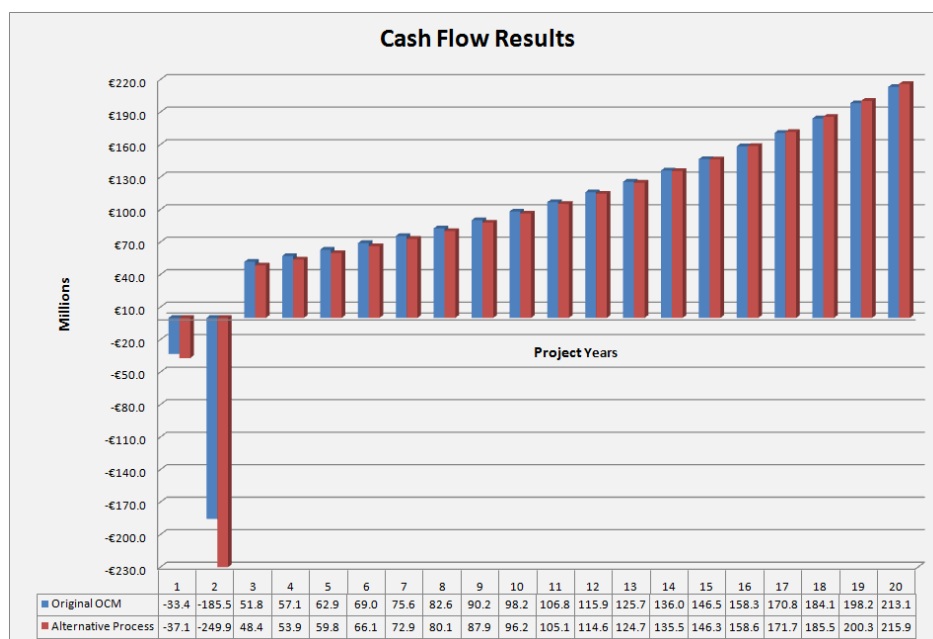
Fig. 5.6: Cash flow for the original OCM and alternative OCM proposed projects

5.6   Conclusions

This analysis shows that it should be possible to produce ethylene from the OCM reaction that is suitable to satisfy de ethylene demand worldwide as a precursor for the production of other chemicals. The development of integrating the OCM process technology, including reactor considerations, and a materials survey under severe OCM reaction conditions have been conducted in this project. The inclusion of alternative processes to the traditional OCM process to increase its profitability is indeed feasible. Nevertheless, a bigger capital investment is required, and the benefits obtained from this are still overcome by the margins and pay out time periods of the OCM process, due to the increase on capital expenses and operative costs. As shown in the results of this analysis, the price of methane is the key factor for the success of an OCM process in the ethylene market. For instance, international companies are moving now to countries that provide low feedstock prices (natural gas) in order to obtain greater margins due to this cost advantage. Producers located in mature markets like Europe will have a hard time in the following years, due to the costs advantage of the other markets and globalization. Middle East represents the best option for every project, even with the strong

competition expected in that region during the coming years. The recent discovery of huge off shore gas reservoirs in the northern coast region near Carúpano in Venezuela and the new trade agreements between this country and China, for the exportation of natural gas, oil and chemicals, could open the way for new projects in that region. Nevertheless, the lack of infrastructure and investors protection could affect its value.

Further work is needed in order to reduce total investment cost especially costs for compressors, furnaces and reactor operation at enhanced pressure should be considered. The investment costs for the reactor are still influenced by uncertainty in the reactor construction. The economic evaluation showed that the minimum performance of the OCM catalyst is more than 30% methane conversion and 80% C_2+ selectivity under some inverse correlation of conversion and selectivity. Based on this economic studies the above consumptions were confirmed that further catalyst improvement is required with respect to an increase of C_2+ selectivity and this would be certainly beneficial for process economics. The OCM alternative process proved to be more economical in terms of the net total expenses than the OCM single process. Furthermore, in general, the OCM technologies were confirmed to be more economically feasible in the case of installation to deal with a natural gas containing large hydrocarbons deposits.

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Chapter 6:
Techno-Economic Analysis for Ethylene and Oxygenates Production using the OCM Reaction

Methane, which is the principal component of natural gas reserves, is currently been used for home and industrial heating and for the generation of electrical power. In many aspects methane is an ideal fuel because of the existence of distribution systems in most populated centers, its ease of purification and the fact that it has the largest heat of combustion compared to the amount of CO_2 formed, among all hydrocarbons. On the other hand, methane is an under-utilized resource for chemicals and liquid fuels. Large resources of natural gas have made methane and also the NGL components (ethane and propane) important raw materials for the chemical industry. Natural gas reserves are increasing more rapidly than those of petroleum, and it is anticipated that this trend will extend well into the 21st century, according to Holmen [1]. Large amounts of methane are found in regions that are located far away from industrial complexes and often methane is found off shore that means its transportation is uneconomical or even impossible. Because of these large reserves in remote locations, gas transport to user locations is more difficult and expensive. It is more advantageous to convert the natural gas to the useful products and transport the end product to users. Thus, several researchers [2 - 5] are making great efforts to direct conversion of methane to value added products, such as ethylene (feedstock for petrochemicals), aromatics (ethyl benzene) and liquid hydrocarbon fuels (methanol) rather than through synthetic gas. With this in mind, new processes have been proposed such as direct conversion of methane into liquid fuel (e.g., gasoline) or an alternative approach: operating reactive separation of ethylene, combining separation of ethylene and production of a useful product. The separation of ethylene via alkylation of benzene to ethyl

benzene has been carried out by Graf and Lefferts [6]. The indirect routes for methane conversion are based on partial oxidation. The most used reaction is the highly energy consuming steam reforming to produce synthesis gas (CO and H_2). The synthesis gas is converted either to liquid fuels through Fischer-Tropsch or to methanol and subsequently to olefins or gasoline. These two or three steps processes require high investments and operational cost. Considerable efforts have been made for many years to develop direct conversion reactions producing partially oxidized compounds (methanol and formaldehyde) and products derived from oxidative coupling of methane (ethane and ethylene). The direct partial oxidation of methane to methanol is one of the attractive potential industrial processes for the use of abundant natural gas resources. Being an exothermic reaction, the direct conversion of methane to methanol would be superior to the conventional industrial process for the production of methanol via syngas by steam reforming of methane in terms of energy efficiency. Techno-economic evaluation, mentioned by Zhang et al. [7], has demonstrated that giving over 70% methanol selectivity at 8–15% methane conversion, the direct process is able to compete with the indirect one. This chapter describes a feasibility study on the production of methanol and formaldehyde using the non-reacted methane coming from the Oxidative Coupling of Methane (OCM) reaction process right after the separation of the ethylene produced.

6.1 Brief Description of the OCM Process

The OCM reaction is a highly exothermic process that is performed on metal oxide catalysts at temperatures between 700 and 900 °C. The process products are C_2H_6, C_2H_4, CO, CO_2, H_2 and H_2O. The CO_x (CO and CO_2) are formed from the complete combustion of hydrocarbons, which leads to point out the difficulties of achieving high performance in the OCM reaction process [8]. The complete process consists of three main sections: reaction, purification and separation section. As discussed earlier in previous chapters, novel process design strategies has

conducted in new downstream alternatives that has being improved the reaction part and the catalyst design as well by means of for instance minimize the carbon dioxide concentration for the reaction product. Figure 6.1 shows the general flowsheet for this process.
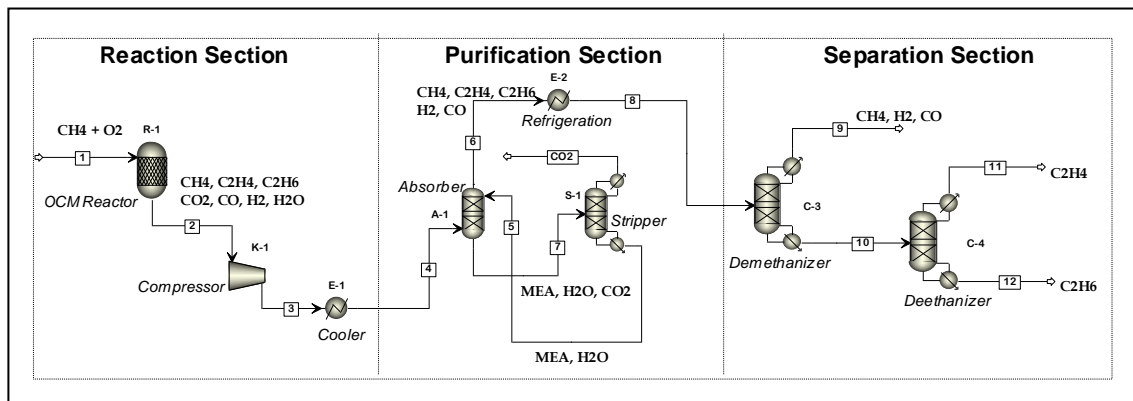
Figure 6.1: General Flowsheet for the Oxidative Coupling of Methane Process.

