

A SYSTEMS FRAMEWORK FOR SHALE GAS MONETIZATION

A Thesis

by

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ABSTRACT

The aim of this study is to provide a systems perspective on shale gas monetization to fuels and chemicals. The properties of shale reservoirs and shale gas production processes will be discussed briefly before focusing on four main building blocks of the chemicals industry: methanol, ethylene, propylene, and butadiene. For each of these building blocks, the main derivatives and their chemical processes are discussed as well as the changes incurred on their markets because of the shale gas boom. In addition, the chemistry of gas-to-liquids (GTL) technology and existing commercial applications of it are detailed. Also, an overview of existing and proposed plants for each of the five monetization pathways will be given. Based on this survey, an optimization formulation is developed and solved to determine the optimal pathways of a given shale gas resource. The objective of the optimization formulation is to maximize profit based on capital and operating costs of the given processes, feedstock prices, the sales prices of the produced chemicals while accounting for supply, demand, technical, and environmental factors (e.g., CO₂). A case study is solved for the Barnett and Eagle Ford shale formations.

DEDICATION

This work is dedicated to my parents, Firas Al-Douri and Zaineb Abdullah, for their continued love and support.

Also, for my two brothers, Abdulhamid and Omar, for being the best brothers anyone can have.

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NOMENCLATURE

MTA = Metric tons per annum

MMT = Million metric tons

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CHAPTER I

INTRODUCTION AND LITERATURE REVIEW

Traditionally, the optimization of chemical processes has concentrated on maximizing an economic criterion (e.g. profit, sales). Recently, there has been heightened awareness of the need to incorporate environmental and safety aspects in the decision-making process as well (Grossmann and Guillén-Gosálbez, 2010). As a result, the goal in process systems engineering (PSE) has been expanded from maximizing profitability to finding alternatives that are also more sustainable and inherently safe.

Environmental and safety factors can be included in PSE applications at different levels of the decision-making process. **Fig. 1.1** illustrates the breakdown of the hierarchical levels in PSE applications in terms of their spatial and temporal scale. As it can be seen from the figure, the bottom section of the pyramid corresponds to the optimization of single units of equipment, production lines, and entire chemical plants. On the other hand, the top section corresponds to multi-site problems involving a wider temporal and spatial scope. While the previous focus in the PSE community has been on the development of optimization tools for single-site applications, recent advances in optimization theory and software application have allowed for an expansion of the analysis beyond the manufacturing stage (Grossmann and Guillén-Gosálbez, 2010). Consequently, supply chain management (Shapiro, 2001) and enterprise-wide optimization (Grossmann, 2005) have recently emerged as active areas of research.

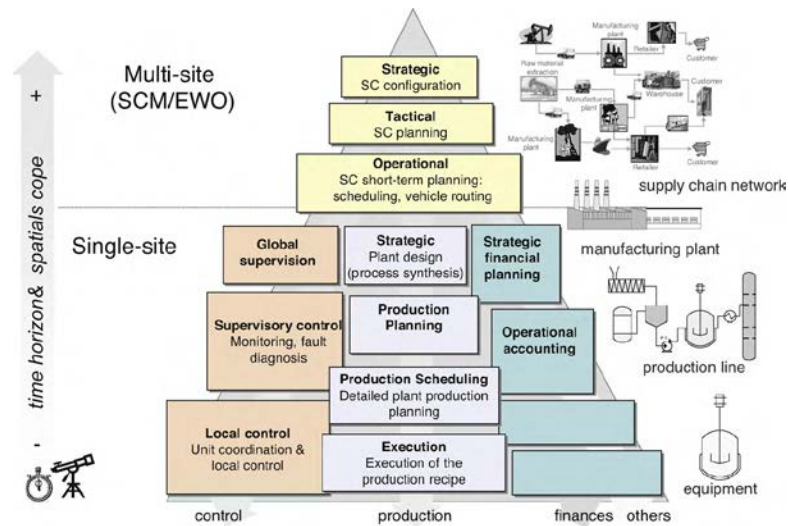


Fig. 1.1- Decision-support levels in process systems engineering. Reprinted from Grossmann and Guillen-Gosalbez (2010).

Papageorgiou (2009) presented a critical review of mathematical programming models for supply chain optimization problems at the strategic and tactical levels. As shown in Fig. 1, this means that the reviewed works will focus on supply chain design and planning/scheduling. Sabri and Beamon (2000) developed a steady-state mathematical model for a multi-objective supply chain model that combined strategic and operational design and planning decisions. Tsiakis et al. (2001) described a mixed integer linear programming model to determine production capacity allocation among different products, optimal layout and flow allocations of the distribution network by minimizing an annualized network cost. Also, Tsiakis and Papageorgiou (2008) developed a mixed integer linear program (MILP) model to determine the optimal configuration of a production and distribution network subject to operational and financial constraints. The authors used a case study for the coatings business unit of a global specialty chemicals manufacturer to prove the applicability of their approach.

Pooley (1994) presented the results of a MILP model used by the Ault Foods company to restructure their supply chain. In this work, the objective of the company was to minimize the total operating cost of a production and distribution network. Camm et al. (1997) combined integer programming, network optimization, and geographical information systems (GIS) for Procter and Gamble's North American supply chain. The authors reported annual savings of \$200 million. Ferrio and Wassick (2008) presented a MILP model capable of optimizing a multi-product supply chain network made up of production sites, an arbitrary number of echelons of distribution centers, and customer sites. In their work, the authors emphasized the redesign of existing supply chain networks by dealing with individual customer demand to address the customer's preferred mode of transport at each location. By doing so, the model avoids lumping customer demand into zones.

Elia et al. (2011) developed a mixed-integer nonlinear programming (MINLP) formulation to analyze U.S. energy supply chain network for hybrid coal, biomass, and natural gas to liquids (CBGTL) facilities. The model in the study selects the optimal locations of these facilities, their feedstock combination, and the size of each facility in a way that gives the minimum overall production cost. The authors present two case studies to investigate the effects of various technologies and hydrogen prices and perform life cycle analysis on each facility in the supply chain network. They conclude that U.S. fuel demands can be fulfilled with an excess of 50% emissions reduction compared to petroleum-based products.

Floudas et al. (2012) provided a detailed review of the key contributions made within the energy community with regards to thermochemically based hybrid energy systems for liquid transportation fuels. The authors were the first to provide a comprehensive description of the contributions for the supply chains of single-feedstock energy systems and hybrid-feedstock energy systems.

Gao and You (2015) used a mixed-integer nonlinear programming (MINLP) approach to address the life cycle economic and environmental optimization of a shale gas supply chain network based on the Marcellus shale play. The authors proposed a model covering the well-to-wire life cycle of electricity generated from shale gas and the resulting Pareto-optimal frontier revealed the trade-off between the economic and environmental objectives.

Onel et al (2015) investigated the co-production of liquid transportation fuels and olefins from a natural gas feedstock. The authors modeled a superstructure of alternatives (multiple natural gas conversion routes, hydrocarbon production and upgrading methods, olefins purification options) as a MINLP. This program was solved to goal optimality using a branch-and-bound framework.

Cafaro and Grossman (2014) addressed the long-term planning of the shale gas supply chain by presenting a MINLP. The model focused on determining aspects of the upstream portion of the supply chain such as the number of wells to drill at every location and the size of gas processing plants, among other items. The objective of this model was to maximize the net present value of the project by optimally determining the

previously mentioned items. The authors followed a decomposition approach based on successively refining a piecewise linear approximation of the objective function.

Garcia and You (2015) identified the challenges and opportunities in supply chain design and optimization. The authors determined three major areas where knowledge gaps exist: multi-scale challenges, multi-objective and sustainability challenges, and multi-player challenges. Then, they proceeded to provide an overview of these areas, a description of the technical challenges that exist in each area, and a perspective on how to address these challenges in supply chain design.

Environmental Considerations

Green supply chain management (GrSCM) is a new discipline that has evolved recently through the combination of environmental management and supply chain management into a single framework (Grossmann and Guillén-Gosálbez, 2010). Srivastava (2007) has done an exhaustive review of the work done in GrSCM and identified two main types of approaches in this discipline: empirical studies and mathematical modeling. Within the latter group, there exist a variety of tools and techniques such as mathematical programming (LP, NLP, MILP, MINLP, and dynamic programming), Markov chains, Petri nets, input-output models, game theory, fuzzy logic data envelopment analysis (DEA), descriptive statistics and simulations.

The above-mentioned techniques can be applied to the design of sustainable processes following two different approaches. The first, which has been the most common approach, has included them as additional constraints to be satisfied by the optimization model. However, Cano-Ruiz and McRae (1998) pointed out that

environmental concerns should be regarded as new design objectives and not merely as constraints on operations. The latter approach is particularly suited for considering environmental issues at the design stage, since it can lead to both environmentally and economically conscious strategic investment planning (Hugo and Pistikopoulos, 2005).

Unfortunately, this approach leads to more complex problems that require the use of multi-objective optimization methods, at times in conjunction with some of the mathematical tools previously described. Azadeh et al. (2015) used a multi-objective multi-period fuzzy linear programming model that considered both economic and environmental objectives to evaluate and optimize a natural gas supply chain.

One of the most important topics considered in literature is the definition of a suitable metric to assess the environmental performance of a process or product. Researchers have not yet reached an agreement to support objective environmental assessments. As a result of this lack of consensus over a general binding value system, a plethora of performance indicators have been evolving over time in order to capture a wide range of environmental effects. Cano-Ruiz and McRae (1998) suggested four main types of environmental objectives according to their exhaustive literature review on these metrics. These environmental objectives are the minimization of: (1) the emissions of pollutants of concern (Chang and Hwang, 1996); (2) the mass of waste generated Hilaly and Sikdar, 1995); (3) the contribution to specific environmental problems (Grossmann et al. 1982); and (4) specific overall indicators of the environmental impact (Cabezas, et al. 1997).

Regardless of the environmental objective followed, it has become clear as of late that the environmental performance of a process should be assessed over its entire life cycle. Traditionally, environmental concerns were included within the decision making process focused at the plant level. While this could lead to decreased environmental impact locally, it can increase the overall damage in other stage of the life cycle of the process (Grossmann et al. 2002). In response to this situation, the life cycle assessment (LCA) methodology arose as a tool to evaluate the environmental loads associated with a product, process, or activity over their entire life cycle (Guinée et al. 2002). This method is based on identifying and quantifying the energy and materials used in a process in order to translate them into a set of meaningful environmental indicators that inform about the impact caused in different categories (i.e., human health, eco-system quality, and resources). The performance achieved in these damage categories can be employed to assess different process alternatives that can be implemented to achieve environmental improvements (Grossmann and Guillén-Gosálbez, 2010).

CHAPTER II

NATURAL GAS VALUE CHAIN

Introduction

In the previous chapter, existing literature on shale gas supply chains was reviewed. In this part of the study, a review of shale gas monetization from a life cycle perspective is presented in three main parts: (1) shale gas treatment and processing, (2) production processes for the major chemical building blocks (methanol, ethylene, and propylene) and their derivatives, and (3) an overview of the current market outlook for these building blocks.

Shale Gas Production Overview

With the recent discovery of unconventional shale gas resources, the potential supply of natural gas has increased significantly. Fig. 2.1 shows the increase in proved shale gas reserves in the United States between 2007 and 2013. Natural gas in shale formations is more difficult to extract than natural gas in conventional ones due to the low permeability of unconventional reservoirs. A combination of horizontal drilling and hydraulic fracturing is used to retrieve the gas from such formations.

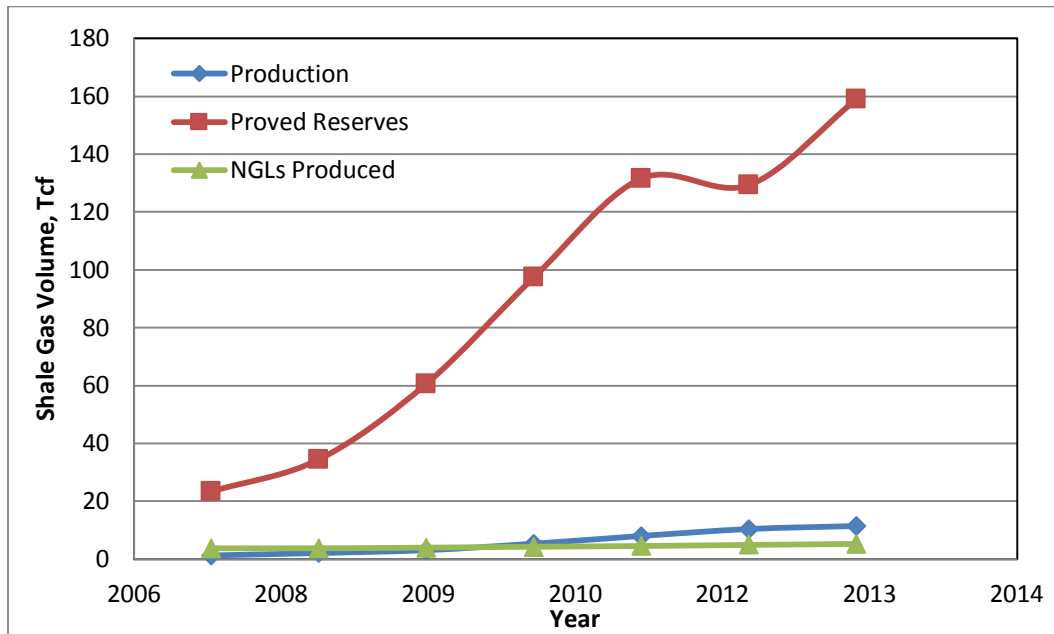


Fig. 2.1- Proved shale gas reserves, production, and NGLs produced in the United States, Tcf (EIA, July 2015).

Shale gas is primarily composed of methane, with heavier hydrocarbons like ethane and propane, in addition to other inorganic gases such as nitrogen, carbon dioxide and hydrogen sulfide, also being present. The composition of the produced gas varies from one formation to another and can also vary between wells located within the same formation.

Production from shale gas plays has increased from 1.3 trillion cubic feet in 2007 to 11.4 trillion cubic feet in 2013, as shown in Fig. 2.1. This accounts for approximately 47% of the total United States natural gas production in 2013 (EIA AEO 2015). With the increase in shale gas production, the volume of the heavier hydrocarbons, also known as natural gas liquids (NGLs), has increased and is expected to reach more than 3.1 MMBD in 2016 (“The Great NGL Surge” Nov. 11, 2011). After several processing and

fractionation steps, the produced NGLs are used by the chemicals industry to produce a variety of derivatives and products which become raw materials for multiple manufacturing sectors (PWC report “Reshaping the US chemicals industry”).

Shale Gas Composition

Shale gas has different compositional makeup depending on the formation, as well as the well it is produced from. This is illustrated in Table 2.1, which shows the composition of different shale plays in volume percent (Noureldin, 2013). The Antrim play has the highest nitrogen content while the Haynesville play has the lowest. The New Albany shale play has the highest amount of carbon dioxide with an average of 7.9 vol% for the tested wells. Also, the carbon content (sum of C1-C3) of the Antrim shale play varies greatly between 32.0 and 90.3 vol%. The Marcellus shale contains the highest amount of carbon with a range of 98.8-99.6 vol%. In the Marcellus shale formation, there is relatively little carbon dioxide and nitrogen but the gas composition varies greatly across the field, in that it contains NGLs in the western portions, while the eastern ones are generally dry. This is illustrated in the data shown in Table 2.1, where wells 1-3 contain 15.0-20.1 vol% of NGLs (C2 and C3), while well 4 contains only 4 vol%. The differences between shale formations highlight the need to assess gas processing operations and the ability of a processing plant to treat a variety of shale gases to pipeline specifications (Speight 2013: Shale Gas Production Processes)

Table 2.1: Shale gas composition (vol%), adapted from Nouredin (2013)

Well	C ₁	C ₂	C ₃	CO ₂	N ₂	Well	C ₁	C ₂	C ₃	CO ₂	N ₂
Antrim Shale Gas						Marcellus Shale Gas					
1	27.5	3.5	1.0		65.0	1	79.4	16.1	4.0	0.1	0.4
2	57.3	4.9	1.9	0.3	5.9	2	82.1	14.0	3.5	0.1	0.3
3	77.5	4.0	0.9	3.3	14.3	3	83.8	12.0	3.0	0.9	0.3
4	85.6	4.3	0.4	9.0	0.7	4	95.5	3.0	1.0	0.3	0.2
Barnett Shale Gas						New Albany Shale Gas					
1	80.3	8.1	2.3	1.4	7.9	1	87.7	1.7	2.5	8.1	
2	81.2	11.8	5.2	0.3	1.5	2	88.0	0.8	0.8	10.4	
3	91.8	4.4	0.4	2.3	1.1	3	91.0	1.0	0.6	7.4	
4	93.7	2.6	0.0	2.7	1.0	4	92.8	1.0	0.6	5.6	
Fayetteville Shale Gas						Haynesville Shale Gas					
1	97.3	1.0	0.0	1.0	0.7	1	95.0	0.1	0.0	4.8	0.1

Shale Gas Processing

After shale gas is extracted, it must undergo a series of processing steps at the wellhead and at a processing plant in order to make it marketable and up to pipeline specifications. In general, shale gas processing has the same steps that are undertaken for conventional gas processing. The sequence consists of the removal of condensates and free water, dehydration, acid gas removal (carbon dioxide and hydrogen sulfide), and nitrogen removal. Then, the gas stream is sent to a de-methanizer which separates NGLs from pipeline-quality natural gas. The pipeline-quality natural gas is taken by transmission pipelines from processing facilities to market centers, where they tie into existing local distribution systems, where it is used for heat, power, and transportation (Goellner, 2012). Fractionation is a process that separates out the NGLs one by one based on their individual normal boiling points, which are shown below in **Table 2.2**. The fractionators used are placed in the following order: de-ethanizer, de-propanizer, de-

butanizer, and butane splitter (separates iso-butane and n-butane) (Speight “Natural Gas: A Basic Handbook” 2007). **Fig. 2.2** is a schematic of the shale gas processing steps outlined above.

Table 2.2: Normal boiling point of natural gas components

Hydrocarbon	Formula	Normal Boiling Point (°C)	Normal Boiling Point (°F)
Methane	CH ₄	-162	-259
Ethane	C ₂ H ₆	-89	-128
Propane	C ₃ H ₈	-42	-44
Butane	C ₄ H ₁₀	-1	30
Pentane	C ₅ H ₁₂	36	97
Hexane	C ₆ H ₁₄	68	154
C ₇ + and heavier		98+	209+

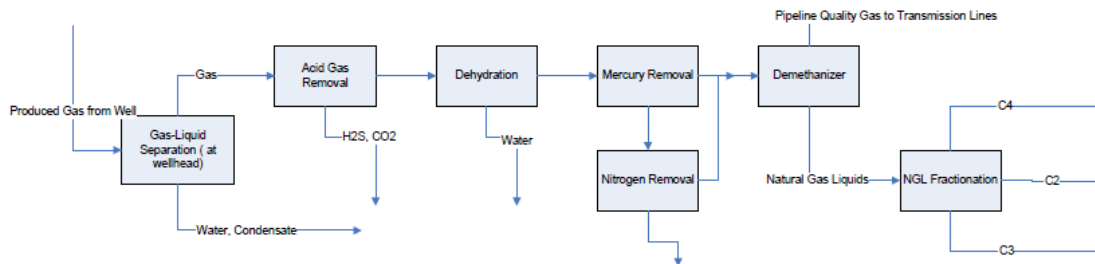


Fig. 2.2- Shale gas processing scheme, adapted from Goellner (2012).

Natural Gas Value Chain

Methane, the principal component of natural gas, is used for home and industrial heating, electrical power generation, and as a source for chemicals and fuels. Methane can be converted to a variety of derivatives either directly or indirectly. Indirect methods of methane utilization require synthesis gas, which is produced by one of the following

processes or a combination thereof: steam reforming, autothermal reforming, or partial oxidation. **Fig. 2.3** shows a diagram of the major chemicals that represent the natural gas value chain. The focus will be on five major pathways for natural gas monetization: methanol, gas-to-liquids (GTL), ethylene, propylene, and butadiene. For each one, the production chemistry, existing and future plants, and value chain will be discussed.

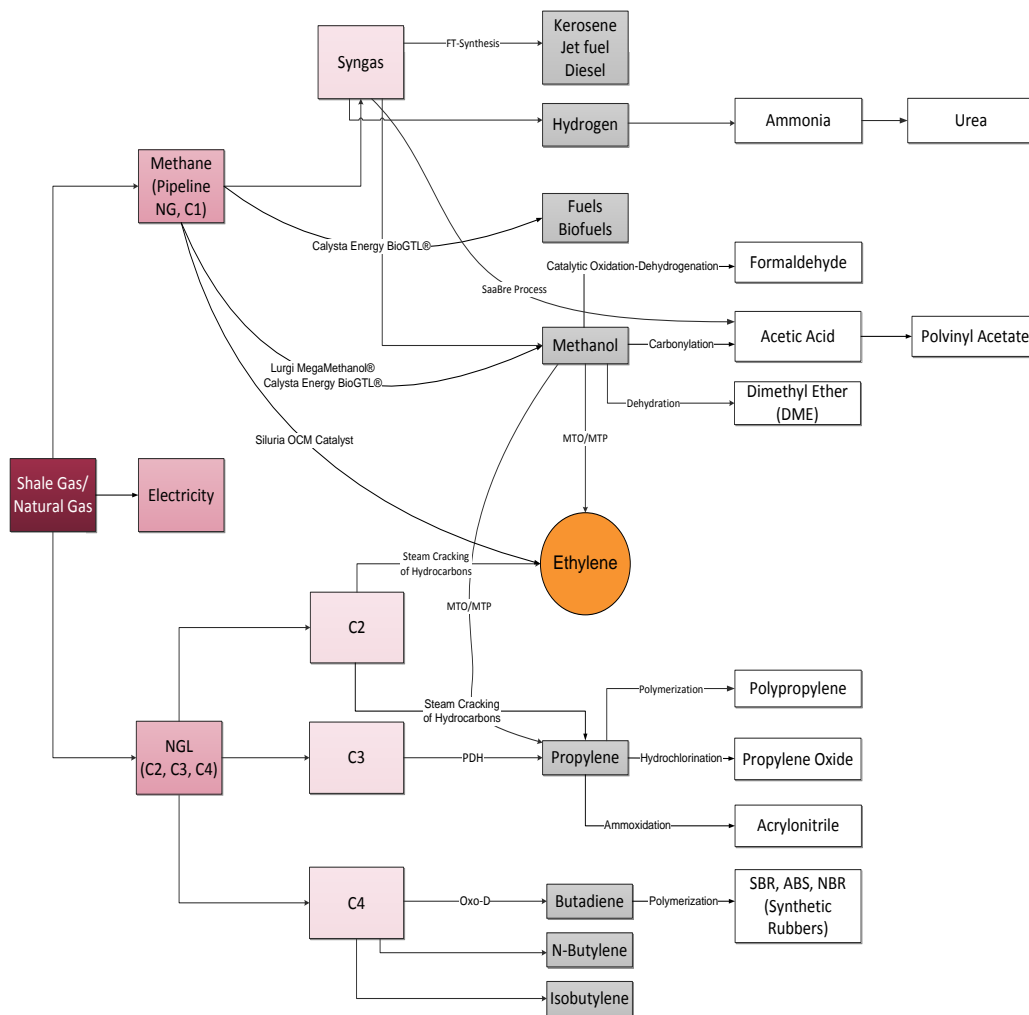


Fig. 2.3- Natural gas value chain

Methanol

Methanol is an important chemical building block that affects human lives daily. It is used in the manufacture of paints and adhesives, and also has applications in the transportation fuel industry. With over 80,000 MT of methanol shipped daily from one continent to another, it is considered a global commodity (www.methanol.org, July 28, 2015).

Methanol Production Chemistry

Methanol production is carried out in two steps: production of synthesis gas, then catalytic synthesis of methanol. **Fig. 2.4** provides an illustration of the steps outlined in this section.

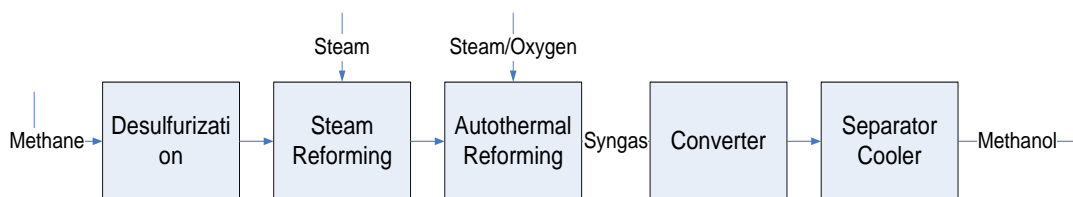
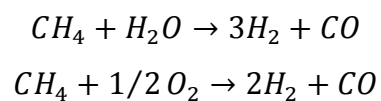
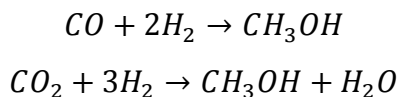


Fig. 2.4- Methanol production scheme.

The first step is achieved through a combined reforming process in which desulfurized natural gas and steam are passed to the primary reformer and the exit gases are then led to an autothermal reformer. Also, preheated oxygen mixed with steam is fed into the oxygen-blown autothermal reformer. The amounts of natural gas and steam are adjusted to generate synthesis gas with stoichiometric ratio of just over two (Wells, 1999). The two steps described above are:



For the methanol synthesis step, either one of the following reactions can occur, depending on the composition of the synthesis gas:



Methanol Plants

Globally, there are ninety methanol plants with a combined production capacity of about 100 MMT/year (www.methanol.org, July 28, 2015). **Table 2.3** lists some of the major plants around the world. The largest producer of methanol is Methanex Corporation, and the largest share of this production comes from the three plant in Taranaki, New Zealand which ship their products to the Asia Pacific markets (www.methanex.com, Methanex: Global Methanol Production Facilities).

Table 2.3: Major methanol production plants in the world

Company	Location	Production Capacity (MT/year)	Source
Methanex	Geismar, Louisiana	1,000,000	www.methanex.com
Statoil	Tjeldbergodden, Norway	900,000	www.statoil.com
Methanex	Medicine Hat, Alberta, Canada	470,000	www.methanex.com
Saudi International Petrochemical Corp.	Al-Jubail, Saudi Arabia	967,000	www.chemicals-technology.com
Methanex	Taranaki, New Zealand (3 plants)	2,400,000	www.methanex.com
Methanex	Damietta, Egypt	1,300,000	www.methanex.com

The availability of cheap natural gas in the United States has resulted in the proposal of several new methanol production plants. After relocating one of their Chile plants to Louisiana and starting production in January 2015, Methanex is relocating a second plant to the same location and expects to start production there in the first quarter of 2016 (www.methanex.com, Methanex: Global Methanol Production Facilities). **Table 2.4** lists the proposed facilities in the United States.

Table 2.4: Proposed methanol plants in the United States.

Company	Location	Production Capacity (MT/year)	Source
Zero Emission Energy	La Place, Louisiana	1,800,000	adi-analytics.com
Cleanese Corp.	Clear Lake, Texas	1,300,000	adi-analytics.com
Valero Energy Corp.	St. Charles, Louisiana	1,600,000	adi-analytics.com
Methanex Corp.	Geismar, Louisiana	1,000,000	adi-analytics.com
North West Innovations	Kalama, Washington/Westward, Oregon	3,800,000	adi-analytics.com
OCI Partners LP	Beaumont, Texas	1,800,000	adi-analytics.com
G2X Energy	Pampa, Texas	60,000	adi-analytics.com

Methanol Value Chain

Methanol is used primarily as a chemical feedstock. One of the most important outlets for methanol is the production of formaldehyde, which accounts for about 33% of methanol demand (ADI Analytics, April 6 2015). Formaldehyde is produced by the catalytic oxidation of methanol, commonly known as the Formox process shown in Fig. 2.5. The main outlet for formaldehyde is the preparation of resins and adhesives, used in the production of plywood and particle board. Another major use of formaldehyde is as an intermediate for the manufacture of polyacetal and polyurethane resins, surface coatings, plasticizers, cross-linking agents, and slow-release fertilizers (Wells, 1999).

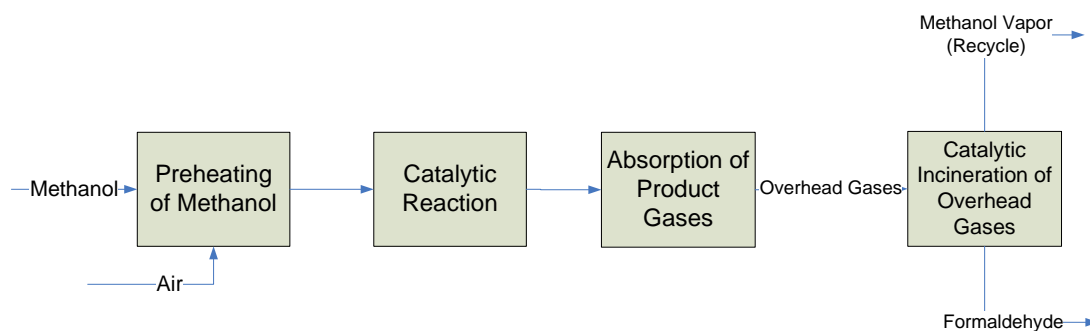


Fig. 2.5- Catalytic oxidation of methanol (Formox process).

Aside from formaldehyde, other significant chemicals produced from methanol are acetic acid, dimethyl ether, and methylamines. Acetic acid is one of the most important organic chemicals and is produced mainly by the carbonylation of methanol process shown in **Fig. 2.6**. Other routes include the oxidation of butane or naphtha and the oxidation of acetaldehyde. The largest application of acetic acid is in the production of vinyl acetate monomer used to manufacture polyvinyl acetate, which is used in paints,

adhesives, and plastics (Wells, 1999). It is also used in the production of purified terephthalic acid (PTA) which is used to manufacture polyester fibers (Grand View Research, February 2014).

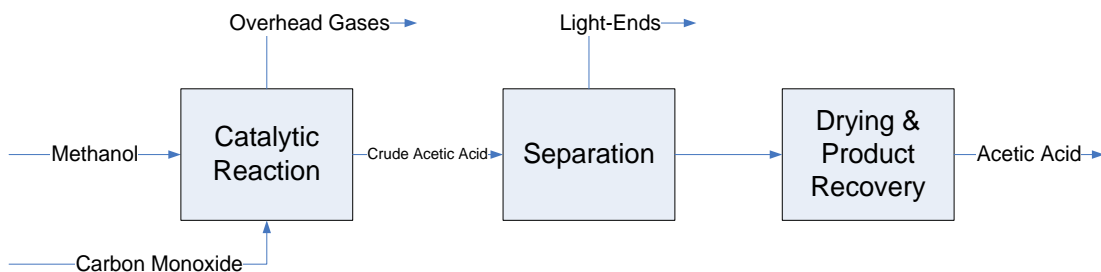


Fig. 2.6- Acetic acid production by the carbonylation of methanol.

Furthermore, methanol is used in the production of fuel additives such as methyl-tert-butyl-ether (MTBE) and tertiary-amyl-methyl-ether (TAME). Although MTBE is no longer used in the United States, it is still used around the world. For example, 7 MMT of methanol were blended in the Chinese gasoline pool in 2014 (Nash, 2015). It is produced by the catalytic addition of methanol to isobutylene from a butadiene-free C₄ stream, a process shown in **Fig. 2.7**.

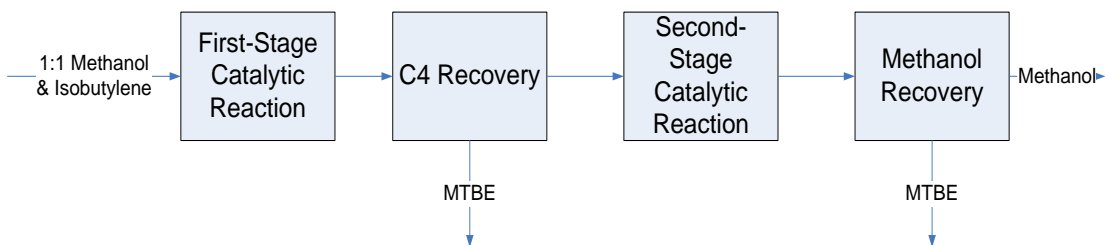


Fig. 2.7- MTBE production by addition of methanol and Isobutylene.