6.1.1 Reaction Section

The reactor is continuously fed with natural gas and oxygen. The feed gas is preheated to 700 °C, catalytic partial oxidized at pressure of 115 kPa and the reaction is carried out at 850 °C. The exothermic reaction heat has to be immediately removed. The cooling of the cracked gas in the transfer line exchanger is carried out by vaporization of high-pressure boiler feed water, which is separated in the steam drum and subsequently superheated in the convection section to high-pressure superheated steam. The reaction products are compressed in a multi-compaction section to 1090 kPa and cooled down to 40 °C later on. This stream is fed to the following purification section.

6.1.2 Purification Section

In this section the reactor effluent gasses are cooled and then are fed into the bottom stages of a series of absorber columns that uses monoethanolamine (MEA) as absorbent solution. The MEA solvent is then regenerated in stripper

columns thereby releasing the CO_2 captured in a dilute stream with water vapor product. The CO_2 removal simulation model consists of an absorber and a stripper using rate-based calculation. The operation data from a pilot plant at TU-Berlin were used to specify feed conditions and unit operation block specifications in the model.

6.1.3 Separation Section

This section consists of two cryogenic distillation columns. The first one is the demethanizer and the unconsumed methane is separated from the product stream (ethylene and ethane). Demethanization of OCM gas separates methane as an overhead component from C_2+ bottom components; concurrently, hydrogen is removed from the OCM gas stream and may be obtained as a product by purification before or after demethanization. The product stream consists of ethane and ethylene that is separated in the deethanizer.

6.2 Design of the Formaldehyde and Methanol Plant Model

The designed process is different from a commercial methanol plant based on auto-thermal reforming of natural gas. It uses the non-reacted methane from the OCM reaction process, a gas phase by-product stream composed by H_2O, CH_4, CO_2, CO and H_2. Although this is a by-products stream with low economic value for the ethylene production process, the amount of CO produced is attractive enough to be used in the production of synthesis gas. First those gases are purified by removing the components that may affect the conversion into synthesis gas (ethylene traces), before being used in the methanol process. The unreacted methane is used as raw material for the formaldehyde reaction. The reactor uses the selective oxidation of methane yielded essentially CH_2O, CO, CO_2, and H_2O, which takes into account chemical kinetics obtained from the fixed-bed reactor experiment by Yang et al. [9]. Additional oxygen as oxidant is required to fulfill the reaction conditions; the CH_4/O_2 molar ratio was about 7.5/1. By the oxygen fed the reactor produces the equivalent of 75.9 metric tons of formaldehyde per day; this lower conversion is coupled with

high selectivity, according to Lintz et al. [10]. All CH_2O formed in this reactor has been purified using two distillation columns. After the formaldehyde production follows the synthesis gas production using the stream coming from the top of the demethanizer column of the formaldehyde purification section. For this section the synthesis gas comes from a fixed-bed reactor for the catalytic partial oxidation of methane at conditions suitable for the production of methanol used by de Smet [11]. Addition of CO_2 (from the OCM purification process with amines) is possible in order to adjust the carbon/hydrogen ratio, which depends on the concentrations of CO and CO_2 from the non-reacted methane. The gas exiting the reformer is cooled with water generating the steam for the reformer. The synthesis gas is compressed to 30 bar by intercooled compressors before entering the synthesis reactor. The reactor operates at 250 °C and the composition of the outlet gas is calculated assuming chemical equilibrium. The chemical equations used in the production of methanol are given in equations (6.2-1 to 6.2-3), and kinetic data were taken from Gallucci et al. [12]. The flowsheet of the process is shown in Figure 6.2.

$$CO + 2\,H_2 \leftrightarrow CH_3OH \qquad\qquad\qquad (6.2\text{-}1)$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O \qquad\qquad\qquad (6.2\text{-}2)$$

$$CO_2 + 3\,H_2 \leftrightarrow CH_3OH + H_2O \qquad\qquad (6.2\text{-}3)$$

Figure 6.2: Simplified flowsheet for oxygenates plant process.

The gas from the methanol reactor is cooled, and condensation of methanol and water occurs. Approximately 35% of the unconverted gas is recycled to the synthesis reactor to get maximal methanol conversion with one reactor set. The

heat generated by synthesis process is used for the distillation. Before entering the distillation column, the crude methanol stream is depressurized in a turbine generating 6525 kW of electricity that counts for 23% of the compressor requirements. With this process, pure liquid methanol is obtained (8510 kg/h) after water removal in the distillation column that operates at 9 bar.

6.3 Economic Model and Design Assumptions

The intention of this part of the project was to evaluate the economics of the OCM reaction in an industrial scale. The most important aspect to work with is the comparative economic aspects and to identify critical costs on this basis rather than estimating the absolute costs. In order to achieve this goal the sensitivity of the economics to the OCM process location and raw material costs was studied. A discount cash flow analysis is used to assess the process economics which are modeled using the Aspen Process Economic Analyzer. The purchased equipment cost (PEC) was estimated using data from the same Aspen software mentioned before. Total installed equipment cost (TIC) and indirect plant expenses have been set as a fraction of purchased equipment cost. Installation costs include charges for equipment installation, instrumentation, piping, electrical connections, building, warehouse and site development. Indirect expenses include costs for engineering and supervision, construction expenses, legal and contractor fees. Contingency cost is estimated as 18% of the total direct and indirect plant costs. The total direct and indirect costs along with the contingency give an estimate of the fixed capital investment (FCI) required for the project. Working capital accounts for the startup costs and is estimated as 15% of FCI. The FCI and working capital constitute the total capital investment (TCI) in the project. The prices for feedstock, raw materials and by-products have been derived from market data (e.g. ICIS chemical and oil price reports) and conservative estimates based on assumptions. It is assumed that utilities required for the plant are purchased and the wastewater treatment is carried out for a fixed price at an external facility. Labor costs are estimated based

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on general assumptions for employee hours required per day for the number of operating steps. Overhead expenses are accounted as a fraction of labor costs and maintenance costs are calculated as a fraction of the total purchased equipment cost. Insurance and legal fees are calculated as a fraction of installed equipment costs. These costs comprise the operating costs for the process. The discounted cash flow analysis is based on certain assumptions and takes into account cash flows over the entire plant life. In the discounted cash flow analysis the project investment is spent over three years following the assumptions stated below. The total operating costs are incurred every year and also include credit from sale of co-products (electricity, formaldehyde and methanol). The plant depreciation costs are recovered in the first eight years of operation following Modifies Accelerated Cost Recovery system method (MACRS). The annual sales of ethylene follow the selling price in €/1000 kg and annual plant output from the process. The difference between these annual costs and the annual sales of ethylene give the net revenue in the respective year. Income tax is incurred at the rate between 15% - 35%, depending on plant location, on the taxable income derived after covering the losses forwarded from the previous operating year. Deducting the income tax from the net revenue gives us the annual cash income for each operating year. These revenue streams from the operating years and the investment costs are discounted to the 2010 year of reference following a 10% internal rate of return. The sum of these costs and revenues in the year of reference give us the net present value (NPV) of the project. The following items are some of the major assumptions critical to the analysis [13]:

- The process has been modeled to utilize 22.6×10^5 m^3 per day of methane (at 15 °C, 1 atm) which is assumed to be produced on-site in remote gas field locations.

- The detailed reaction kinetics for the OCM reaction was taken from Stansch et al. [14]. The reactor size is estimated using residence time and catalyst bulk density.

- The plant operates on a continuous basis for 8000 h every year.

- The methane price is assumed to be different, depending on plant location, between 6.82 and 88.37 €/1000 m^3. The oxygen price (for the formaldehyde production) also depends on the location and it is in the range between 17 and 19 €/1000 kg.

- The plant is 100% equity financed and the lifetime is assumed to be 20 years.

- The construction period is assumed to be 3 years, with 32% of the capital investment spent in 1st year, 60% in year 2 and 8% in year 3.

- The start-up time is assumed to be 18 weeks during which period the revenues have been assumed to be 50% of normal capacity.

- The income tax rate depends on plant location and it is in the range between 15% - 34% and the plant is depreciated following the IRS Modified accelerated Cost Recovery System (MACRS).

- The Internal Rate of Return (IRR) for this project is set at 10%.

- All the costs and prices are updated to 2010 Euro value using appropriate indexes (1 € = 1.31337 US$).

6.4 Results and Discussions

6.4.1 Process Analysis

Before deciding what to do with the amount of non-reacted methane in the OCM process, an economic analysis was performed to compare the costs associated with recycling of this methane. Table 6.1 summarizes the economic overview of this analysis. Economic analysis of both alternatives are based on a total annual production capacity of 240000 metric tons of ethylene with a selling price of 1135 €/ton. Operating and Utilities costs differences represent 4.2% and 4.8% respectively, and both values are for the unreacted methane no-recycling alternative. Since the differences between raw material costs for both alternatives represent only 3%, and the Project Capital Cost are only 7.8% more expensive for the recycled case, the decision was made to use the non-reacted methane in the production of oxygenated products, such as formaldehyde and methanol, in order to give added value to the OCM reaction process.

Table 6.1: OCM Process Economic Results

Investment (Millions €)	OCM Process without CH_4 Recycling	OCM Process with CH_4 Recycling
Total Project Capital Cost	170.67	183.94
Total Operating Cost	266.05	255.34
Total Raw Material Cost	83.77	81.31
Total Utilities Cost	154.89	147.71
Total Products Sales (C_2H_4)	272.40	272.40
Payout Period (Years)	12.16	10.54

The steady state flow rates of raw materials, products and by-products streams are summarized in Table 6.2.

Table 6.2: OCM and Oxygenated Process Economic Results

	OCM Process Alone	OCM & Oxygenated Process Proposed
Raw Materials	(metric ton/day)	
Methane	2593.2	2593.2
Mono Ethanol Amine	676.7	676.7
Products		
Ethylene	396.0	396.0
Formaldehyde	---	117.1
Methanol	---	204.2
Ethylene purity (mass %)	99.6	99.2
By-products		
H_2O	1438.9	229.2
C_2H_6	19.6	25.7
CO_2	1675.2	518.8
CO	126.5	1512.9
H_2	72.0	108.6
Non-reacted CH_4	1421.1	502.2

Both simulated processes (OCM alone and proposed alternative) consume a 2593 t/d pure methane as feed-stock, resulting in a production of 396 t/d of 99% purity ethylene. This amount represents 55% of the total capacity of ethylene production plant. The difference in water production in both processes can be explained because the alternative process goes through more equipment to produce steam to be the raw material for the syngas reaction before its final use in

the methanol reactor. The CH_4/O_2 molar feed ratio in the OCM reactor for the original and alternative OCM process is 1.7; as a result in both processes a gas phase by-product stream composed by H_2O, C_2H_6, CO_2, CO and H_2 is obtained. Although this is a by-products stream with low economic value, the flow of CO and H_2 are sufficiently attractive to separate it from the mixture and used it as synthesis gas in a methanol synthesis reactor. The non-reacted methane in the initial process is 2.8 times higher than the alternative, because it is employed in the production of synthesis gas and formaldehyde. The CO_2-enriched stream obtained after the amine process section together with the CO_2 and H_2O formed as by-products of both, formaldehyde and OCM reaction, can be used for the methanation of carbon dioxide reaction by hydrogen reduction [15], and then recycled to the syngas reactor. As shown in Table 6.2, the final CO_2 emissions in the alternative process are 3 times lower than OCM process because it is used in the methanol production process. All these improvements in the process can result in a more favorable economic analysis. In the case of the OCM process the nitrogen obtained from the air separation unit, which is at 95% wt. purity, can be sold for many applications in a wide variety of areas including its use as purge-gas in the reactors when carrying out the catalyst regeneration and as feedstock for ammonia plants as raw material for the production of nitrogen based fertilizers.

6.4.2 Economic Analysis

Prior to starting the economic study of the OCM process a preliminary analysis of possible plant locations should be developed. Natural Gas (methane) is a commodity which price varies strongly from one region to another. Moreover, not only the price of raw materials is affected by the location of the plant but also the costs associated with the production, namely: steam, refrigeration, electricity, fuel, wages, etc., affecting strongly the profitability of a petrochemical project. Table 6.3 shows the operating costs of different regions. Due to low natural gas prices in Venezuela, which has the highest production potential in South America, and the

highest ethylene sales for the European market, this geographical location has been chosen for economic analysis of this project.

Table 6.3: Plant Location Economic Analysis for the OCM Process

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

The capital expenses for the production of ethylene and oxygenates products for both processes are summarized in Table 6.4. The common sections to both processes are: Air Separation Unit, OCM Reaction, Gas Compression, CO_2 Removal and Ethylene Separation. The differences in capital costs results show that the alternative process is two times more expensive than the OCM process alone; this is evidently due to the alternative process uses a lot more equipment for the production of oxygenated products.

A close look for the operating expenses values, shown in Table 6.5, may notice that the cost of the utilities (refrigeration, cooling water, steam) are the major contributor to the operating expenses that accounts for the 82.5% of the total operating costs for the OCM original process and 87.9% for the OCM alternative process. In order to decrease utility costs in the OCM alternative process the condensed water coming from the OCM reactor is used to generate HP steam (30 bars) for the reboilers in the demethanizer and ethylene-ethane separation columns. The other costs represent general and administrative costs incurred during production such as administrative salaries/expenses, Research & Development,

product distribution and sales costs. The by-product sales in the alternative process include the formaldehyde and methanol production.

Table 6.4: Capital expenses for both processes using OCM reaction

Process Section	Price (Million EUR)	
	Original OCM Process	OCM-OXY Process
1. Air separation Unit	44.37	38.11
2. OCM Reactor	24.44	22.99
3. Gas Compression	30.88	21.79
4. CO_2 Removal	11.89	72.31
5. C_2H_4 Separation	8.71	8.62
6. Methane Conditioning	---	2.01
7. Formaldehyde Reaction	---	47.29
8. CH_2O Separation	---	20.47
9. Syngas Production	---	7.65
10. Syngas Compression	---	13.07
11. Methanol Reaction	---	0.78
12. CH_3OH Separation	---	4.04
Total Installed Equipment Cost	120.29	259.21
Total Direct and Indirect Costs	167.02	326.86
Contingency	29.31	58.47
Fixed Capital Investment	180.47	352.67
Working Capital	29.31	63.48
Total Capital Investment	195.43	403.06
Lang Factor	5.7	5.7

The Lang factor used (5.7), is based on a same name method developed at the end of the decade of the forties of the twentieth century by H. J. Lang, which is the sum of the equipment prices and multiplied by a factor (Lang factor) that provides a better estimate of the prices of these equipment, which could vary from one provider to another, besides the origin of this equipment. For each type of chemical process there is a corresponding value of Lang factor, namely: for a solid process plant, one for processing solids and liquids and finally a value for processing fluids only (liquid and gases) [13].