Another outlet for methanol is the production of olefins, which has become a reality in China. The methanol-to-olefins (MTO) technology is enabled by the use of silicoaluminophosphate (SAPO) molecular sieve catalysts, whose unique properties

enabled a more selective route for methanol conversion to ethylene and propylene with reduced heavy byproducts (Shale Gas Monetization-How to Get into the Action, 2013).

Methanol Market Outlook

The methanol market is expanding, from both a capacity and demand perspective, and the pathways in which methanol is utilized are changing as well. For example, methanol production capacity is expected to increase from approximately 80 MMT in 2010 to about 160 MMT in 2020 (Mark Eramo, IHS). Also, global methanol demand is expected to increase from 60.7 MMT in 2013 to more than 109 MMT in 2023 (IHS, August 29 2014). The major driver in methanol demand is China, which is expected to double its methanol consumption from 30 MMT in 2013 to 60.7 MMT in 2023, and increase its imports from 4 MMT to 25 MMT in the same time span (IHS, August 29, 2014). The rising Chinese demand will be addressed mostly by the aforementioned methanol-to-olefins (MTO) technology that is employed in five active plants, plus 13 planned MTO facilities with a capacity of about 9 MMTA (ICIS Chemical Business, 26 September 2014).

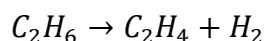
Ethylene

Ethylene is the primary hydrocarbon used in the petrochemical industry, and the most consumed of the olefin building blocks. It is produced by steam cracking of a wide range of hydrocarbons such as naphtha, ethane, propane, butane, LPGs, and gas oils (Wells, 1999). While the traditional feedstock has been naphtha, the shale gas boom in the United States has created many opportunities to use of lighter feedstock. From 2005

to 2013, the share of ethane as a feedstock for steam crackers in the U.S. increased from 45% to 65% (Nexant APIC 2014).

Production Chemistry

Steam cracking of hydrocarbons is a process in which high-pressure steam is used to break molecular bonds to produce olefins. The cracking of ethane to produce ethylene is given by the following equation:



In this process, steam and hydrocarbons are fed into a tubular reactor where cracking takes place at a temperature of 750-870°C. To prevent secondary reactions, the exit gases are quenched to 550-600°C in a quench tower. The exit stream is then compressed in a multi-stage compression system to pressure of 32-38 bar. After each stage, liquids are removed and the remaining gases are treated to remove acid gases. The stream then passes through a cooling train to condense water, and molecular sieves to dry the gases. Finally, a series of fractionators are used to remove methane, ethane, propane, and heavier fractions (Wells, 1999). **Fig. 2.8** shows the important steps in a steam cracking process.

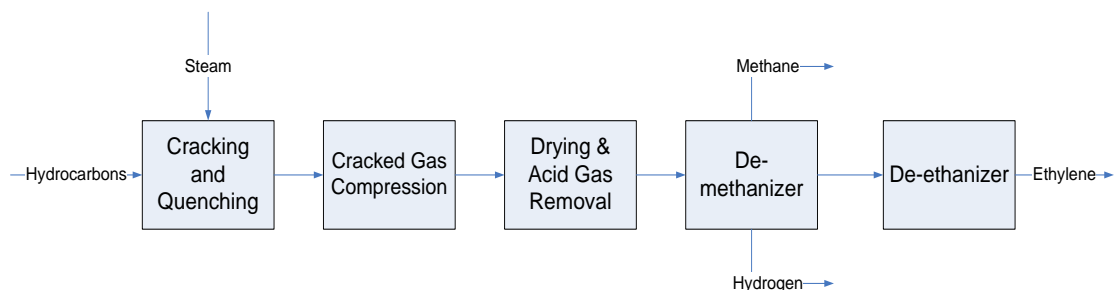


Fig. 2.8- Ethylene from steam cracking process.

Existing/Planned Plants

As of 2014, global ethylene production capacity is more than 146 MMTA (Robert Brelsford, 2014, Oil & Gas Journal). The ten largest ethylene production plants worldwide as of 2014 are shown in **Table 2.5**. This list may change as new facilities are commissioned, existing capacities increased or decreased.

Table 2.5: Ten largest ethylene plants, adapted from (OGJ, July 7 2014).

Company	Location	Production Capacity (MTA)
ExxonMobil	Jurong Island, Singapore	3,500,000
Formosa	Yunlin, Taiwan	2,935,000
Nova Chemicals	Alberta, Canada	2,811,792
Arabian Petrochemical	Jubail, Saudi Arabia	2,250,000
ExxonMobil	Baytown, Texas, U.S.A	2,197,000
Chevron Phillips	Sweeny, Texas, U.S.A	1,865,000
Dow	Terneuzen, Netherlands	1,800,000
Ineos	Chocolate Bayou, Texas, U.S.A	1,752,000
Equistar Chemicals	Channelview, Texas, U.S.A	1,750,000
Yanbu Petrochemical	Yanbu, Saudi Arabia	1,705,000

In the United States, ethylene production capacity was about 28 MMTA, as of 2014. The shale gas boom has provided a flood of low-cost feed which, coupled with rising demand, spurring proposals for 10 new ethane cracking facilities, or around 12.5

MMTA of ethylene capacity (ICIS Chemical Business, January 16 2014). **Table 2.6** lists these facilities and their expected startup dates. It is important to note that these facilities are at different stages of planning or construction, and may experience delays in those processes.

Table 2.6: Planned ethylene facilities in the U.S., adapted from (ICIS Chemical Business, January 16 2014).

Company	Location	Expected Capacity (MTA)	Start-up Date Projection
Chevron Phillips	Cedar Bayou, Texas	1,500,000	Mid-late 2017
ExxonMobil	Baytown, Texas	1,500,000	Late 2016
Dow	Freeport, Texas	1,500,000	2017
Sasol	Lake Charles, Louisiana	1,500,000	2017
Formosa	Point Comfort, Texas	1,000,000	2017
Formosa	Louisiana	1,200,000	N.A.
Occidental Chemical/Mexichem	Ingleside, Texas	544,000	2017
Axiall/Partner	Louisiana	World-scale	2018
Shell	Monaca, Pennsylvania	World-scale	2019-2020
Odebrecht	Wood County, West Virginia	World-scale	N.A.

Value Chain

Ethylene is utilized exclusively as a chemical intermediate. As shown in **Fig. 2.9** there are three main derivatives produced from ethylene: polyethylene, ethylene dichloride, and ethylene oxide. Also, acetaldehyde is another derivative but it will not be discussed in detail because its global market has been trending downward due to the commercialization of more efficient technologies for products formerly based on acetaldehyde (IHS, April 1 2013).

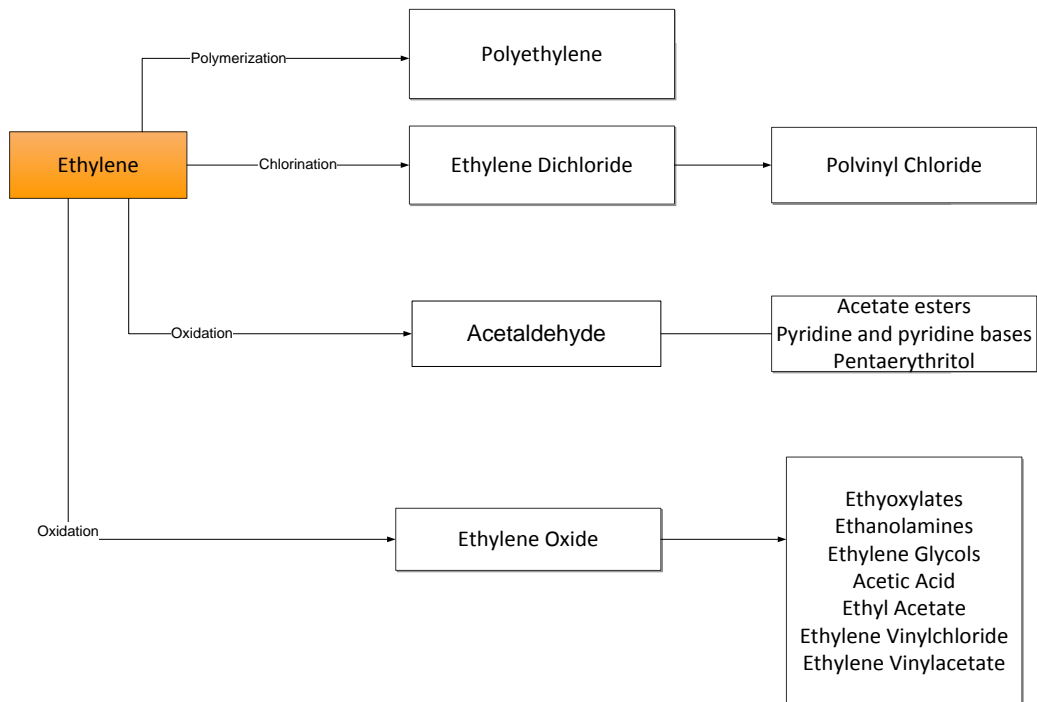


Fig. 2.9- Ethylene value chain.

For polyethylene, several types of it exist for different applications. Low density polyethylene (LDPE) is produced by the polymerization of ethylene in tubular or stirred autoclave reactors and its largest applications being in films (food packaging, industrial

liners) and sheathing for electrical communication cables. The process variant where tubular reactors are used is shown in **Fig. 2.10**.

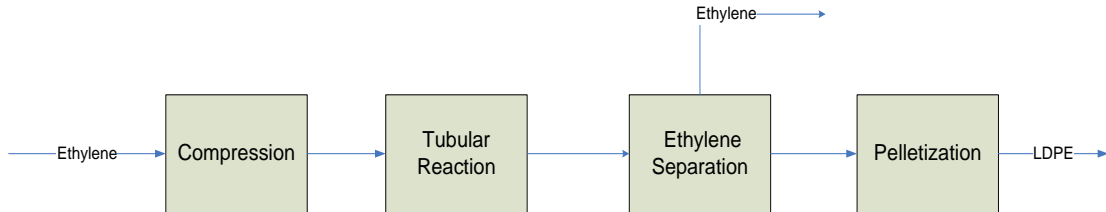


Fig. 2.10- LDPE production process.

Also, high density polyethylene (HDPE) and linear low density polyethylene (LLDPE) are made by one of the following types of ethylene polymerization: gaseous, slurry (suspension), or solution. **Fig. 2.11** shows the steps of a gaseous polymerization process. The major applications of HDPE are blow molding and film and sheet (wrapping, industrial liners) and those of LLDPE are film applications where it is seen as a replacement for LDPE.

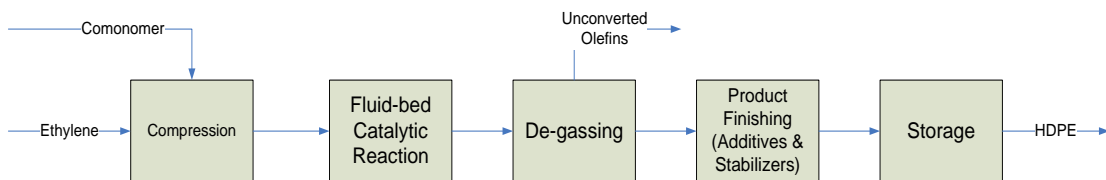


Fig. 2.11- HDPE/LLDPE production process.

Ethylene dichloride (EDC) is produced industrially by the direct chlorination of ethylene with chlorine or by oxychlorination using hydrogen chloride. In practice, both routes are utilized in an integrated ethylene-EDC-vinyl chloride process. **Fig. 2.12** shows the direct chlorination route. Ethylene dichloride is used almost exclusively to produce

vinyl chloride, which in turn is used to make polyvinyl chloride (PVC). The major uses of the latter are in the cyclical and automotive industries.

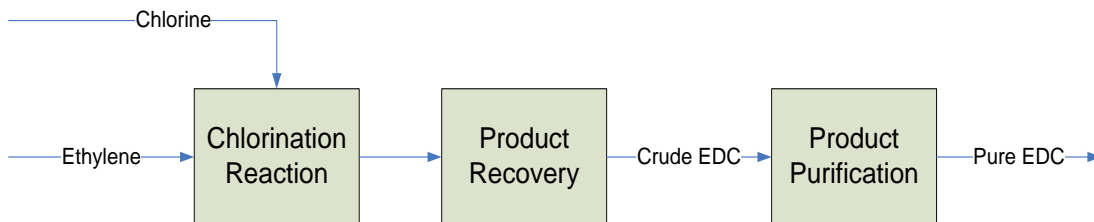


Fig. 2.12- EDC production process.

The third ethylene derivative, ethylene oxide, is produced by the direct oxidation of ethylene in the presence of air or oxygen over a silver oxide catalyst. **Fig. 2.13** shows the major steps of this process. Ethylene oxide is used as a raw material to produce ethylene glycol, ethoxylates, ethanolamines, glycol ethers, and triethylene glycols.

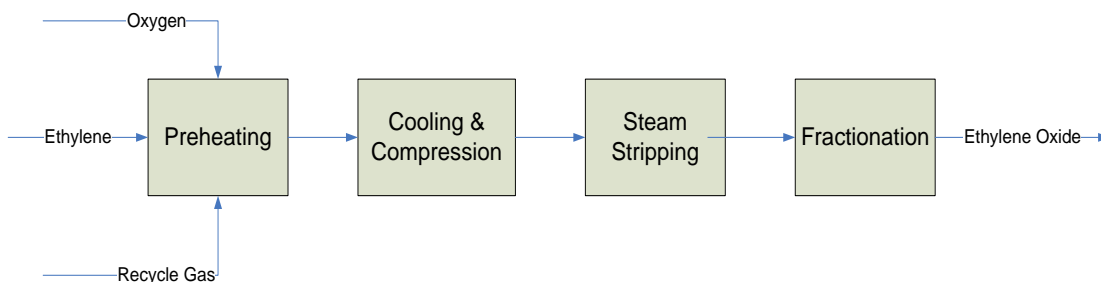


Fig. 2.13- Ethylene oxide production process.

Ethylene is the most important raw material in the petrochemical industry, with approximately 130 MMT of it processed globally in 2013 and global capacity expected to reach 200 MMT by 2020 (Mark Eramo, IHS). The shale gas boom in the United States has had a considerable effect on the ethylene market. With the increasing supply of ethane, twelve new ethane crackers have been announced and are slated to for start-up in the next five years, representing a 60% increase over current U.S. ethylene capacity

(ICIS Chemical Business, January 19 2015). These projects flourished because of the record profits gained by U.S. petrochemical producers, who have enjoyed the benefit of low costs based on natural gas prices and high chemical prices based on high crude oil prices until the second half of 2014. In addition, the abundance of ethane supply has moved many European manufacturers to announce their intention to change over to using imported ethane as feedstock (IHS Chemical Week, March 2014). However, it is forecasted that the increase in ethylene production capacity will outpace the increase in demand, which will negatively influence price trends. Thus, revenue generated by ethylene globally is expected to increase by 3.2% per annum (p.a.) between 2013 and 2021, which is significantly lower than the period of 2005-2013 (Ceresna Ethylene Market Study).

Propylene

Propylene is the second most important petrochemical feedstock. It is produced by steam cracking of a wide range of hydrocarbons as a by-product of ethylene manufacture and is separated out from the C₃ stream. The shift from naphtha cracking to ethane cracking has led to a shortfall in propylene and butadiene (Hydrocarbon Processing, 27 February 2015). This is due to the lower propylene yield of ethane feedstock (2%) in comparison to its naphtha counterpart (15%) (Robert Brooks USAEE, 31 May 2013). To fill this propylene shortfall, two new technological advances have gained attention in industry: propane dehydrogenation (PDH) and methanol-to-olefins (MTO).

Production Chemistry

In steam cracking, mixed gases (propane, propylene, propadiene, and propyne) exit a depropanizer and are fed into a selective dehydrogenation unit containing a palladium catalyst at a pressure of 18 bar. This process is shown in **Fig. 2.14**. The reaction shown below is carried out either in the gas phase at a temperature of 50-120°C, or in the liquid phase below 25°C (Wells, 1999).