Table 6.5: Operating expenses for both processes using OCM reaction

Operating Expenses	Original OCM Process (millions EUR/year)	OCM-OXY Process (millions EUR/year)
Methane feed	0.95	0.98
Utility costs	130.86	246.14
Labor costs	1.03	0.32
Overhead and maintenance	3.92	7.18
Others	20.85	25.37
Total expenses before credit	157.61	279.99
By-product credit ($CH_3OH + CH_2O$)	---	81.41
Profitability Index	0.000	1.1953
Net total expenses	**157.61**	**198.58**

The volatility of the market for oil and natural gas trades, mainly because the political situations of the producing countries, makes the prices always changing. For this reason, the value for the actual C_2H_4 prices is higher for the 3rd. quarter 2011 than last year (around 35%). However selling by-products compensates any future fluctuation for these high price ethylene sales for this process. Finally, the payout period, the expected number of years required to recover the original investment in the project, is 8 years for OCM process in Venezuela and 9 years for the OCM & Oxygenates process in the same country.

This value indicates the length of time that the facility needs to operate in order to recover the initial capital investment (total capital cost plus working capital). For a project of 20 years, these results clearly show that it is possible to invest in the ethylene processing technology using the scheme suggested here. Figure 6.3 shows the cash flows for the OCM alternative project for the 20 years period.
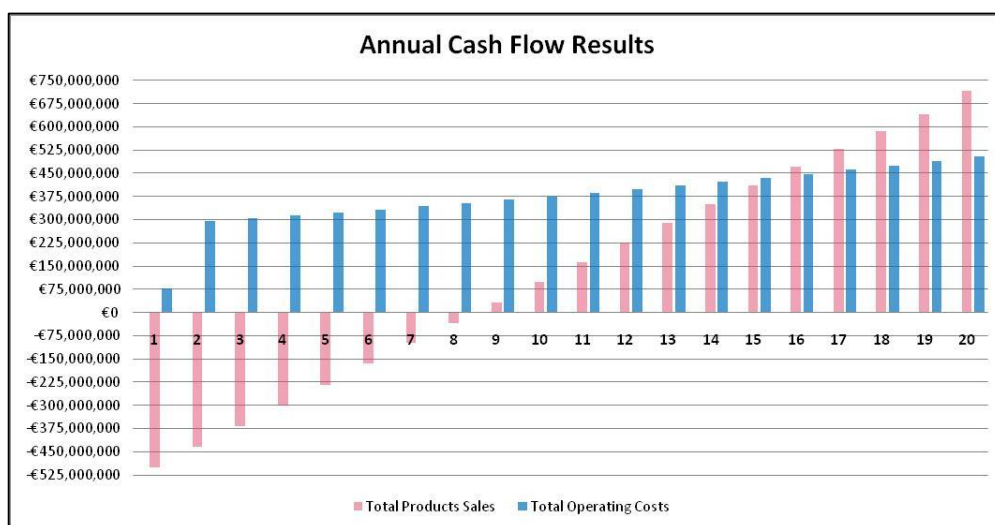
Figure 6.3: Cash flow for the Ethylene, Formaldehyde and Methanol process using OCM reaction

6.5   Conclusions

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

As shown in the results of this analysis, the price of methane is the key factor for the success of an OCM process in the ethylene market. For instance, international companies are moving now to countries that provide low feedstock prices (natural gas) in order to obtain greater margins due to this cost advantage.

Producers located in mature markets like Europe will have a hard time in the following years, due to the costs advantage of the other markets and globalization. Middle East represents the best option for every project, even with the strong competition expected in that region during the coming years. The recent discovery of huge offshore gas reservoirs in the northern coast region near Carúpano, Venezuela and the new trade agreements between this country and China, for the exportation of natural gas, oil and chemicals, could open the way for new projects in that region. Nevertheless, the lack of infrastructure and investors protection could affect its value.

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

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Chapter 7: Conclusions and Future Work

The research work in this thesis has been done on various process schemes proposals for an industrial process for ethylene production using the Oxidative Coupling of Methane reaction. It had started from the first experimental results carried out by Jašo in his fluidized bed reactor [1], and it was found a match between the experimental values reported for conversion, selectivity and yield and the simulation results performed using the plug-flow reactor model in Aspen Plus simulator software.

Generally the use of process simulator software comes after knowing in detail the process flow diagram of any particular section of a plant or for the complete process. This work started from the experimental results of the OCM reaction and then the reaction section diagrams were made for the entire process. Once the design of the reaction section for the OCM process was done, the decision was taken to design the whole plant for obtaining ethylene at an industrial level with production values that moved closer to those obtained in ethylene production plants globally, in order to perform the economic analysis of the process based on the sizing of equipment.

The OCM process alone was economically evaluated for different world locations in order to find the best place to get profits for this process. Natural Gas (methane) is a commodity which price varies strongly from one region to another. Additionally, not only the price of raw materials is affected by the location of the plant but also the costs associated with the production, namely: steam, refrigeration, electricity, fuel, wages, etc., affecting strongly the profitability of a petrochemical project. As a result of this evaluation two sites offer the best advantage for the potential location of the OCM plant: Middle East and Venezuela. Considering the knowledge of the country, access to raw material costs, utilities, tax

laws, domestic and export market potentials, Venezuela was selected to perform the economic evaluation process. Also Venezuela has low natural gas prices, with highest production potential in South America, and profitable sales earnings from the European market.

Once the location was decided, the initial analysis of the economic evaluation resulted in great energy consumption in the ethylene-ethane separation column, so the application concept of feed-splitting gave the following conclusions:

- The goal of significantly reducing the heat duty required by the condenser has been achieved by 26% and simultaneously has been reduced (27.5%) the amount of heat duty required by the reboiler.
- The advantages of applying the feed-splitting concept in a pilot plant is highly profitable, in order to save as much energy as possible and reduce the expenses, in 5 million €/year (almost 26%), in the amount of refrigerant used in the condenser thus achieving saving resources, both energetically and financially.

As mentioned in the introduction, the processes analyzed in this study did not include those who have gasoline and diesel as the final product from the ethylene oligomerization reaction. These six processes were initially suggested for technical and economic evaluation and possible improvement, using the OCM reaction, namely:

1) OXCO Process
2) UCC Process
3) ARCO Process
4) Suzuki Process
5) Schwittay - Turek Process
6) Co-generation Process

Of these six, the first four were directed principally to gasoline production through the olefin oligomerization reaction. A short list of advantages and disadvantages is presented below:

Process Name	Advantages	Disadvantages
OXCO	- Gasoline and Diesel are the main products. - Uses on-site natural gas resources.	- Its economic viability is very sensitive to international market prices. - Demands an Air Separation Unit for pure O_2 production.
UCC	- Uses OCM and steam cracker reactor to produce olefins and heavier paraffins for gasoline production. - It is more like classical refinery process using natural gas (methane) as raw material.	- There is no easy information source available in the literature reviews (journals). - Demands pure O_2 and CH_4 as raw material; this means that no natural gas is used directly.
ARCO	- Uses natural gas directly as an on-site raw material. - Gasoline and LPG are the final products, as an alternative to the oil refinery production process.	- Requires olefin conversion, and this aspect is a waste for the C_2H_4 production goal of the OCM reactor product. - Its economic viability is very sensitive to the international gasoline and LPG market prices.
Suzuki	- Use of natural gas as an on-site raw material. - Gasoline is the final product.	- Requires at least three (3) different reactor types: OCM, Alkanes and Oligomerization. - Its economic viability is very sensitive to the international gasoline market prices.

7.1   Co-generation Process

Starting from the initial schematics shown in Figure 7.1, it was successfully achieved the process flow diagram model for the co-generation process using the OCM reaction (Figure 7.2).
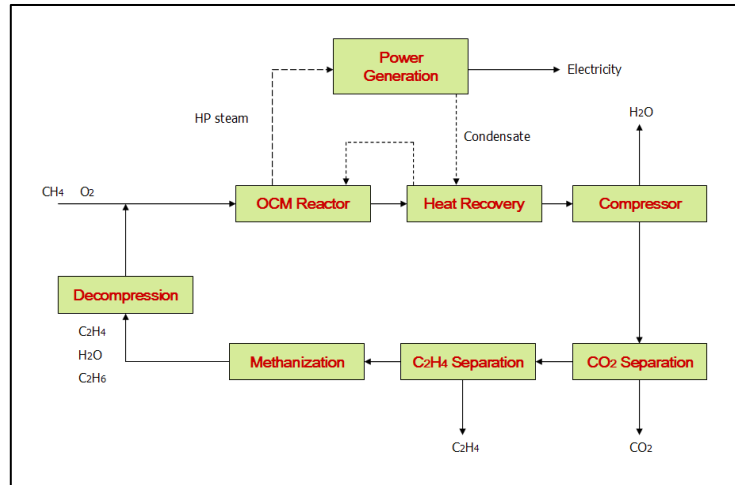
Figure 7.1: Initial OCM co-generation scheme to ethylene and electricity
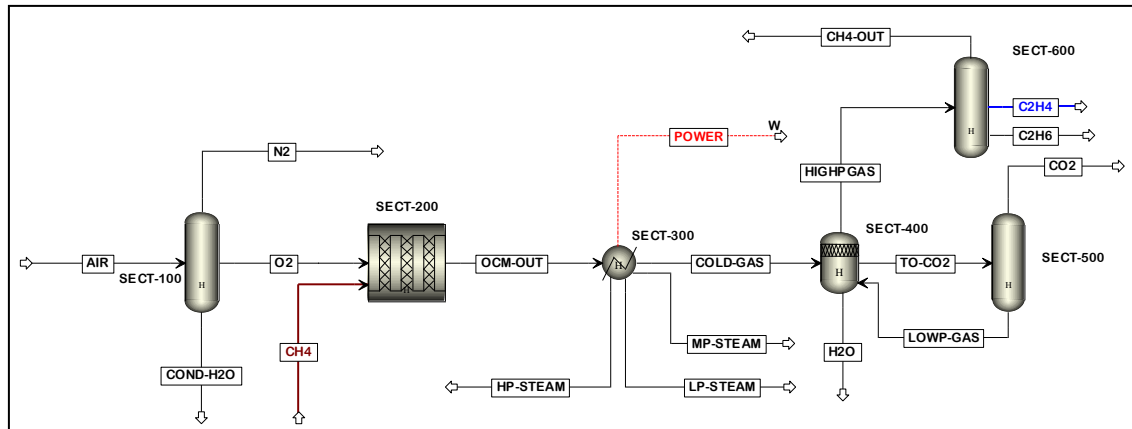
Figure 7.2: Proposed OCM schematic to produce ethylene and electricity

Despite having annually average ethylene sales about 490 million Euros, exceeding the annual production costs (376 million Euros), annual cash flows are not enough to consider the process economically profitable. This process requires large amounts of energy to be implemented and the electricity demand is almost the

same produced. Payout period is too high, more than 15 years, meaning that co-generation process has a negative profitability index value, which proves then that the project appears not to be profitable.

7.2   Ethylene, Formaldehyde and Electricity Co-generation Process

The principal difference of this process, compared to that proposed by Schwittay [2], is in the separation process of the ethylene produced by the OCM reaction before using the unreacted methane for formaldehyde production.

As another contribution, this alternative process requires the same amount of water used for cooling the compressor stages in Air Separation Unit, suitable to be used for heat recovery and electricity production.

As the main disadvantage it can be mention the low methane conversion in the formaldehyde production reactor. Also the process demands an energy-waste procedure for decompressing the non-reacted methane before the formaldehyde reaction, since this reaction is carried out at atmospheric pressure.

The comparison of this alternative process with the original OCM process has resulted in a payout period of 8 years. Besides this promising payout period, the profitability index for this process is below zero.

7.3   Ethylene, Formaldehyde and Methanol Process

Because the non-convincing economic results for the processes discussed above, it was decided to use the remaining unreacted methane, from the formaldehyde reactor, and together with the syngas produced in the OCM reaction ($CO + H_2$) carrying out a methanol production process, using this raw material discarded from the above reactions. The cost is zero, as they are waste streams; so that the additional investment required was applied to the reactors necessary for the production of synthesis gas and methanol.

The economic analysis of the processes studied here has shown that it is feasible to implement a process that combines OCM reaction (for ethylene production) and oxygenates generation (formaldehyde and methanol), via synthesis gas, taking advantage of low natural gas prices offered by Venezuela. Payout period, 9 years, and profitability index of 1.1953 confirm this assertion.

Initial estimates made to locate the probable region for the installation of this plant have confirmed Venezuela as the right place. The country has the lowest prices of the raw material necessary for the OCM process, natural gas, in addition to have the highest potential production of South America.

7.4 Future Work

Studies on the OCM reaction have not been left alone in ethylene production by improving catalysts to achieve better conversion and selectivity values towards C_2+ products. New catalytic processes have been proposed for exploiting the energy from the exothermic OCM reaction. A process concept called tri-reforming of methane has been proposed using CO_2 in the flue gases from fossil fuel based power plants without CO_2 separation [3]. The proposed tri-reforming process is a synergetic combination of CO_2 reforming, steam reforming, and partial oxidation of methane in a single reactor for effective production of industrially useful synthesis gas (syngas). New reactor concepts have appeared for very promising application of auto-thermal reactors, coupling endothermic and exothermic reactions, where the product of the endothermic reaction is the desired one. Therefore, a reactor in which oxidative coupling of methane (OCM) and steam re-forming of methane (SRM) reactions take place simultaneously was modeled [4].

Finally, carbon dioxide reforming of methane or dry reforming of methane (DRM) to synthesis gas has lately attracted renewed interest [5]. An advantage of producing synthesis gas by this route, instead of using steam reforming or partial oxidation, is the low H_2/CO ratio obtained, which is of particular interest in the

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synthesis of valuable oxygenated products, such as alcohols and aldehydes. Kinetic models have been developed for the mixed (steam and dry) reforming of methane using a wide variety of catalysts [6 – 8].

Far from being considered an outdated reaction, the potential for the OCM reaction has a promising future as long as new catalysts and processes are found to make use of the exothermic energy of this reaction, taking advantage to the maximum use of methane and consequently the natural gas.

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List of Activities for UNICAT Research Area C: Complex Reaction Engineering

Process simulation with hierarchic models
C3.3 Process synthesis - Design of process alternatives
Coordinators: Prof. G. Wozny; Dr. H. Arellano-Garcia
PhD-Student: Daniel Salerno

PAPERS PUBLISHED:

1. Ethylene Separation by Feed-Splitting from Light Gases. Daniel Salerno, Harvey Arellano-Garcia, Günter Wozny. (Energy Journal **36** (2011) 4518 - 4523).

2. Techno-economic analysis for ethylene, and Oxygenates production using the oxidative coupling of methane reaction. Daniel Salerno, Stanislav Jašo, Harvey Arellano-Garcia, Günter Wozny. (AIDIC Conference Series, Vol. 10, 2011) ISBN 978-88-95608-58-7.

3. Techno-economic analysis of integrating the methane oxidative coupling and methane reforming processes. Hamid Reza Godini, Shengnan Xiao, Stanislav Jašo, Steffen Stünkel, Daniel Salerno, Nghiem Xuan Son, Shankui Song, Günter Wozny. (Fuel Processing Technology, 2012). http://dx.doi.org/10.1016/j.fuproc.2012.10.002

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2. Oral Presentation at 9° CONGRESO INTERAMERICANO DE COMPUTACIÓN APLICADA A LA INDUSTRIA DE PROCESOS CAIP'2009, 25 al 28 de Agosto de

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3. Oral Presentation at 2009 AIChE Annual Meeting Conference Proceedings on CD-ROM. Nashville, TN, November 8 – 13, 2009. ISBN: 978-0-8169-1058-6. "*Performance Evaluation of Biomass Co-Gasification with Coal*". Xiaotao Zhang, Daniel Salerno, Harvey Arellano-Garcia, Günter Wozny.