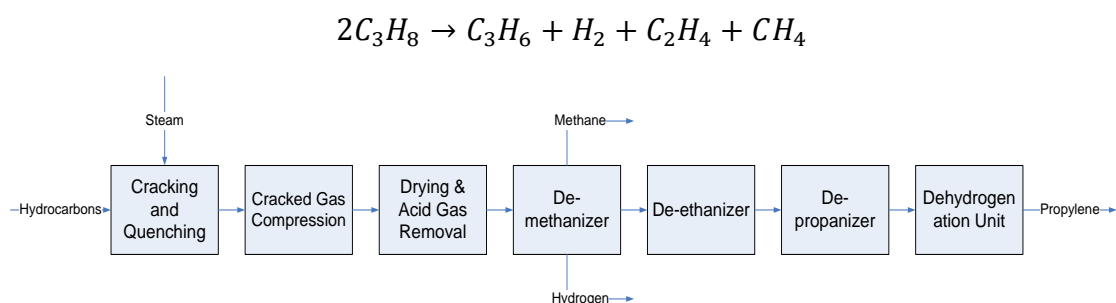
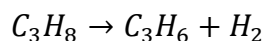


Fig. 2.14- Propylene from steam cracking process.

PDH is a catalytic dehydrogenation process whereby propane, recycle propane, and hydrogen are preheated to a temperature of 500-700°C and fed into a moving or fixed-bed reactor at near atmospheric pressure. A noble metal (e.g. platinum) on activated alumina impregnated with 20% chromium is used as the catalyst (Wells, 1999). There are five licensed technologies (STAR, Catofin, Oleflex, FBD, and PDH) for this process that differ in catalyst type, temperature, and pressure (Witcoff, Reuben, and Plotkin 2013). A block diagram for the process is shown in Fig. 2.15, and the reaction that occurs in it is as follows:



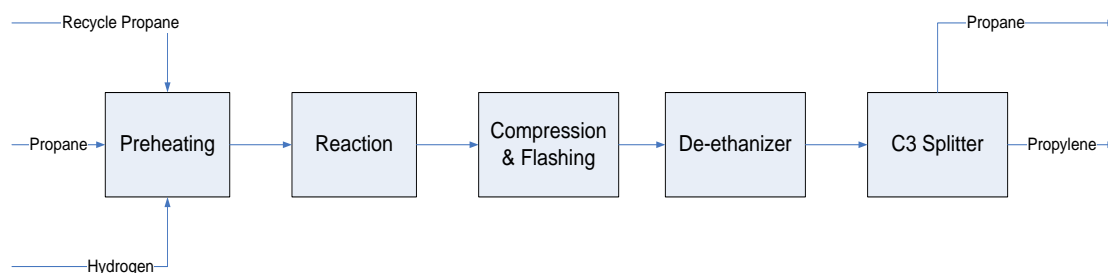


Fig. 2.15- Propylene from PDH process.

Existing/Planned Plants

In 2013, approximately 90 MMT of propylene were produced around the world (Mark Eramo, IHS). A selection of the largest operating propylene production plants is shown in **Table 2.7**.

Table 2.7: Major propylene production plants

Company	Location	Production Capacity (MTA)	Source
LyondellBasell	Channelview, Texas	1,450,000	ICIS
ExxonMobil	Baytown, Texas	1,000,000	ICIS
Total Olefins	Antwerp, Belgium	710,000	Oil & Gas Journal, 2011
Chicago Bridge & Ironworks	Tianjin, China	600,000	www.process-worldwide.com
Naphthachimie	Lavera, France	540,000	ICIS, 2013
Chevron	Port Arthur, Texas	499,000	www. platts.com
Sanyuan Petrochemical	Zhejiang Province, China	450,000	Oil & Gas Journal, 2015

Currently, there is one PDH plant in the United States (Flint Hills Resources facility in Houston) that produces about 657,000 MMTA of propylene. There are six new projects that have been announced and are in various stages of development. As of late 2014, only three to four will be built in the immediate future because of cost issues and questions over propylene derivative demand (ICIS News, 5 October 2014). Table 2.8 shows the proposed units (adapted from ICIS News, 5 October 2014).

Table 2.8: Proposed PDH plants in the United States, adapted from ICIS News (5 October, 2014)

Company	Location	Expected Capacity (MTA)	Start-up Date Projection
Ascend Performance Materials	Chocolate Bayou, Texas	1,173,000	Late 2015
Dow	Freeport, Texas	750,000	Mid-2015
Enterprise Products	Mont Belvieu, Texas	750,000	Early 2016
Williams	Alberta, Canada	500,000	Mid-2016
Formosa	Point Comfort, Texas	658,000	2017

Value Chain

Similar to the ethylene value chain, the propylene chain has two main derivatives: polypropylene (PP) and propylene oxide. As with polyethylene, polypropylene is produced by polymerization of propylene. Historically, slurry

polymerization was the most-used method to produce polypropylene, but gas-phase polymerization has been replacing it. **Fig. 2.16** shows a block diagram of the latter process. This change is due to that the gas-phase process produces a dry polymer and its stereospecific catalysts result in higher yields and greater selectivity (Wells 1999). Polypropylene has a higher melting point, lower density, and better stress cracking than other polyolefins, and is used for injection molding and several applications in the automotive industry (e.g. battery cases).

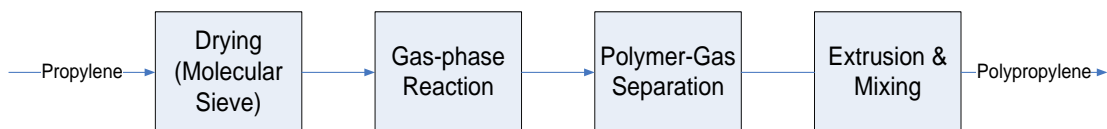


Fig. 2.16- Polypropylene from gas-phase polymerization.

Propylene oxide, the other major derivative, is used to produce polyether polyols, propylene glycols, and propylene glycol ethers. Polyether polyols are used to make polyurethanes for the manufacture of foams, while propylene glycol is used for de-icing aircraft and runways. Consequently, in harsh winters, demand for propylene glycol increases. Propylene oxide is manufactured from propylene by two routes:

chlorohydration and epoxidation. **Fig. 2.17** shows the major steps in a chlorohydration process, while **Fig. 2.18** shows the same for the epoxidation route.

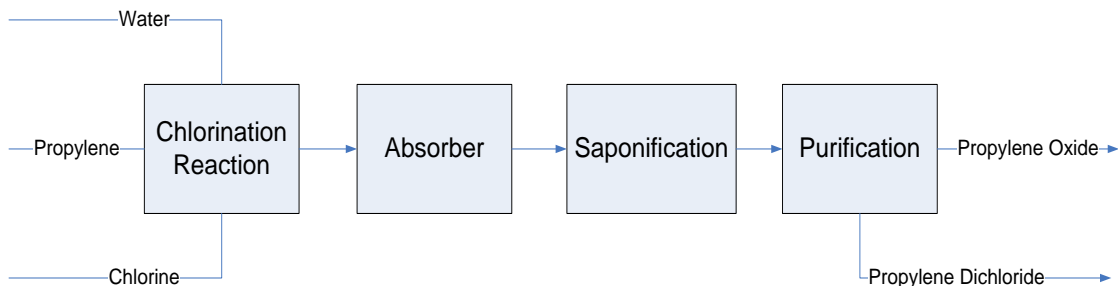


Fig. 2.17- Propylene oxide from chlorohydration.

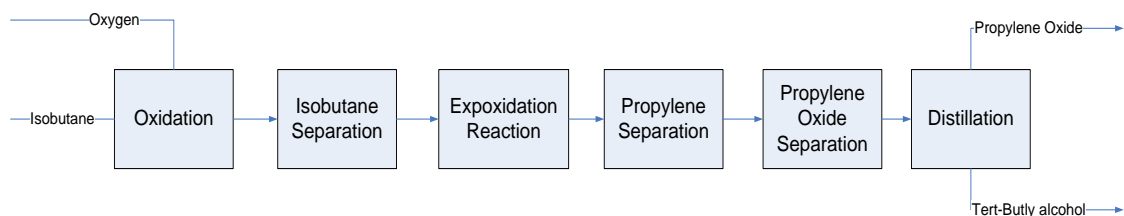


Fig. 2.18- Propylene oxide from epoxidation.

Market Outlook

Propylene is considered the second most important petrochemical feedstock with approximately 85 MMT processed globally in 2013, and capacity is expected to reach 140 MMT by 2020 (Mark Eramo, IHS). While the increasing use of ethane has created a propylene shortfall, PDH and MTO plants are expected to solve that problem. PDH technology already supplies 4 MMT of propylene annually to the global market (ICIS Chemical Business, 16 April 2012). In China, a total of six PDH plants will be in operation by late 2015 and are expected to produce 3.51 MMT of propylene annually. MTO is another technology that is expected to help increase propylene production with UOP having announced four licenses for this technology since 2011. These projects will have a combined propylene/ethylene production capacity of 1.72 MMTA (UOP Press Release, June 18, 2014). As a result, global propylene prices are expected to stabilize (ICIS Propylene: Market Overview, 2015).

Processes Under Development

Aside from the processes mentioned previously, there have been ongoing efforts at finding different pathways to produce the same chemicals. Many of these processes that are undergoing laboratory-scale tests are biologically-based pathways. For example,

catalyst maker Siluria Technologies claims to have developed a catalyst that converts methane into ethylene, from which two-thirds of global chemical production is derived. This process is called the oxidative coupling of methane (OCM). The developers used a virus that is 900 nanometers long and nine nanometers in diameter to serve as a template for forming small nanowires when exposed to metals and other elements under certain conditions. According to them, the catalyst can activate methane at a temperature about 200°C less than the best existing catalyst, which operates between 800 and 950°C (Fairley, 2010).

Conclusions

With over 10 MMT of proposed capacity to be added, the United States is expected to become a net exporter of methanol by 2017. On the other hand, China is the main driver of global growth in methanol consumption. Between 2013 and 2023, it is expected to double its consumption from 30 MMT to 60.7 MMT (IHS, August 29, 2014). This demand is expected to be driven by fuel and MTO applications with 13 MTO units planned over the next several years. Also, with several China-related methanol plants planned in the U.S. as mentioned, it is possible that the coal-to-methanol industry in China will be negatively impacted (ICIS Chemical Business, 26 September 2014). As ethane from shale gas replaces naphtha as the feedstock for ethylene production, propylene co-production will be essentially eliminated (Jasper and El-Halwagi, 2015). Thus, a significant gap between propylene supply and production is expected to grow. In order to deal with this gap, MTO/MTP and on-purpose propylene production (PDH) are gaining an increasing share of global propylene production. For

example, China is expected to add 3.5 MMT of propylene production by the end of 2015 through six PDH plants. This change in supply methods will make propylene prices more prone to the change in feedstock prices and the technological risks and challenges associated with these new processes.

CHAPTER III

METHODOLOGY OF OPTIMIZATION PROGRAM

In the previous chapter, the process chemistry and value chains of three major chemical building blocks (methanol, ethylene, and propylene) was surveyed. In this part of the study, the methodology used to write the optimization program for the chemical production complex being proposed is discussed in three parts: (1) profitability/economics, (2) environmental aspects, and (3) safety considerations.

Introduction

As the review of literature shows, most of the work done hitherto has focused on the optimization of shale gas supply chain for the purposes of electricity production and fuels production. In this work, the focus is on optimization of the production of chemicals from a given resource of shale gas, in this case the annual production of dry gas in the state of Texas. In 2014, dry gas production in Texas was 7,146,549 MMSCF, which can be converted into metric tons per annum (MTA) as follows:

$$\begin{aligned} & \frac{7,146,549 \text{ MMSCF}}{\text{yr}} \times \frac{1 \times 10^6 \text{ SCF}}{1 \text{ MMSCF}} \times \frac{1 \text{ lb} - \text{mol } CH_4}{379.5 \text{ SCF}} \times \frac{16.04 \text{ lb}}{1 \text{ lb} - \text{mol } CH_4} \\ & \times \frac{0.000453592 \text{ MT}}{1 \text{ lb}} = 137,010,656 \text{ MTA} \end{aligned}$$

The methodology followed in the optimization program is based on the chemical reactions that occur in the reactor(s) of the given processes. The optimization program takes into account three separate criteria: profitability/economics, safety, and the environment.

Profitability/Economics

For this part of the optimization study, an input-output block model was developed from each of the process designs to mathematically represent the chemical processes in the superstructure being studied. The statement for the optimization problem in the chemical production complex can be given as follows:

Optimize: Objective function

Subject to: Constraints from plant model

The objective function in this study is a simple profit function shown here:

$$\text{Profit} = \sum \text{Product sales} - \sum \text{Capital Costs} - \sum \text{Raw material costs} - \sum \text{Energy costs}$$

The constraint equations describe the relationship among variables and parameters in the processes and in this optimization program, they are material balances. In other works, they are material and energy balances, chemical reaction rates, thermodynamic equilibrium relations, and others (Sengupta “Chemicals from Biomass”, 2012). The objective of optimization in this study is to find optimal solutions that maximize profit from a given resource of shale gas produced in Texas.

Also, the program involves three different cases: a base case, a reduced methanol price sensitivity case, and an urea price sensitivity case.

For the first case, which will be called the base case, the sales prices for natural gas and chemicals as of November 2015 are utilized in the program. All prices are on a dollar per metric ton basis (\$/MT). The Henry Hub price of natural gas as of November 2015 was \$2.260/MMBtu, which can be converted to \$/MT as follows:

$$\frac{\$2.260}{\text{MMBtu}} \times \frac{1 \text{ MMBtu}}{1,000 \text{ CF}} \times \frac{379.5 \text{ SCF}}{1 \text{ lb - mol}} \times \frac{1 \text{ lb - mol}}{16.04 \text{ lb}} \times \frac{1 \text{ lb}}{0.00045359 \text{ MT}} = \frac{\$117.88}{\text{MT}}$$

For the second case, the price of methanol, which is the main intermediate, will be reduced from its current level of \$366/MT to \$130/MT to account for what may happen when several new methanol production facilities are expected to come online by 2017. As mentioned in the previous chapter, methanol production in the U.S. is expected to increase by about 12 MMT over the next five years if all the proposed plants come online. Naturally, this is expected to drive global prices for methanol down. Since the chemical superstructure has two main intermediates (methanol and ammonia), a change in the price of one of them will have an impact on the quantity that will be produced of that intermediate and how it will be monetized. This includes whether it will be sold as methanol, or further processed into any of dimethyl ether, acetic acid, or formaldehyde.

Environmental Emissions

Under this criterion, the aim is to find the most environmentally-friendly processes in the chemical complex being studied. The harmful emissions being studied to make this determination will be greenhouse gases (GHG) and criteria air pollutants (CAP). This is what distinguishes this research study from others, in that the emissions examined are beyond GHG. While greenhouse gas emissions are mostly concerned with carbon dioxide and methane emissions, CAP are defined as commonly found air pollutants found all over the United States (www3.epa.gov/airquality/urbanair). They include six major air pollutants and they are: carbon monoxide (CO), particulate matter (PM), lead, sulfur dioxide (SO₂), and nitrogen oxides. The data for CAP can be obtained from the National Emission Inventory (NEI), which estimates both Criteria and Hazardous air pollutants from all air emissions sources. The NEI is prepared by the

Environmental Protection Agency (EPA) and is prepared every three years based upon emission estimates and emission model inputs provided by state, local, and tribal air agencies for sources in their jurisdictions, and is also supplemented by data developed by the EPA (www3.epa.gov/ttn/chief/net/2011inventory.html).

The environmental aspect of this study aims to find the most environmentally friendly processes in the proposed chemical production complex from shale gas. Most of the previous research work. Most of the previous research work related to shale gas, only greenhouse gases have been considered for environmental criteria. In this research, criteria pollutants in addition to GHGs have been considered for a complete environmental profile of the chemicals produced. GHGs are carbon dioxide, methane, nitrous oxide (N_2O), and fluorinated gases. On the other hand, CAPs are defined as commonly found air pollutants found all over the United States (www3.epa.gov/airquality/urbanair). They include six major air pollutants and they are: carbon monoxide (CO), particulate matter (PM), lead, sulfur dioxide (SO₂), and nitrogen oxides. The data for CAPs is reported by facilities producing a certain chemical in the United States every three years. The EPA compiles this data based on reports by state, local, and tribal air agencies.

Safety Considerations

For safety factors, the metric taken into account in this study is the Dow Fire & Explosion Index. It is used to analyze the hazards associated with the reactor(s) in each process focusing on fires and explosions. The basic starting value in the computation of F&EI is the Material Factor (MF), which is a measure of the intrinsic rate of potential

energy release from fire or explosion produced by combustion or other chemical reaction (AIChE, 1987). The index is calculated based on two areas: general process hazards and special process hazards. **Fig. 3.1** shows a sample of the form used to determine Dow Fire & Explosion Index. Since this calculation will be done mainly to gain a rough idea of the risks associated with each process in the chemical superstructure, there are several items in the F&EI form that will not be considered such as: enclosed or indoor process units, access, drainage and spill control, and rotating equipment.

Under “General Process Hazards”, the main item for which a penalty is assessed is “Exothermic Chemical Reactions”. In each process, the reaction that occurs is unique and requires a certain penalty as specified in the Fire & Explosion Index Hazard Classification Guide. This penalty is determined from the type of reaction that occurs in the process and under what exotherm category it falls under. The categories of exotherms and their corresponding penalties are given in **Table 3.1**.

Table 3.1: Exotherm categories and their corresponding penalties.

Exotherm	Penalty
Mild	0.30
Moderate	0.50 except for addition reactions (0.75) and oxidation reactions (1.00)
Critical-to-control	1.00
Particularly sensitive	1.25

Another important item under “General Process Hazards” for which a penalty is assessed is “Material Handling and Transfer”. This item takes into account the potential for fire involving the reactor(s) during handling, transfer, and warehousing of materials (AIChE, 1987). For the purposes of this study, a penalty of 0.50 will be used for any loading or unloading operation involving Class I flammables or LPG-type materials where transfer lines are connected or disconnected (AIChE, 1987).

FIRE AND EXPLOSION INDEX			
AREA / COUNTRY	DIVISION	LOCATION	DATE
SITE	MANUFACTURING UNIT	PROCESS UNIT	
PREPARED BY:	APPROVED BY: (Superintendent)	BUILDING	
REVIEWED BY: (Management)	REVIEWED BY: (Technology Center)	REVIEWED BY: (Safety & Loss Prevention)	
MATERIALS IN PROCESS UNIT			
STATE OF OPERATION [] DESIGN [] START-UP [] SHUT-DOWN [] NORMAL OPERATION		BASIC MATERIAL(S) FOR MATERIAL FACTOR	
MATERIAL FACTOR (See Table 1 or Appendices A or B) <small>Note: requirements when unit temperature over 140 °F (60 °C)</small>			
1. General Process Hazards		Penalty Factor Range	Penalty Factor Used ⁽¹⁾
Base Factor _____		1.00	1.00
A. Exothermic Chemical Reactions		0.30 to 1.25	
B. Endothermic Processes		0.20 to 0.40	
C. Material Handling & Transfer		0.25 to 1.05	
D. Enclosed Or Indoor Process Units		0.25 to 0.90	
E. Access		0.20 to 0.35	
F. Drainage And Spill Control _____ gals or cu. m.		0.25 to 0.50	
General Process Hazards Factor (F ₁) _____			
2. Special Process Hazards			
Base Factor _____		1.00	1.00
A. Toxic Material(S)		0.20 to 0.80	
B. Sub-Atmospheric Pressure (-500 mm Hg)		0.50	
C. Operation In Or Near Flammable Range [] Inerted [] Not Inerted			
1. Tank Farms Storage Flammable Liquids		0.50	
2. Process Upset Or Purge Failure		0.30	
3. Always In Flammable Range		0.80	
D. Dust Explosion (See Table 3)		0.25 to 2.00	
E. Pressure (See Figure 2) Operating Pressure _____ psig or kPa gauge Relief Setting _____ psig or kPa gauge			
F. Low Temperature		0.20 to 0.30	
G. Quantity Of Flammable/Unstable Material: Quantity _____ b or kg H = _____ BTU/lb or kcal/kg			
1. Liquids, Gases And Reactive Materials In Process (See Figure 3)			
2. Liquids Or Gases In Storage (See Figure 4)			
3. Combustible Solids In Storage, Dust In Process (See Figure 5)			
H. Corrosion And Erosion		0.10 to 0.75	
I. Leakage – Joints And Packing		0.10 to 1.50	
J. Use Of Fired Heaters (See Figure 6)			
K. Hot Oil Heat Exchange System (See Table 5)		0.15 to 1.15	
L. Rotating Equipment		0.50	
Special Process Hazards Factor (F ₂) _____			
Process Unit Hazards Factor (F ₁ x F ₂ = F ₃) _____			
Fire And Explosion Index (F ₃ x MF = F&EI) _____			

(1) Furno penalty use 0.00

Fig. 3.1- Dow Fire & Explosion Index form (www.processoperations.com).

Under “Special Process Hazards”, the penalty for the item labeled “Toxic Material(s)” is determined from the health factor N_h found in Appendix A of the Hazard Classification Guide. N_h is the health factor of a material as defined in the National Fire Protection Association 704 standard (AIChE, 1987). The health factor used is that of the

basic material in the process and the penalty assessed is: $0.20 \times N_h$. Another important item is “Pressure”, where a penalty is applied to offset the effect of high pressure on the potential for leaks with higher release rates (AIChE, 1987). This item is determined from a chart, a modification of which is shown in **Table 3.2**, in the Hazard Classification Guide which gives a penalty based on the operating pressure of the process unit.

Table 3.2: Pressure penalty for flammable and combustible liquids.

Pressure (psig)	Penalty Factor
1,500	0.92
2,000	0.96
2,500	0.98
3,000-10,000	1.00
>10,000	1.50

The last two items of relevance in the F&EI form in this study were the items “Quantity of Flammable/Unstable Material” and “Corrosion and Erosion”. The penalty for the former is determined using Figure 3 in page 24 of the Hazards Classification Guide, while the penalty for the latter is determined by searching for values of corrosion rates of the chemicals being examined in the F&EI study. **Table 3.3** shows corrosion rates and their corresponding penalties.

Table 3.3: Corrosion rates and their corresponding penalty factors, modified from the Hazards Classifications Guide (AIChE, 1987).

Corrosion Rate (mm/year)	Penalty Factor
<0.50	0.10
0.50<CR<1.00	0.20
>1.00	0.50

Afterwards, the items under each of the “General Process Hazards” and “Special Process Hazards” are summed up and two values are obtained, F1 and F2. F1 refers to the General Process Hazards Factor and F2 refers to the Special Process Hazards Factor. Then, they are multiplied to obtain a Process Unit Hazards Factor, labelled F3. Finally, the Dow Fire & Explosion Index is obtained by multiplying the Process Unit Hazards Factor by Material Factor mentioned earlier in this chapter. In order to understand the significance of the Dow F&EI, **Table 3.4** shows a qualitative level of hazard for various Dow F&EI values modified from Turton and Bailie’s textbook from 2012.

Table 3.4: Dow Fire & Explosion Index (adapted from Turton et al. 2012).

Fire & Explosion Index	Qualitative Hazard Level
1-60	Light
61-96	Moderate
97-127	Intermediate
128-158	Heavy
159-	Severe

CHAPTER IV

CHEMICAL PRODUCTION COMPLEX OPTIMIZATION: RESULTS AND DISCUSSION

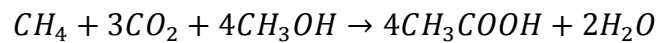
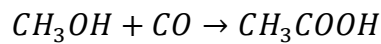
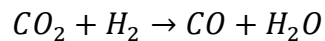
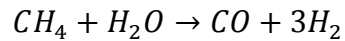
In the previous chapter, the methodology behind the formulation of the optimization program was explained. In this part of the study, the objectives are to: (1) examine the results of the optimization program based on market conditions as of November 2015, (2) examine the effects of a reduction in the price of methanol (a major intermediate), (3) determine the impact urea prices have on the monetization pathway chosen, (4) determine carbon dioxide emissions for the base case and see effects of limiting CO₂ emissions, and (5) obtain Dow Fire & Explosion Index values to provide a safety metric for the processes in the complex.

Introduction: Superstructure Processes

The superstructure contains processes for the production of the following chemicals: methanol, acetic acid (2), dimethyl ether (2), formaldehyde, ethylene, propylene, ammonia, and urea. Methanol is a major intermediate and is subsequently used in the production processes of acetic acid, dimethyl ether, formaldehyde, and olefins. While methanol has been produced from syngas previously, it can also be produced from methane directly by a two-step reforming process. The chemistry has been explained previously in Chapter 2 of this study.

One of the major chemicals globally is acetic acid, and it can be produced by one of two methods: a two-step process from methanol, and the recently-developed integrated three-step SaaBre process by BP. Both processes are included in the

chemical superstructure. For the two-step process, it is a well-established one developed by Monsanto and is used in Dow Chemical's Hahnville plant which part of the company's St. Charles Operations (Xu, 2004). The reactions involved in this process are as follows:



The first two equations are the steam reforming reaction and the water-gas shift reaction, respectively. The third equation is the reaction of methanol and carbon monoxide to form acetic acid while the fourth reaction is an overall reaction for this process obtained by summing up the three previous reactions. **Fig. 4.1** illustrates the block diagram for this process with the stream names as they appear in the chemical superstructure, while **Table 4.1** defines those streams.

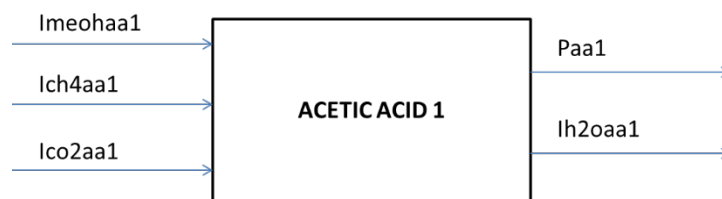


Fig. 4.1- Block diagram of methanol to acetic acid plant.

Table 4.1: Process streams in methanol to acetic acid plant.

Name of Stream	Description
Ich4aa1	Natural gas to acetic acid plant
Imeohaa1	Methanol to acetic acid plant
Ico2aa1	CO ₂ to acetic acid plant
Paa1	Total production of acetic acid from acetic acid plant
Ih2oaa1	Water produced from acetic acid plant

As for the BP SaaBre process, it eliminates the need for the purchase of methanol and the purification of carbon monoxide (BP, 2013). The reaction for the process can be represented the following equation:

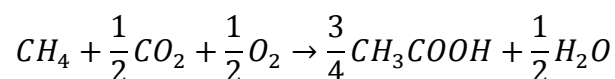


Fig. 4.2 illustrates the block diagram for the SaaBre process, with the stream names as they appear in the chemical superstructure defined in **Table 4.2**.



Fig. 4.2- Block diagram of synga to acetic acid (BP SaaBre) plant.

Table 4.2: Process streams in syngas to acetic acid plant.

Name of Stream	Description
Ich4aa2	Natural gas to BP SaaBre plant
Io2aa2	Oxygen to BP SaaBre plant
Ico2aa2	CO ₂ to BP SaaBre plant
Paa2	Total production of acetic acid from BP SaaBre plant
Ih2oaa2	Water produced from BP SaaBre plant

The second major derivative of methanol is dimethyl ether (DME), and it is produced by one of two processes: the dehydration of methanol, or the syngas-to-DME route. First, the reaction for the dehydration of methanol process can be represented by the following equation:

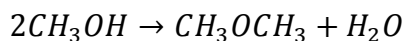


Fig. 4.3 shows the block diagram for the dehydration of methanol to DME, with **Table 4.3** containing the definitions for the process inlet and outlet streams.

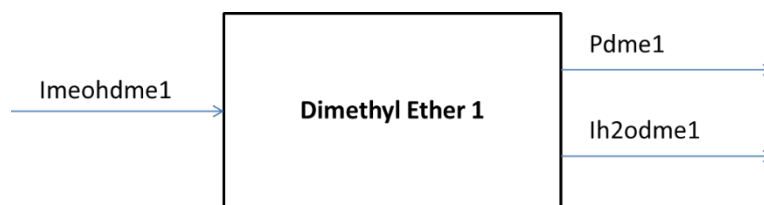
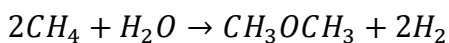


Fig. 4.3- Block diagram of methanol to DME plant.

Table 4.3: Process streams in methanol to acetic acid plant.

Name of Stream	Description
Imeohdme1	Methanol to dimethyl ether plant
Pdme1	Total production of dimethyl ether from plant
Ih2odme1	Water produced from dimethyl ether plant

In addition to the previous method, DME can be produced in an integrated process using the syngas route. While there are different approaches for producing the syngas, the method used in this reaction is steam reforming (Peng, 1999). The equation for the reaction is as follows:



A block diagram showing the inlet and outlet streams for the process is given below in **Fig. 4.4**, while Table 4.4 defines these streams.

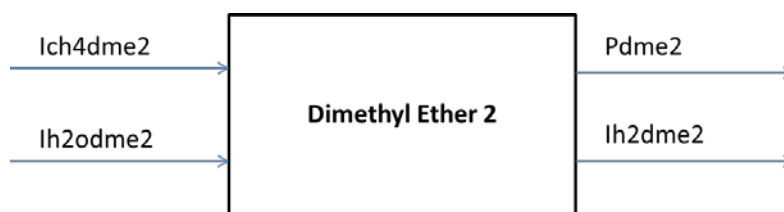
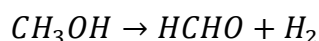
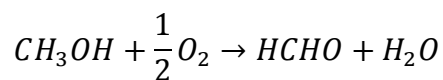


Fig. 4.4- Block diagram of syngas to DME plant.

Table 4.4: Process streams in syngas to DME plant.

Name of Stream	Description
Ich4dme2	Natural gas to syngas-to-DME plant
Ih2odme2	Water to syngas-to-DME plant
Pdme2	Total production of DME from syngas-to-DME plant
Ih2dme2	Hydrogen produced from syngas-to-DME plant

In addition to acetic acid and dimethyl ether, methanol is used in the production of formaldehyde, an important precursor in the manufacture of industrial resins. The process can occur by one of two routes, both starting with methanol: oxidation-dehydrogenation, and oxidation with air. In this study, the latter process will be considered in the superstructure and the chemical reactions for it are as follows:



The oxidation of methanol to formaldehyde occurs at a temperature of 470°C in a reactor containing tubes filled with a catalyst based on iron, molybdenum, or vanadium oxide. In order to write the material balances for this process, an overall reaction was obtained by summing up the two equations above, resulting in the following reaction equation:

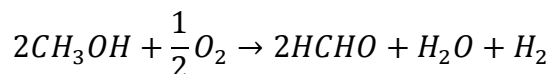


Fig. 4.5 is a block diagram illustration of the oxidation of methanol to formaldehyde showing all the inlet and outlet streams. These streams are then defined in **Table 4.5**.

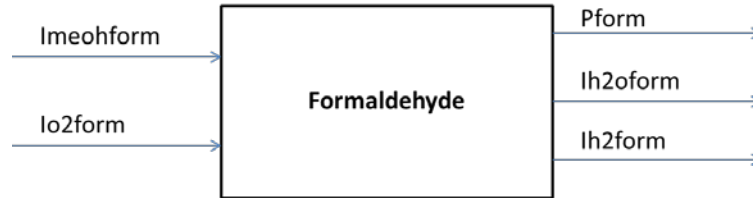


Fig. 4.5- Block diagram of formaldehyde plant.

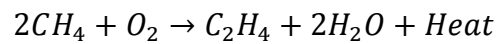
Table 4.5: Process streams in formaldehyde plant.

Name of Stream	Description
Imeohform	Methanol to formaldehyde plant
Io2form	Oxygen to formaldehyde plant
Pform	Production of formaldehyde from plant
Ih2oform	Water produced from formaldehyde plant
Ih2form	Hydrogen produced from formaldehyde plant

Methane can also be used in the production of olefins (ethylene, propylene) and there are three such processes included in the superstructure: oxidative coupling of methane, the methanol-to-olefins process, and the methanol-to-propylene process. The oxidative coupling of methane (OCM) process has been the subject of research interest for almost thirty years because of its potential to reduce costs, energy, and environmental emissions in the production of ethylene (http://siluria.com/Technology/Oxidative_Coupling_of_Methane). The first demonstration plant commercializing this technology was commissioned around April of

2015 and produces approximately 1 metric ton/day of ethylene (ICIS “US Siluria starts up methane-to-ethylene demo plant”, April 1 2015). The reason for this breakthrough is Siluria’s development of a process that uses viruses as a design tool to create a biological template for nanowire catalysts.

In this process, methane and oxygen react over a catalyst environment to produce ethylene and water, as shown in the following reaction:



The nanowire catalyst can activate methane at a temperature that is “a couple of hundred degrees” lower than the best existing catalyst, which operate between 800°C to 950°C (Fairley, 2010). **Fig. 4.6** shows a block diagram representation of the process with the reactants and products streams defined in **Table 4.6**.