4. Oral Presentation at 2010 AIChE Annual Meeting Conference Proceedings on CD-ROM. Salt Lake City, UT, November 7- 12, 2010. "*An Alternative Process for Oxidative Methane Coupling for Ethylene, Electricity and Formaldehyde Production*". Daniel Salerno, Harvey Arellano-Garcia, Günter Wozny.

5. Oral Presentation at ESCAPE-21 European Symposium on Computer-Aided Process Engineering. "*Techno-Economic Analysis for Ethylene and Methanol Production from the Oxidative Coupling of Methane Process*". Daniel Salerno, Harvey Arellano-Garcia, Günter Wozny. Chalkidiki, Greece, 29 May – 1st June, 2011.

6. Oral Presentation at ICheap-10, the 10th International Conference on Chemical and Process Engineering. "*Techno-Economic Analysis for Ethylene and Oxygenates Products from the Oxidative Coupling of Methane Process*". Daniel Salerno, Harvey Arellano-Garcia, Günter Wozny. Florence, Italy, 8-11 May, 2011.

7. Oral Presentation at 11th International Symposium on PSE-2012, Singapore, July 15 – 19, 2012. "Techno-Economic Analysis for the Synthesis of Downstream Processes from the Oxidative Coupling of Methane Reaction". Daniel Salerno, Harvey Arellano-Garcia, Günter Wozny. Edited by I.A. Karimi and Rajagopalan Srinivasan, Year: 2012.

Declaration

I, Daniel Salerno herewith declare that I have produced this thesis without the prohibited assistance of third parties and without making use of aids other than those specified; notions taken over directly or indirectly from other sources have been identified as such. This paper has not previously been presented in identical or similar form to any other German or foreign examination board.

The thesis work was conducted from October 2008 until September 2011 under the supervision of Prof. Dr. -Ing Günter Wozny at the chair for Process Dynamics and Operation (DBTA) at the TU-Berlin.

Erklärung

„Ich erkläre an Eides Statt, dass die vorliegende Dissertation in allen Teilen von mir selbständig angefertigt wurde und die benutzen Hilfsmittel vollständig angegeben worden sind."

„Veröffentlichungen von irgendwelchen Teilen der vorliegenden Dissertation sind von mir nicht / wie folgt vorgenommen worden."

"Weiter erkläre ich, daß ich nicht schon anderweitig einmal die Promotionsabsicht angemeldet oder ein Promotionser-öffnungsverfahren beantragt habe."

Berlin, 12.04.2012

Daniel Salerno

Appendix I: Original OCM Process
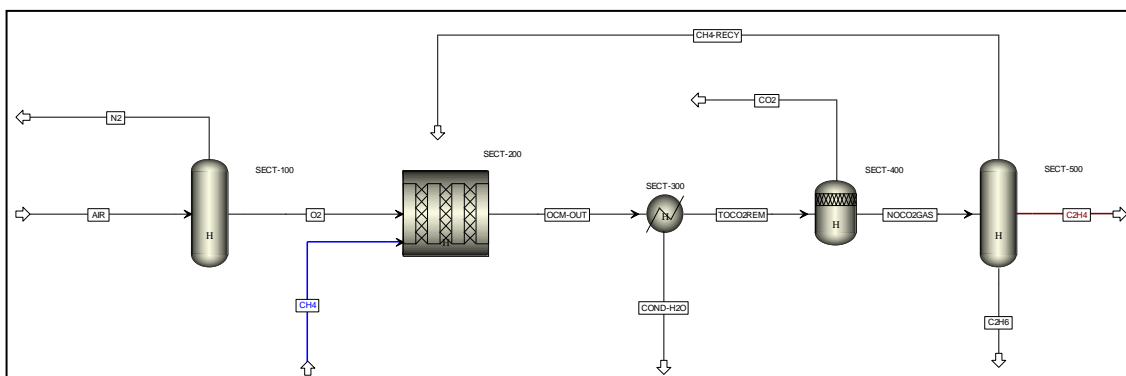
Variable	AIR	C2H4	C2H6	CH4	CH4-RECY	CO2
Temperature (°C)	32.00	-8.40	9.20	25.00	51.80	107.70
Pressure (bar)	1.013	33.800	33.805	1.200	34.990	1.013
Mole Flow (kmol/hr)	25899.75	588.00	40.63	6735.00	5335.00	7715.30
Mass Flow (kg/hr)	750000.00	16501.45	1205.23	108047.99	67643.93	159491.20
Volume Flow (m^3/hr)	648301.01	223.27	3.28	138772.96	4041.65	239591.68
Mass Flow (kg/hr)						
Ar	9311.79	0.00	0.00	0.00	88.81	0.09
O_2	174039.80	0.00	0.00	0.00	0.00	0.00
N_2	566648.41	0.00	0.00	0.00	0.00	0.00
H_2O	0.00	0.00	0.04	0.00	0.00	124690.63
CH_4	0.00	0.00	0.00	108047.99	59057.26	55.31
C_2H_6	0.00	87.07	976.99	0.00	0.09	1.06
C_2H_4	0.00	16414.38	228.16	0.00	344.03	48.16
CO_2	0.00	0.00	0.00	0.00	0.00	34561.14
CO	0.00	0.00	0.00	0.00	5225.22	3.80
H_2	0.00	0.00	0.00	0.00	2928.52	2.36
MEA	0.00	0.00	0.03	0.00	0.00	128.65
Molecular Weight	28.96	28.06	29.67	16.04	12.68	20.67

Variable	COND-H2O	N2	NOCO2GAS	O2	OCM-OUT	TOCO2REM
Temperature (°C)	85.40	14.60	40.00	14.60	486.50	40.00
Pressure (bar)	1.106	1.100	9.950	1.100	1.150	10.090
Mole Flow (kmol/hr)	3272.75	21354.03	6009.32	3336.82	10874.46	7601.71
Mass Flow (kg/hr)	58960.44	604518.17	86174.40	106791.77	214841.83	155881.39
Volume Flow (m^3/hr)	74.26	464301.88	15580.41	72509.63	597270.26	19264.18
Mass Flow (kg/hr)						
Ar	0.00	9190.68	88.81	88.90	88.90	88.90
O_2	0.00	28678.99	0.00	106702.87	0.00	0.00
N_2	0.00	566648.50	0.00	0.00	0.00	0.00
H_2O	58958.35	0.00	822.86	0.00	59918.46	960.11
CH_4	0.21	0.00	59057.26	0.00	59112.78	59112.57
C_2H_6	0.01	0.00	1064.15	0.00	1065.22	1065.21
C_2H_4	0.11	0.00	16986.58	0.00	17034.85	17034.74
CO_2	1.76	0.00	0.00	0.00	69461.71	69459.95
CO	0.00	0.00	5225.22	0.00	5229.03	5229.03
H_2	0.01	0.00	2928.52	0.00	2930.89	2930.88
MEA	0.00	0.00	1.00	0.00	0.00	0.00
Molecular Weight	18.02	28.31	14.34	32.00	19.76	20.51

Appendix II: Ethylene, Formaldehyde and Electricity Cogeneration Process using the OCM Reaction
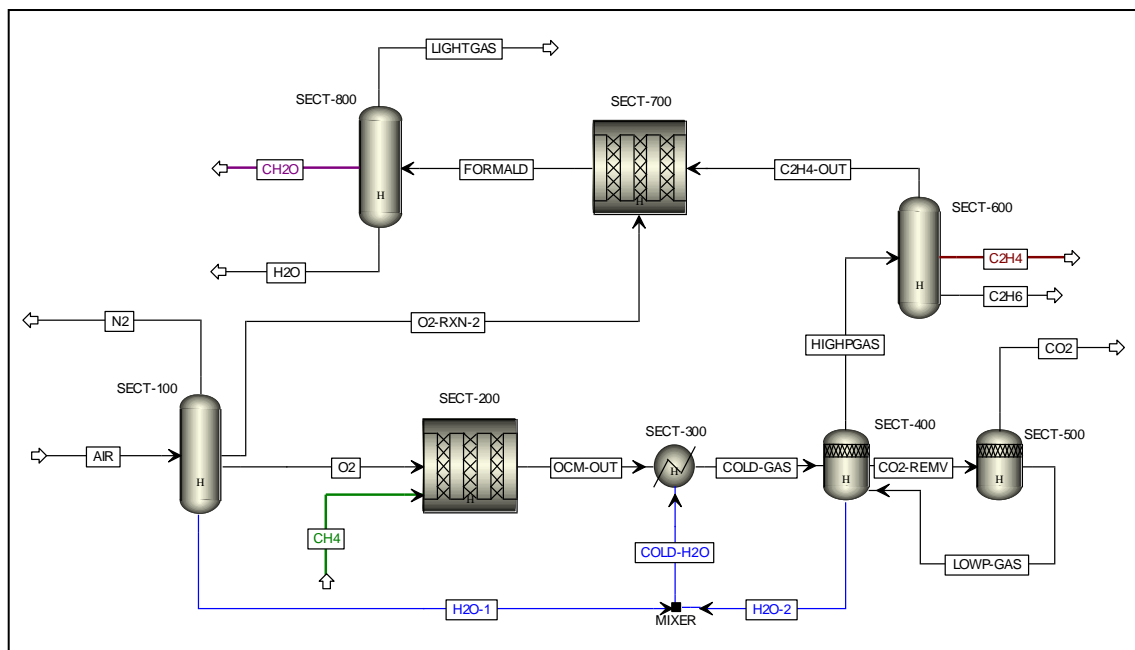
Variable	AIR	C2H4	C2H4-OUT	C2H6	CH2O	CH4
Temperature (°C)	32.00	-6.80	-18.80	-2.70	6.70	25.00
Pressure (bar)	1.013	33.800	34.990	33.802	2.800	1.200
Mole Flow (kmol/hr)	25896.76	479.48	4318.55	84.23	102.00	5650.00
Mass Flow (kg/hr)	750000.00	13452.92	50926.82	2412.72	3054.76	90641.59
Volume Flow (m^3/hr)	648226.18	187.80	2494.26	6.37	3.98	116416.81
Mass Flow kg/hr						
Ar	9662.45	0.00	97.24	0.00	0.00	0.00
O_2	173870.56	0.00	0.00	0.00	0.00	0.00
N_2	566466.98	0.00	0.00	0.00	0.00	0.00
H_2O	0.00	0.00	0.00	0.03	11.89	0.00
CH_4	0.00	4.44	43745.20	0.00	0.00	90641.59
C_2H_4	0.00	13373.19	0.00	1671.56	0.00	0.00
C_2H_6	0.00	75.29	0.00	741.11	0.00	0.00
CO_2	0.00	0.00	0.00	0.00	0.04	0.00
CO	0.00	0.00	4181.42	0.00	0.00	0.00
H_2	0.00	0.00	2902.96	0.00	0.00	0.00
MEA	0.00	0.00	0.00	0.03	0.00	0.00
CH_2O	0.00	0.00	0.00	0.00	3042.84	0.00
Molecular Weight	28.96	28.06	11.79	28.64	29.95	16.04

Variable	CO2	CO2-REMV	COLD-GAS	COLD-H2O	FORMALD	H2O
Temperature (°C)	108.40	40.00	68.00	32.30	217.70	131.10
Pressure (bar)	1.490	10.557	1.110	1.013	1.380	2.803
Mole Flow (kmol/hr)	7977.15	6572.76	8548.84	5501.16	6121.69	1802.19
Mass Flow (kg/hr)	165826.16	139871.16	175471.38	99105.62	110640.34	32474.95
Volume Flow (m^3/hr)	168263.90	15903.49	217749.12	100.50	180854.80	36.73
Mass Flow kg/hr						
Ar	0.11	97.35	97.35	0.00	132.49	0.00
O_2	0.00	0.00	0.00	0.04	2.28	0.00
N_2	0.00	0.00	0.00	0.01	0.00	0.00
H_2O	128292.28	796.23	36395.32	99104.32	32466.91	32455.02
CH_4	47.74	43797.38	43797.42	0.05	28470.88	0.00
C_2H_4	49.78	15094.55	15094.57	0.03	0.00	0.00
C_2H_6	0.95	817.35	817.35	0.00	0.00	0.00
CO_2	37289.60	72177.65	72178.71	1.06	42936.05	0.00
CO	3.55	4184.96	4184.96	0.00	665.69	0.00
H_2	2.73	2905.69	2905.69	0.00	2902.96	0.00
MEA	139.14	0.00	0.00	0.11	0.00	0.00
CH_2O	0.00	0.00	0.00	0.00	3063.09	19.93
Molecular Weight	20.79	21.28	20.53	18.02	18.07	18.02

Variable	H2O-1	H2O-2	HIGHPGAS	LIGHTGAS	LOWP-GAS
Temperature (°C)	30.10	30.20	40.00	91.40	40.00
Pressure (bar)	1.013	3.420	35.129	1.350	9.950
Mole Flow (kmol/hr)	3500.00	2001.16	4894.49	4217.50	4919.57
Mass Flow (kg/hr)	63053.53	36052.10	67013.27	75110.63	67465.15
Volume Flow (m^3/hr)	74.55	42.63	3501.00	94637.47	12773.38
Mass Flow kg/hr					
Ar	0.00	0.00	97.24	132.49	97.24
O_2	0.04	0.00	0.00	2.28	0.00
N_2	0.01	0.00	0.00	0.00	0.00
H_2O	63053.48	36050.84	220.16	0.00	671.92
CH_4	0.00	0.05	43749.63	28470.88	43749.64
C_2H_4	0.00	0.03	15044.76	0.00	15044.76
C_2H_6	0.00	0.00	816.40	0.00	816.40
CO_2	0.00	1.06	0.00	42936.01	0.00
CO	0.00	0.00	4181.42	665.69	4181.42
H_2	0.00	0.00	2902.96	2902.96	2902.96
MEA	0.00	0.11	0.70	0.00	0.81
CH_2O	0.00	0.00	0.00	0.32	0.00
Molecular Weight	18.02	18.02	13.69	17.81	13.71

Variable	N2	O2	O2-RXN-2	OCM-OUT
Temperature (°C)	14.60	14.60	14.60	484.90
Pressure (bar)	1.100	1.100	1.100	1.150
Mole Flow (kmol/hr)	21351.04	3337.32	1208.40	9769.44
Mass Flow (kg/hr)	604515.88	106809.74	38674.32	197461.13
Volume Flow (m^3/hr)	464236.32	72520.61	26258.70	535366.75
Mass Flow kg/hr				
Ar	9529.85	97.35	35.25	97.35
O_2	28518.96	106712.39	38639.07	0.00
N_2	566467.07	0.00	0.00	0.00
H_2O	0.00	0.00	0.00	58384.77
CH_4	0.00	0.00	0.00	43797.44
C_2H_4	0.00	0.00	0.00	15094.59
C_2H_6	0.00	0.00	0.00	817.35
CO_2	0.00	0.00	0.00	72178.98
CO	0.00	0.00	0.00	4184.96
H_2	0.00	0.00	0.00	2905.69
MEA	0.00	0.00	0.00	0.00
CH_2O	0.00	0.00	0.00	0.00
Molecular Weight	28.31	32.01	32.01	20.21