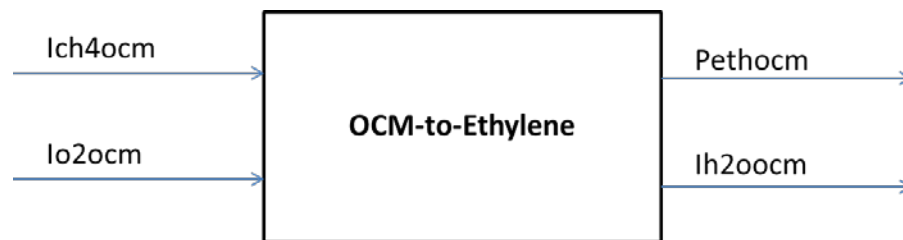
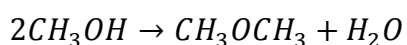


Fig. 4.6- Block diagram of OCM-to-ethylene plant.

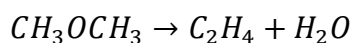
Table 4.6: Process streams for OCM-to-ethylene plant.

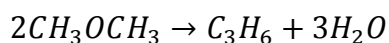
Name of Stream	Description
Ich4ocm	Methane to OCM plant
Io2ocm	Oxygen to OCM plant
Pethocm	Production of ethylene from OCM plant
Ih2oocm	Water produced from OCM plant

The UOP methanol-to-olefins (MTO) process is a means to produce ethylene and propylene from feedstock sources other than crude oil or condensates. The discovery and utilization of the SAPO-34 catalyst in this process provided a technology breakthrough since it created a more selective route for methanol conversion to ethylene and propylene with reduced amounts of heavy byproducts (“Shale Gas Monetization- How to Get Into the Action”, 2013). The reactor in the process operates in the vapor phase at temperatures of 340°C to 540°C and pressures between 15 and 45 psig (1.03 and 3.1 bar). The reaction for MTO occurs in two steps. The first step is the conversion of methanol to dimethyl ether (DME) and water:



The second step is the conversion of DME to both ethylene and propylene. The ratio between ethylene and propylene production depends on the catalyst, reaction parameters, and the technology (Jasper and El-Halwagi, 2015). The reactions, which occur in a fluidized bed reactor, for this step can be represented as follows:





In order to write the material balance equations for the optimization program, one overall equation for each of ethylene and propylene had to be written. These equations are written as follows for ethylene and propylene, respectively:

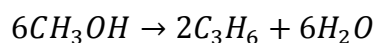
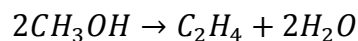


Fig.4.7 shows a block diagram representation of the MTO process with the reactants and products defined in **Table 4.7**.

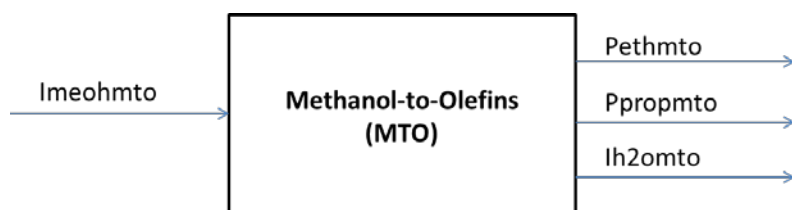


Fig. 4.7- Block diagram of MTO plant.

Table 4.7: Process streams of MTO process.

Name of Stream	Description
Imeohmto	Methane to MTO plant
Pethmto	Production of ethylene from MTO plant
Ppropmto	Production of propylene from MTO plant
lh2omto	Water produced from MTO plant

The Lurgi methanol-to-propylene (MTP) process differs from the MTO process in that crude methanol has to be purified prior to the reaction. **Fig. 4.8** is a block diagram

illustration of the MTP process and its inlet and outlet streams, while **Table 4.8** gives the stream definitions. The process also produces liquefied petroleum gases (LPGs) and gasoline.

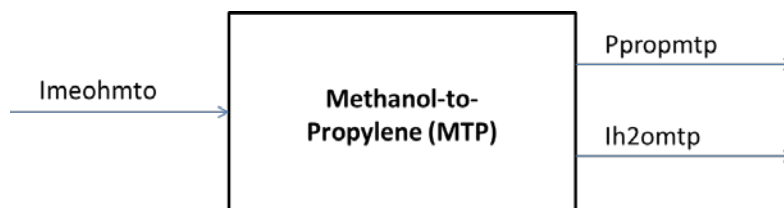
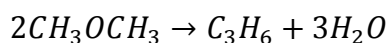
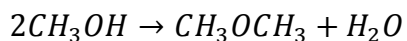


Fig. 4.8- Block diagram of MTP plant.

Table 4.8: Process streams of MTP process.

Name of Stream	Description
Ich4amm	Natural gas to ammonia plant
Ih2oamm	Steam to ammonia plant
In2amm	Air to ammonia plant

As for the reaction, methanol is first converted to DME and water, and then is further reacted to propylene on a zeolite-based catalyst (ZSM-5) in a fixed bed reactor (Jasper and El-Halwagi, 2015). Similar to the MTO process, the reactions of the MTP process are written as follows:



In addition to the chemicals above, ammonia is another widely-produced chemical that is included in the superstructure. **Fig. 4.9** gives the block diagram for the

ammonia process and **Table 4.9** gives the definitions of the inlet and outlet streams. After natural gas is desulfurized, it is fed to a steam reformer, where part of the methane is converted to carbon oxides and hydrogen over a nickel catalyst. Then, the gas mixture enters an autothermal reformer where air is injected to provide nitrogen needed in ammonia synthesis. Since carbon oxides are poisonous to the ammonia synthesis catalyst, the reformed gas mixture is shifted for more H_2 . Also, carbon monoxide is oxidized to carbon dioxide. Then, a methanator is utilized to remove remaining CO_2 traces by reaction with H_2 to produce methane and water. In the last step, the syngas is compressed and converted to ammonia in the synthesis reactor.

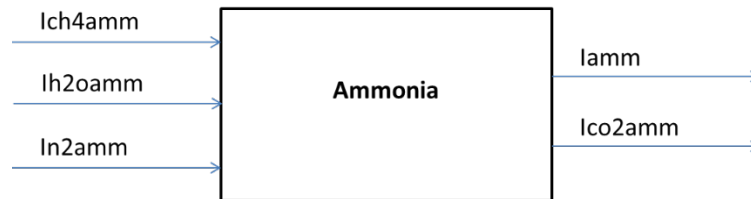
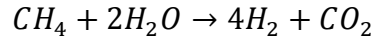


Fig. 4.9- Block diagram for ammonia production plant.

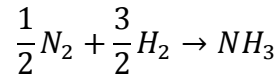
Table 4.9: Process streams for ammonia production plant.

Name of Stream	Description
Ich4amm	Natural gas to ammonia plant
lh2oamm	Steam to ammonia plant
ln2amm	Air to ammonia plant
lamm	Total production from ammonia plant
lco2amm	CO_2 production from ammonia plant

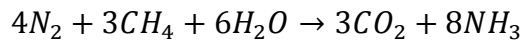
The steam reforming reaction and water-gas shift reaction can be summed up into the following reaction equation:



The ammonia synthesis reaction is as follows:



In order to write the material balance equations for this block, the summation of the steam reforming and water-gas shift reactions was multiplied by 3 and the ammonia synthesis reaction was multiplied by 8 (in order to eliminate hydrogen) resulting in the following overall equation for the process:



In this study, there were two options for the monetization of ammonia: to be sold as ammonia, or to be further processed into urea. The major outlet for urea (about 80% of total consumption) is as a fertilizer, and it is also used in the manufacture of urea-formaldehyde resins produced by the condensation reaction between urea and formaldehyde. Subsequently, these resins are used in adhesives for paper, board, plywood, surface-coatings molding resins and textile processing (Wells, 1999). **Fig. 4.10** is an illustration of the urea production process, and **Table 4.10** shows the inlet and outlet streams.

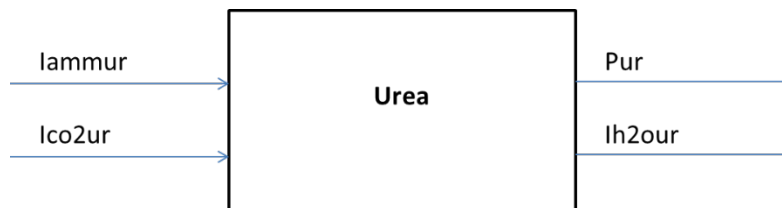
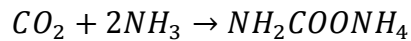


Figure 4.10- Block diagram for urea production plant.

Table 4.10: Process streams for urea production plant.

Name of Stream	Description
Iammur	Ammonia to urea plant
Ico2ur	CO ₂ to urea plant
Pur	Urea produced from urea plant
Ih2our	Water produced from urea plant

The formation of ammonia occurs in two steps, which are represented by the following two equations:



Usually, these two reaction steps are expressed as the following overall reaction:



The reaction occurs at a temperature between 180°C and 210°C and a pressure of 150 bar, and around 70% of the carbamate (NH_2CONH_2) formed is decomposed into urea (Wells, 1999).

Economics/Profitability

Base Case

As previously mentioned, the prices of chemicals and of natural gas as of November 2015 are used in the calculation of the objective profit equation. The superstructure is a mixed-integer nonlinear programming problem (MINLP), solved with

the global solvers in LINGO. The results of the chemical production complex for this case can be seen in **Fig. 4.11**. The methanol produced in the complex was distributed between three pathways: the formaldehyde production process, the MTO process, and sold as is. Thus, no methanol was used to produce acetic acid or DME. Instead, acetic acid was produced by the BP SaaBre process, while DME was produced through the syngas route. Ethylene was produced through the oxidative coupling of methane (OCM) process, a new technology for which the first pilot plant started up in April 2015. Propylene, the other major olefin, was produced by the MTO technology. Also, 2.0 MMTA of ammonia was produced and sold as is, so no urea was manufactured in this case of the complex.

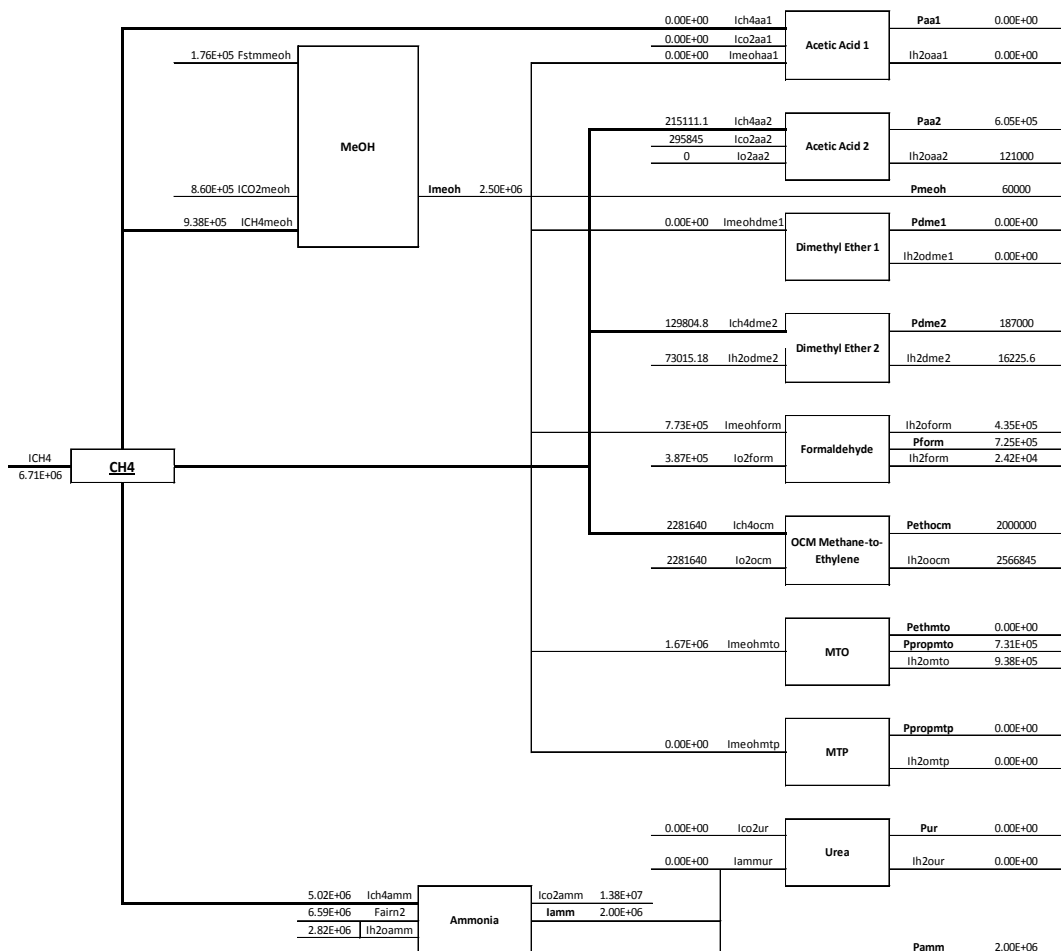


Fig. 4.11- Chemical production complex base case.

In this case, it is observed that out of 2.50 MMTA of methanol produced, approximately 60,000 MTA of it was sold as is to the market. From the 2.44 MMTA remaining, 1.67 MMTA of methanol is used to produce 0.73 MMTA of propylene (sold for \$819/MT) via the MTO process. The remaining 0.773 MMTA of methanol is converted through the formaldehyde production unit to formaldehyde which is subsequently sold in the market at \$830/MT. While 1.16 MMTA of carbon dioxide were consumed, it should be noted that 13.8 MMTA was produced in this case of the

production complex. As for water, 2.90 MMTA of it were consumed in the complex compared to 4.06 MMTA of it being produced. Also, there were 0.044 MMTA of hydrogen, an important chemical building block, produced in the complex. The annual profit obtained in this case was \$3,731 million per year. These results are shown in **Table 4.11**.

Table 4.11: Sales and costs associated with base case.

Category	Value (\$ millions)
Income from Sales	5,183
Annualized fixed costs	268
Raw material costs	912
Utility costs	232
Gross Profit	3,771

Methanol Price Sensitivity Case

After the base case, the objective was to examine the effect of price sensitivity on the type and quantity of chemicals produced. Specifically, the effects of fluctuations in the price of methanol will be examined here. After the middle of 2015, the price of methanol declined again to approximately \$161/MT in response to the 60% increase in U.S. production capacity (ICIS, January, 15, 2016). Thus, the price of methanol in the program was changed from \$366/MT to \$161/MT to examine how the effects of that price change on the chemical production complex. From the results in **Fig. 4.12**, it can be seen that no methanol was sold as is to the market. This can possibly be explained by the drop in methanol price, thus rendering the product less likely to make a profit than if it was further processed into formaldehyde or olefins. In this case of the complex, of the

2.5 MMTA of methanol that were produced: 0.773 MMTA were used to produce 0.725 MMTA of formaldehyde, and the remaining 1.73 MMTA were used to produce 0.757 MMTA of propylene via the MTO process. By comparing these values to the base case, it can be concluded that the methanol that was previously sold as is (60,000 MTA) was further processed into propylene in the MTO process. As a result, the amount of propylene produced was slightly higher in this case (0.757 MMTA) than in the base case (0.73 MMTA). Similar to the base case, 2.00 MMTA of ammonia, and no urea, were produced and sold as is to the market. As for the amounts of water, carbon dioxide, and hydrogen that were reacted and produced in the complex, the numbers were very similar to the base case, with the exception being a slight increase in the amount of water produced to 4.09 MMTA (up from 4.06 MMTA). This slight increase can be attributed to the increase in the amount of propylene produced in comparison to the base case.