Appendix III: Ethylene, Formaldehyde and Methanol Process using the OCM Reaction
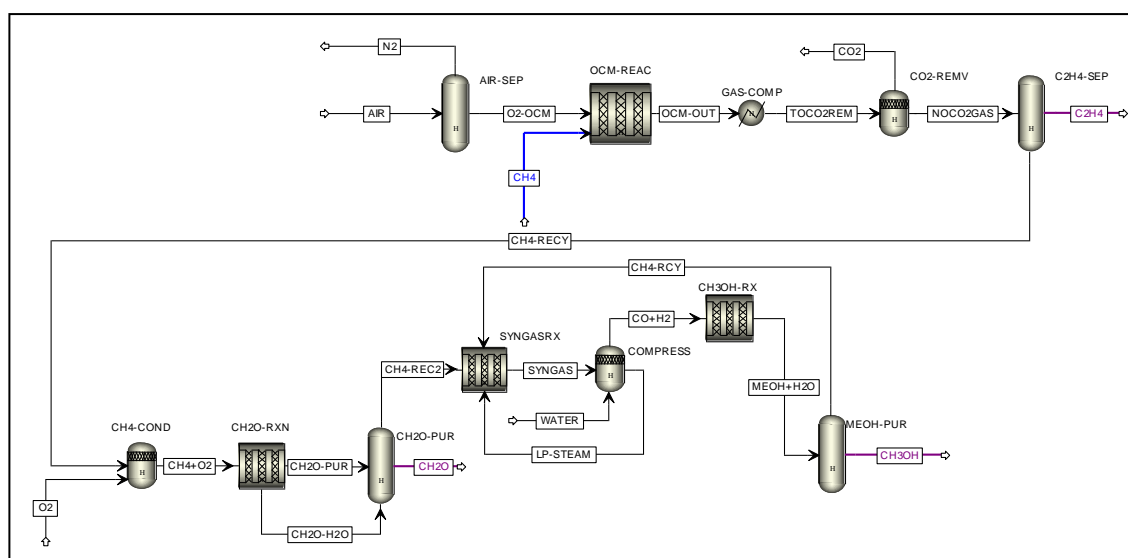
Variable	AIR	C2H4	CH2O	CH2O-H2O	CH2O-PUR	CH3OH
Temperature (°C)	32.00	-8.30	54.10	57.90	-108.80	132.80
Pressure (bar)	1.013	33.800	11.800	1.027	1.020	9.000
Mole Flow (kmol/hr)	25906.86	592.50	163.00	2170.00	5185.05	266.00
Mass Flow (kg/hr)	750000.00	16630.51	4887.73	41062.86	93695.50	8517.23
Volume Flow (m^3/hr)	648479.00	225.04	7.27	46.55	68868.69	13.16
Mass Flow (kg/hr)						
Ar	8279.42	0.00	0.00	0.00	90.85	0.00
O_2	174916.57	0.00	0.00	0.00	14.56	0.00
N_2	566804.01	0.00	0.00	0.00	0.00	0.00
H_2O	0.00	0.00	9.84	36138.81	0.00	7.69
CH_4	0.00	0.08	0.00	0.00	41843.95	0.00
C_2H_6	0.00	130.05	0.00	0.00	0.00	0.00
C_2H_4	0.00	16500.37	0.00	0.00	0.00	0.00
CO_2	0.00	0.00	0.00	0.00	47898.02	0.01
CO	0.00	0.00	0.00	0.00	885.53	0.00
H_2	0.00	0.00	0.00	0.00	2928.99	0.00
MEA	0.00	0.00	0.00	0.00	0.00	0.00
CH_2O	0.00	0.00	4877.89	4924.05	33.60	0.00
CH_3OH	0.00	0.00	0.00	0.00	0.00	8509.54
Molecular Weight	28.95	28.07	29.99	18.92	18.07	32.02

Variable	CH3OH	CH4	CH4+O2	CH4-RCY	CH4-REC2	CH4-RECY
Temperature (°C)	132.80	25.00	25.00	50.00	162.70	51.80
Pressure (bar)	9.000	1.200	1.150	1.200	5.600	34.990
Mole Flow (kmol/hr)	266.00	6735.00	6543.91	6555.70	5185.05	5335.00
Mass Flow (kg/hr)	8517.23	108047.99	106324.23	115244.12	93695.50	67635.82
Volume Flow (m^3/hr)	13.16	138772.96	140900.37	146755.12	33529.86	4042.06
Mass Flow (kg/hr)						
Ar	0.00	0.00	90.85	94.80	90.85	66.67
O_2	0.00	0.00	37418.41	0.00	14.56	0.00
N_2	0.00	0.00	0.00	0.00	0.00	0.00
H_2O	7.69	0.00	467.60	73.05	0.00	0.00
CH_4	0.00	108047.99	59051.12	20508.14	41843.95	59051.12
C_2H_6	0.00	0.00	0.00	0.00	0.00	0.02
C_2H_4	0.00	0.00	0.00	0.00	0.00	364.06
CO_2	0.01	0.00	1142.29	22753.42	47898.02	0.00
CO	0.00	0.00	5224.97	66353.57	885.53	5224.97
H_2	0.00	0.00	2928.99	4764.09	2928.99	2928.99
MEA	0.00	0.00	0.00	0.00	0.00	0.00
CH_2O	0.00	0.00	0.00	0.73	33.60	0.00
CH_3OH	8509.54	0.00	0.00	696.33	0.00	0.00
Molecular Weight	32.02	16.04	16.25	17.58	18.07	12.68

Variable	CO+H2	CO2	LP-STEAM	MEOH+H2O	N2	NOCO2GAS
Temperature (°C)	90.00	108.50	247.80	175.70	14.60	40.00
Pressure (bar)	30.145	1.490	5.100	29.990	1.100	9.950
Mole Flow (kmol/hr)	7415.57	7716.12	2370.90	7523.75	21361.14	6008.65
Mass Flow (kg/hr)	109678.94	159512.35	42712.43	140013.01	604524.18	86147.61
Volume Flow (m^3/hr)	7459.22	162802.88	19786.68	9344.64	464443.93	15578.80
Mass Flow (kg/hr)						
Ar	95.58	0.07	0.00	95.58	8188.51	66.67
O_2	0.00	0.00	0.00	0.00	29531.58	0.00
N_2	0.00	0.00	0.00	0.00	566804.09	0.00
H_2O	3220.48	124701.73	42712.43	9561.35	0.00	822.86
CH_4	20926.57	54.88	0.00	20926.48	0.00	59051.20
C_2H_6	0.00	1.05	0.00	0.00	0.00	1064.35
C_2H_4	0.00	47.71	0.00	0.00	0.00	16987.57
CO_2	13799.73	34571.98	0.00	28643.02	0.00	0.00
CO	64937.61	3.78	0.00	66659.07	0.00	5224.97
H_2	6645.01	2.35	0.00	4764.09	0.00	2928.99
MEA	0.00	128.55	0.00	0.00	0.00	1.00
CH_2O	33.59	0.00	0.00	33.59	0.00	0.00
CH_3OH	20.39	0.00	0.00	9329.83	0.00	0.00
Molecular Weight	14.79	20.67	18.02	18.61	28.30	14.34

Variable	O2	O2-OCM	OCM-OUT	SYNGAS	TOCO2REM	WATER
Temperature (°C)	14.60	14.60	484.10	575.00	40.00	35.00
Pressure (bar)	1.100	1.100	1.150	5.000	10.090	5.100
Mole Flow (kmol/hr)	1208.91	3336.82	10874.57	10618.68	7601.26	2370.90
Mass Flow (kg/hr)	38688.41	106787.36	214837.42	167391.42	155865.04	42712.43
Volume Flow (m^3/hr)	26265.98	72507.68	595335.68	149820.09	19263.00	43.40
Mass Flow (kg/hr)						
Ar	24.18	66.74	66.74	95.59	66.73	0.00
O_2	38664.23	106720.62	0.00	0.00	0.00	0.00
N_2	0.00	0.00	0.00	0.00	0.00	0.00
H_2O	0.00	0.00	59926.78	60915.17	960.05	42712.43
CH_4	0.00	0.00	59106.63	20927.23	59106.09	0.00
C_2H_6	0.00	0.00	1065.42	0.00	1065.40	0.00
C_2H_4	0.00	0.00	17035.57	0.00	17035.28	0.00
CO_2	0.00	0.00	69476.19	13802.05	69471.40	0.00
CO	0.00	0.00	5228.75	64937.88	5228.74	0.00
H_2	0.00	0.00	2931.36	6645.05	2931.35	0.00
MEA	0.00	0.00	0.00	0.00	0.00	0.00
CH_2O	0.00	0.00	0.00	33.64	0.00	0.00
CH_3OH	0.00	0.00	0.00	34.81	0.00	0.00
Molecular Weight	32.00	32.00	19.76	15.76	20.51	18.02