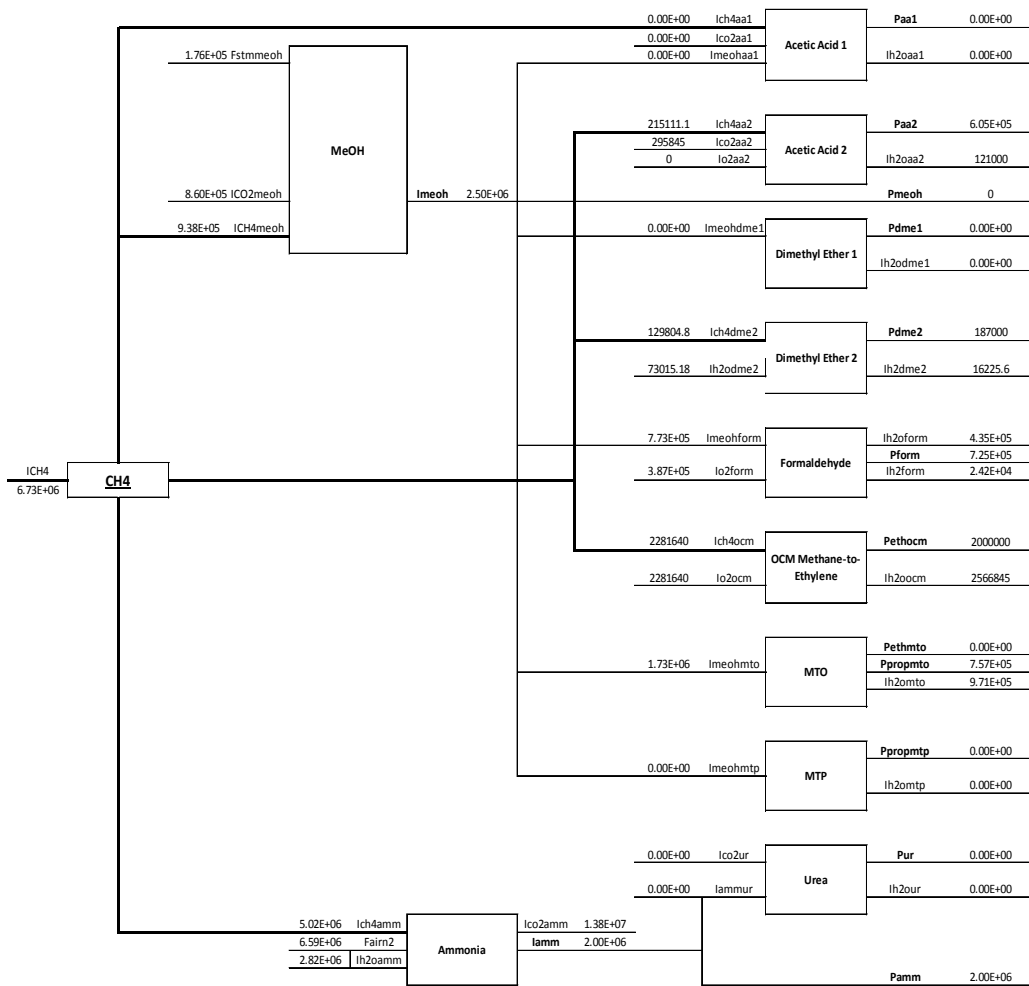


Fig. 4.12- Chemical production complex for methanol price sensitivity case.

The total profit generated in this case of the production complex was \$3,766 million, which is almost the same as the base case. **Table 4.12** shows the breakdown of the sales and costs associated with the profit equation.

Table 4.12: Sales and costs associated with methanol price sensitivity case.

Category	Value (\$ millions)
Income from Sales	5,183
Annualized fixed costs	268
Raw material costs	915
Utility costs	234
Gross Profit	3,766

Urea Price Sensitivity Case

In both the base and the lower methanol price cases, it was noted that no urea was produced in the production complex. This raises the opportunity to experiment with the LINGO program to determine the conditions under which urea is produced and the changes that will incur on the quantity and types of chemicals manufactured in the complex as well as the profit. It should be noted that the methanol price in this case of the program is the same as it was in the base case (\$366/MT). To gain a better idea of the changes that urea prices have gone through over the past ten years, **Fig. 4.13** shows that urea has experienced a steady decline over the last four years after reaching \$500/MT in early 2012. Looking back earlier, the price of urea was around \$750/MT around the time of the 2008 recession before crashing to \$250/MT (www.indexmundi.com).

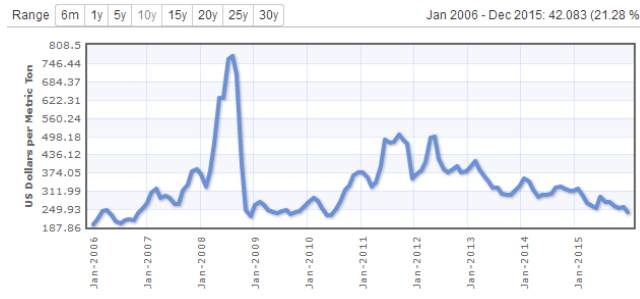


Fig. 4.13- Urea price history over the period 2006-2015 (www.indexmundi.com).

For this case of the production complex, the price of urea was \$500/MT, an increase from the base case price of \$255/MT. This change resulted in urea being manufactured from ammonia, and the results for the complex can be seen in **Fig. 4.14**. Similar to the base case, 2.00 MMTA of ammonia was produced and was processed in two routes: 1.15 MMTA sold as ammonia, and 0.849 MMTA processed into urea. In comparison to the base case, the production of other chemicals such as acetic acid, DME, and olefins was not affected. The addition of the urea process increased the amount of carbon dioxide consumed in the complex to 2.25 MMTA (up from 1.16 MMTA) and the amount of water produced to 4.51 MMTA (up from 4.06 MMTA).

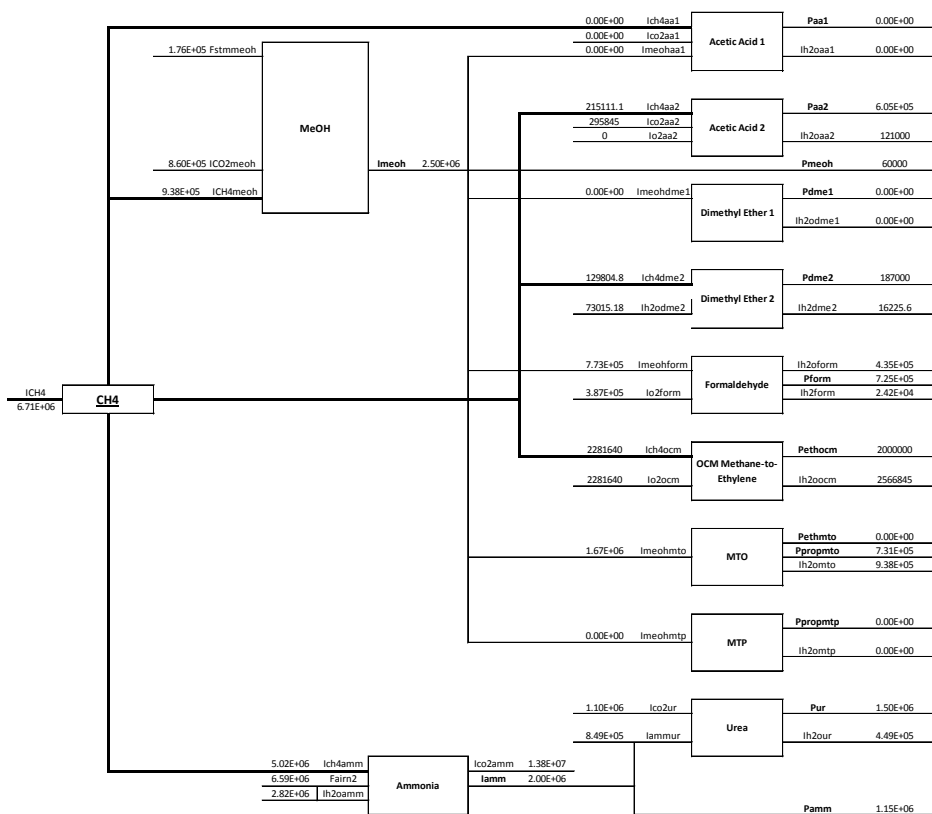


Fig. 4.14- Chemical production complex for urea price sensitivity case.

For this case, the overall profit as \$3,823 million representing an increase of \$92 million in profits attributable to urea sales. **Table 4.13** shows a breakdown of the sales and costs associated with this case of the production complex.

Table 4.13: Sales and costs associated with urea price sensitivity case.

Category	Value (\$ millions)
Income from Sales	5,339
Annualized fixed costs	296
Raw material costs	912
Utility costs	268
Gross Profit	3,863

Restrictions on Available Gas

Another case that was examined is when the amount of natural gas available for usage is less than the total Texas annual production used previously. In reality, only 20-25% of the gas would be available for usage in the proposed chemical production complex because the remainder would have been contracted to other entities. When this was done, the amount of gas available was reduced from 137 MMTA (77,146,549 MMSCF/yr) to 27.4 MMTA 15,429,310 MMSCF/yr). However, as shown in **Fig. 4.15**, no change was incurred on the results. This was due to that only about 5.65% of the available gas is actually being used in the production complex. In the program, the amount of available methane was set by the following equation:

$$I_{CH_4} = F_{ng} * 0.8675$$

The fraction 0.8675 used above is the average volume percent of methane in Barnett shale samples (86.75%) as shown in **Table 2.1** (table in Chapter2). Using the above equation, if the amount of methane of 6.71 MMTA, then the amount of natural gas used is:

$$F_{ng} = \frac{I_{CH_4}}{0.8675} = \frac{6.71 \times 10^6 MTA}{0.8675} = 7.735 MMTA \text{ of gas}$$

The amount of 7.735 MMTA of gas is only 5.65% of the available 137 MMTA of dry natural gas production in Texas.

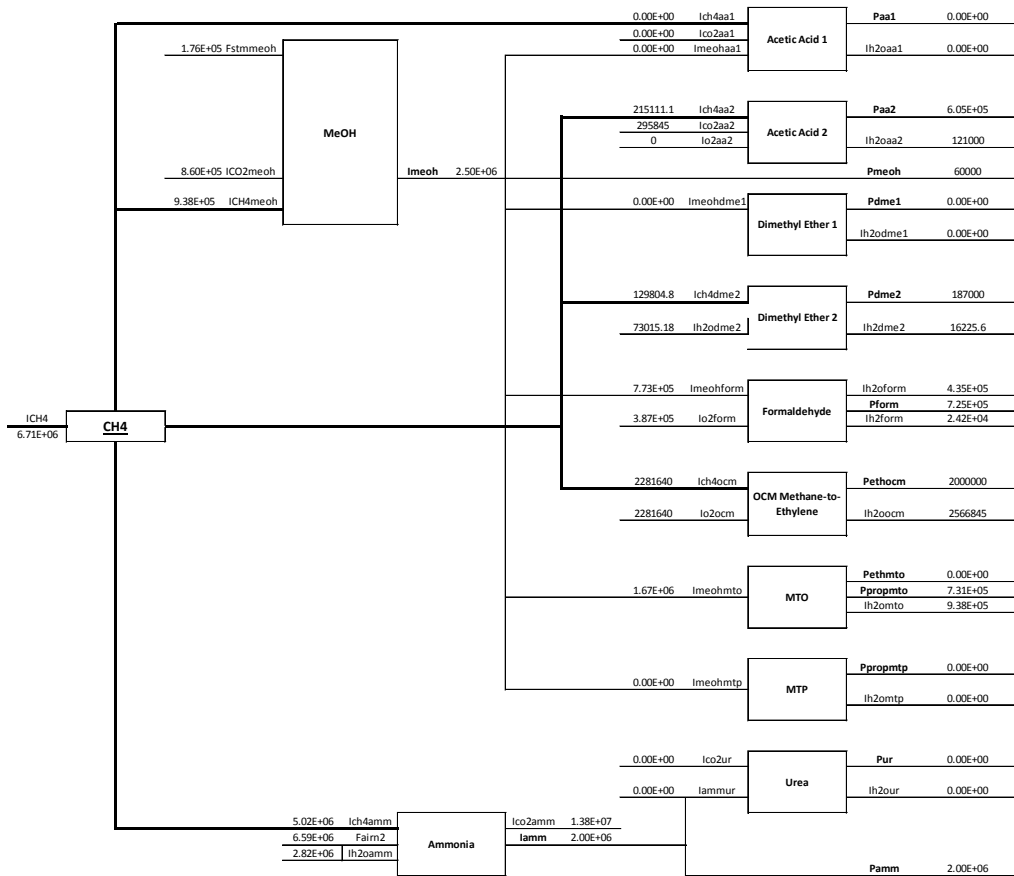


Fig. 4.15- Chemical production complex results for limited available gas case.

Environmental Aspects

Aside from economics/profitability, it is desired to see the effect of environmental aspects or emission restrictions on the results of the chemical production complex. This is done by incorporating CO_2 emissions obtained from literature as rates per metric ton of product. In addition to the CO_2 emissions associated with production, there are emissions resulting from the fuel burned for utilities (heating, cooling, and electric power) in the process. In this complex, it will be assumed that natural gas, which emits 117 lbs CO_2 /MMBtu, is used as fuel (www.eia.gov).

For the methanol production process, there were 182.7 lbmol/hr of CO₂ produced from the process, which can be converted to 28,880 MTA (Ehlinger, 2014). Given that the process produces 1.65 MMTA of methanol, the ratio of CO₂ produced per methanol is 0.0175 MT CO₂/MT methanol. However, this does not account for the CO₂ produced for utilities. The utilities used in the process were reported as follows (Ehlinger, 2014):

Table 4.14: Utilities for methanol production process.

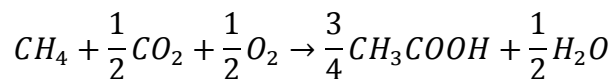
Utility	Value
Heating	1.425×10^6 MMBtu/yr
Cooling	11.2×10^6 MMBtu/yr
Power	398.5×10^3 MMBtu/yr
Total	13.02×10^6 MMBtu/yr

To determine the amount of CO₂ produced as a result of using natural gas for utilities, the following calculation is performed:

$$13.02 \times 10^6 \frac{\text{MMBtu}}{\text{yr}} \times \frac{117 \text{ lbs } CO_2}{\text{MMBtu}} \times \frac{1 \text{ MT } CO_2}{2204.6 \text{ lbs } CO_2} = 0.691 \text{ MMTA } CO_2$$

$$\frac{0.691 \text{ MMTA } CO_2}{1.65 \text{ MMTA Methanol}} + \frac{0.0175 \text{ MTA } CO_2}{1 \text{ MT Methanol}} = \frac{0.437 \text{ MT } CO_2}{\text{MT Methanol}}$$

For the SaaBre process, the amount of CO₂ produced was calculated from the heat of reaction of acetic acid from the reaction equation:



The resultant heat of reaction for the above equation was -234.1 kJ/mol of acetic acid (AA) produced, which can be converted to -221.9 Btu/mol. To estimate the amount of

CO₂ produced as a result of utilities for this process, the following calculation was performed:

$$\frac{221.9 \text{ Btu}}{\text{mol AA}} \times \frac{1 \text{ mol AA}}{60.05 \text{ g}} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1000 \text{ kg}}{1 \text{ MT}} = \frac{3.69 \text{ MMBtu}}{\text{MT AA}}$$

$$\frac{3.69 \text{ MMBtu}}{\text{MT AA}} \times \frac{117 \text{ lbs CO}_2}{\text{MMBtu}} \times \frac{1 \text{ MT CO}_2}{2204.6 \text{ lbs CO}_2} = \frac{0.196 \text{ MT CO}_2}{1 \text{ MT AA}}$$

For the direct syngas-to-DME process, the amount of CO₂ produced from utilities was determined in a similar method to that used for the methanol process. The utilities used by the process were reported as follows (Karagoz, 2014):

Table 4.15: Utilities for syngas-to-DME production process.

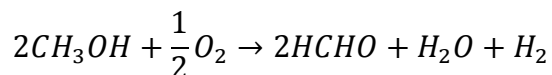
Utility	Value
Heating	1.302×10^6 MMBtu/yr
Cooling	7.252×10^6 MMBtu/yr
Power	589×10^3 MMBtu/yr
Total	9.143×10^6 MMBtu/yr

Given that the production rate was 3,250 MT/day in the study by Karagoz (2014), the amount of CO₂ produced was determined to be:

$$\frac{9.143 \times 10^6 \text{ MMBtu}}{\text{yr}} \times \frac{117 \text{ lbs CO}_2}{1 \text{ MMBtu}} \times \frac{1 \text{ MT CO}_2}{2204.6 \text{ lbs CO}_2} \times \frac{\text{yr}}{1.07 \text{ MMT DME}}$$

$$= \frac{0.452 \text{ MT CO}_2}{1 \text{ MT DME}}$$

Similar to the acetic acid process, the CO₂ emissions from the formaldehyde production process were determined by calculating the heat of formation of the following chemical reaction equation:



The heat of reaction for the above equation was -33.5 kJ/mol of acetic acid (AA) produced, which can be converted to -31.8 Btu/mol. To estimate the amount of CO₂ produced as a result of utilities for this process, the following calculation was performed:

$$\frac{31.8 \text{ Btu}}{\text{mol form.}} \times \frac{1 \text{ mol form.}}{30.031 \text{ g}} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1000 \text{ kg}}{1 \text{ MT}} = \frac{1.058 \text{ MMBtu}}{\text{MT form.}}$$

$$\frac{1.058 \text{ MMBtu}}{\text{MT form.}} \times \frac{117 \text{ lbs CO}_2}{\text{MMBtu}} \times \frac{1 \text{ MT CO}_2}{2204.6 \text{ lbs CO}_2} = \frac{0.0561 \text{ MT CO}_2}{1 \text{ MT form.}}$$

As for the MTO process, the reported numbers which are shown in **Table 4.16** include CO₂ emissions from utilities (Jasper and El-Halwagi, 2015).

Table 4.16: CO₂ emission values used in the optimization program.

Process	Rate of CO ₂ Emissions (MT CO ₂ /MT product)	Source
Methanol	0.437	Ehlinger, 2014
Acetic Acid	0.196	ΔH_{rxn}
Syngas-to-Dimethyl Ether	0.452	Karagoz, 2014
Formaldehyde	0.0561	ΔH_{rxn}
Methanol-to-Olefins	20.9 (MT of propylene)	Jasper and El-Halwagi, 2015

Base Case CO₂ Emissions

First, the rates of CO₂ emissions were added to the base case and it was determined that a total of 30.81 MMTA of CO₂ was produced. Next, it was desired to place restrictions on the amount of carbon dioxide produced and observe the effects that would have on the configuration of products and the profit generated by the complex. Several trials were conducted using the LINGO program with the amount of CO₂ to be generated restricted to 90%, 85%, 80%, and 75% of the amount produced in the base case. The cases at 90% and 80% will be examined in detail here.

90% of Base Case CO₂ Emissions

Starting with the 90% case, the profit declined to \$3,625 million in comparison to the \$3,731 million in the base case, or a reduction of about 2.8%. Aside from profit, there are many differences between the base case and the 90% case. Starting with the raw materials, there was a 2% reduction in the amount of gas used in the complex from 6.73 MMTA to 6.60 MMTA. Also, the amount of methanol produced declined by 7.2% from 2.50 MMTA to 2.32 MMTA, and no methanol was sold to the market whereas 60,000 MTA of it were sold in the base case. The amount of ethylene produced in the OCM process declined from 2.00 MMTA to 1.93 MMTA, with an additional 0.0720 MMTA of ethylene produced from the MTO process. The amount of propylene produced by the MTO process also declined to 0.606 MMTA from 0.757 MMTA which can be attributed to the decline in methanol produced by the complex. **Fig. 4.16** provides a summary of these results.

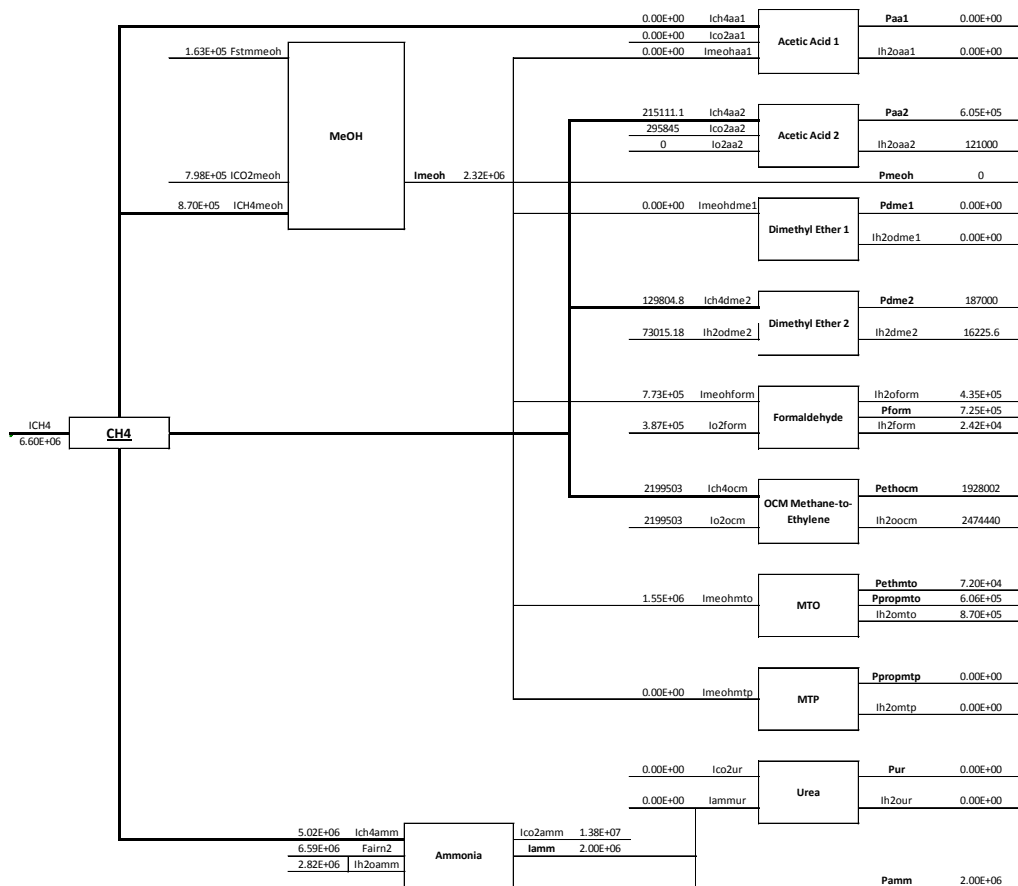


Fig. 4.16- Chemical production complex results for CO2 emissions restricted to 90%.

80% of Base Case CO2 Emissions

As for the 80% case, the profit generated from the production complex further declined to \$3,517 million, representing a decline of about 5.7% compared to the base case (\$3,731 million), and 3% compared to the 90% case (\$3,625 million). The amounts of acetic acid, dimethyl ether, and formaldehyde produced remained the same as in the base case, and similar to the 90% case, no methanol was sold as is to the market. As for olefins, the amount of ethylene produced in the OCM process declined from 1.92

MMTA in the 90% case to 1.78 MMTA, with an additional 0.219 MMTA of ethylene produced from the MTO process. This means that the amount of propylene produced by the MTO process also declined to 0.459 MMTA from 0.606 MMTA which can be attributed to the decline in methanol produced by the complex in this case compared to the base case. **Fig. 4.17** provides a summary of these results.

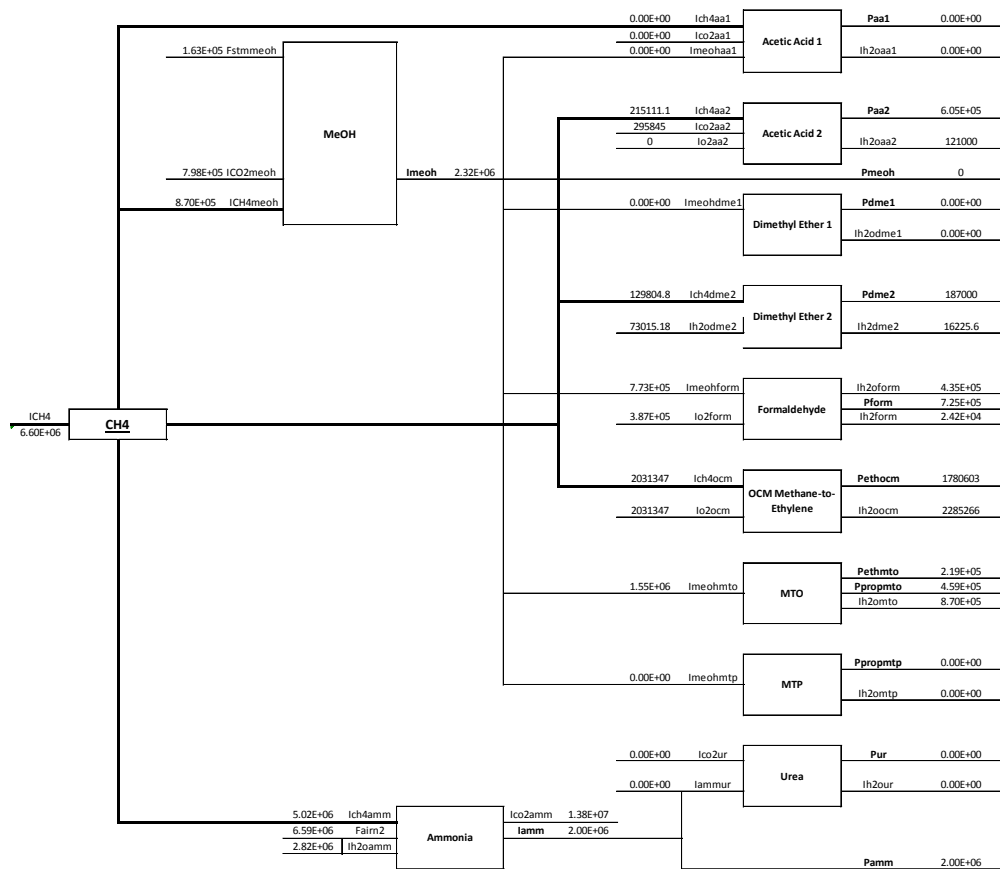


Fig. 4.17- Chemical production complex results for CO₂ emissions restricted to 80% of base case.

From the above cases, it can be determined that as the amount of CO₂ produced is further restricted, three main trends emerge: methanol is not sold as is to the market,

ethylene production gradually switched to the MTO process from the OCM process, and propylene production declined. **Table 4.17** provides the amount of CO_2 produced and the profit generated by the production complex for every case examined via the program, and **Fig. 4.18** shows this relationship in graphical form.

Table 4.17: Profit generated vs. CO2 emissions restriction.

Case	CO2 Produced (MMTA)	Profit (\$ millions)
Base (100%)	30.81	3,731
90	27.73	3,625
85	26.19	3,576
80	24.65	3,517
75	23.11	3,458
65	20.03	3,339
55	16.95	3,224

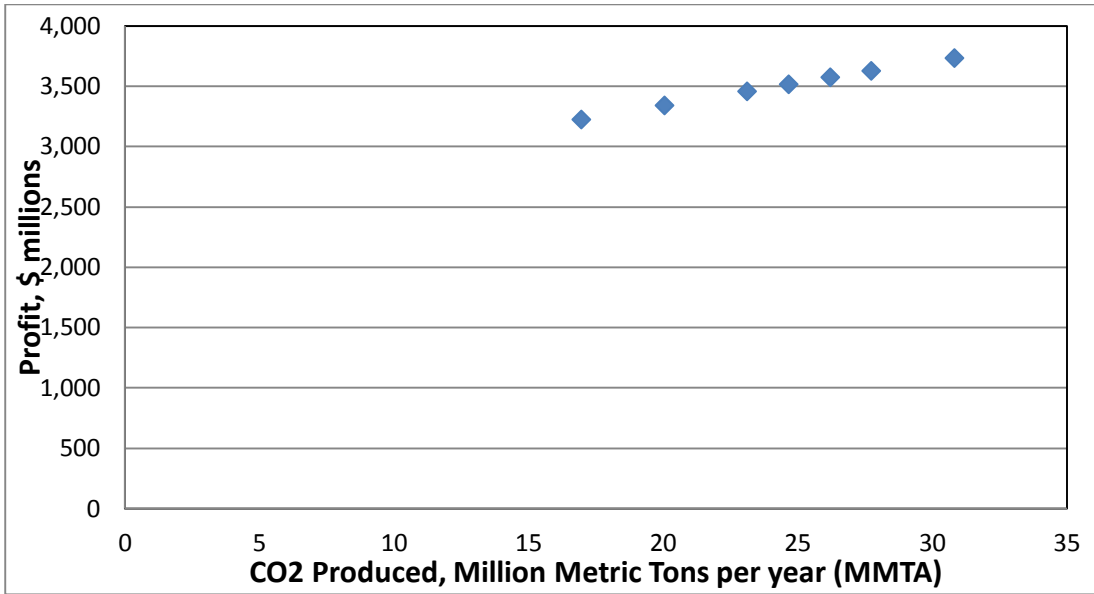


Fig. 4.18- Graphical representation of profit generated vs. CO2 emissions restrictions for the chemical production complex base case.

Safety Considerations

The final set of considerations taken into account for this chemical production complex are safety metrics, which will be done through a Dow Fire & Explosion Index analysis of the reactors of each of the processes involved in the base case of the complex. The DFEI results will not be included in the objective function (profit equation) but provide a starting point for further analysis of the safety aspects of this proposed chemical complex. While the DFEI is useful in identifying process units where hazardous conditions exist, it does not estimate the damage that might result from such an event (Turton, 2012). **Table 3.14** shows the qualitative hazard levels for various values of the DFEI. Throughout the analysis, the following items in the DFEI form were considered: A-C under General Process Hazards, and A, E, and G under Special Process Hazards. Table 4.18 shows the Dow Fire & Explosion Index values that were

obtained using this methodology and their corresponding qualitative hazard levels.

Table 4.18: DFEI values and their corresponding qualitative hazard levels.

Process	Dow Fire & Explosion Index	Qualitative Hazard Level
Methanol	153	Heavy
Acetic Acid	110.5	Intermediate
Syngas-to-Dimethyl Ether	88	Moderate
Formaldehyde	73.6	Moderate
Methanol-to-Olefins	98	Intermediate
Ammonia	153	Heavy

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

The objective of this work was to provide a high-level preliminary analysis of a chemical production complex using natural gas as a feedstock taking into account economic, environmental, and safety considerations. In Chapter I, literature on supply chain optimization was surveyed with a special focus on shale gas. It was determined that while many works focus on a specific process or the whole supply chain, there is little work done on a chemical complex that would utilize shale gas as feedstock and take into account economics, environment, and safety factors.

In Chapter II, a brief overview of shale gas composition, production, and processing was discussed to provide some background on the importance of shale gas and its current role in U.S. energy industry. Also, the production chemistry, value chain, and market outlook was detailed for three major chemical building blocks derived from natural gas: methanol, ethylene, and propylene. In each discussion, the rise of the shale gas industry in the United States and its impact was discussed.

In Chapter III, the methodology used in developing the chemical production complex optimization program was detailed. The amount of available natural gas was determined as the dry gas production for Texas in 2014. The objective function was defined as the maximization of profit based on the constraints which were material balance equations, production constraints for each plant, and capital and utility costs. In addition, the type of environmental and safety considerations that will be taken into

account in the study were detailed to be CO₂ emissions and the Dow Fire & Explosion Index for the reactor unit in each process, respectively.

In Chapter IV, the results of the optimization program were discussed in detail. First, the block diagrams and streams for each process were shown to give a clear idea of the chemical production complex and its component processes. Second, taking into account profitability only, three cases were tested using the program. A base case (latest prices obtained as of November 2015) was presented, as well as two more cases involving a reduced methanol price, and an increased urea price. It was seen that reducing the sales price of methanol no longer made it viable to sell as is to the market and instead was diverted to the MTO process where it is used in the production of more valuable olefins. As for the case where urea price was increased, it was seen that the profit increased in comparison to the base case as urea was made from ammonia and sold, where it had not been in the base case. Another case was tested where the amount of gas available as feedstock was limited to 20% of the available quantity, but that did not have an effect on the results because only 5% of the available gas was being utilized. Afterwards, environmental considerations for the base case were added in the form of CO₂ emissions which were based on peer-reviewed sources or heats of reaction for the chemical equations of the processes in question. It was determined that as the amount of CO₂ was further restricted, profit declined because production of certain chemicals declined to comply with the new CO₂ restrictions. Finally, the Dow Fire & Explosion Index for each process was calculated for the reactor unit and a qualitative hazard level was presented.

Based on the above, there are ample future research opportunities available from this work. The following is a list of these possible avenues:

1. Inclusion of criteria air pollutants (CAP) emissions from data provided by the National Emissions Inventory (NEI).
2. Performing ASPENPlus® simulations on each process to get a more accurate picture of the production quantities.
3. Based on these simulations, a better safety analysis of the chemical production complex can be performed using DFEI or other metrics as determined by the researcher.
4. Inclusion of the safety metrics as a constraint in the optimization program.

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