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Usage of natural gas from Brazilian pre-salt to meet the national needs of methanol, ammonia and urea

Rio de Janeiro

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Tese apresentada, como requisito parcial para obtenção do título de Doutor, ao Programa de Pós-Graduação em Engenharia Química, da Universidade do Estado do Rio de Janeiro. Área de concentração: Fundamentos em Engenharia Química.

Orientador: Prof. Dr. André Luís Alberton
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ABSTRACT

Santos, Walmir Gomes dos, *Usage of natural gas from Brazilian pre-salt to meet the national needs of methanol, ammonia and urea*, Brasil, 2018, 245 f. Tese (doutorado em engenharia química) – Instituto de Química, Universidade do Estado do Rio de Janeiro, Rio de Janeiro, 2018.

Natural gas has increased its share in the energy matrix of major countries consistently in recent years. Several segments of the global industry have already realized the best gas quality and are benefiting from the use of this gas in their production processes. However, it is in the use as raw material, in industrial complexes of chemical transformation, that natural gas finds its use nobler and of better economic value. Considering that chemicals of high strategic value, such as methanol, fertilizers, organic acids, among other chemicals, are still imported in large quantities, requiring the expenditure of millions of dollars in currency of the country and also considering that Brazil currently has the possibility of obtaining the availability of large quantities of natural gas produced in the pre-salt, this work proposes a technical and economically viable solution for the more noble use of part of this gas that is being made available to the domestic market in the form of an industrial complex, where the raw material used is only natural gas. This complex would have the function of producing all the ammonia, urea and methanol currently imported. The dynamics of natural gas prices may make it possible to use gas as a raw material in industrial plants or make it impossible to use it. Countries with lower gas prices have a competitive advantage in the installation of complexes that use natural gas as raw material. Based on this scenario, this work presents an analysis of gas prices in the Brazilian market, as well as an analysis of the cost of implementing an integrated complex for the production of these products. In parallel, a general review is presented on the technologies used by the production processes of the main natural gas derivatives. Then, production units of methanol, ammonia and urea are simulated in a commercial simulator according to good engineering practices, to allow capital cost (CAPEX) calculation of these units, in addition to the analysis of production costs and the expected revenue with the marketing of these products. Concluding the work, a proposal is presented for an integrated industrial complex capable of fully supplying the Brazilian market with these products. The complex uses the most appropriate technologies to maximize the economic result of the project and meets the specific conditions of the Brazilian market.

Keywords: Natural gas. Synthesis gas. Methanol. Ammonia. Urea. Simulation. Techno-economic analysis. Pre-salt.

RESUMO

Santos, Walmir Gomes dos, *Uso do gás natural do pré-sal brasileiro para atender às necessidades nacionais de metanol, amônia e uréia.* Brasil, 2018, 245 f. Tese (doutorado em engenharia química) – Instituto de Química, Universidade do Estado do Rio de Janeiro, Rio de Janeiro, 2018.

O gás natural tem aumentado sua participação na matriz energética dos principais países de forma consistente nos últimos anos. Vários segmentos da indústria mundial já perceberam a melhor qualidade do gás e se beneficiam do uso desse combustível em seus processos de produção. No entanto, é na utilização como matéria-prima, em complexos industriais de transformação química, que o gás natural encontra sua utilização mais nobre e de melhor valoração econômica. Considerando que produtos químicos de alto valor estratégico, como metanol, fertilizantes, ácidos orgânicos, entre outros produtos químicos, são ainda importados em grandes quantidades, exigindo o dispêndio de milhões de dólares em divisas do país e também considerando que o Brasil atualmente tem a possibilidade de contar com a disponibilidade de grande quantidade de gás natural produzido no pré-sal, este trabalho vem propor uma solução técnica e economicamente viável para utilização mais nobre de parte desse gás que está sendo disponibilizado para o mercado interno, na forma de um complexo industrial, em que a matéria-prima utilizada seja apenas o gás natural. Este complexo teria a função de produzir toda a amônia, ureia e metanol atualmente importados. A dinâmica de preços do gás natural pode tornar viável o aproveitamento do gás como matéria-prima em unidades industriais ou impossibilitar o seu uso. Países com mais baixos preços de gás possuem uma vantagem competitiva na instalação de complexos que utilizam o gás natural como matéria-prima. Com base neste cenário, este trabalho apresenta uma análise dos preços do gás e seus principais derivados no mercado brasileiro, assim como uma análise do custo de implantação de um complexo integrado para a produção desses produtos. Em paralelo, é apresentada uma revisão geral sobre as tecnologias utilizadas pelos processos produtivos dos principais derivados do gás natural e em seguida, unidades de produção de metanol, amônia e ureia são simuladas em um simulador comercial, de acordo com as boas práticas de engenharia, para permitir o cálculo do custo de capital (CAPEX) dessas unidades, além da análise dos custos de produção e a receita prevista com a comercialização desses produtos. Concluindo o trabalho, é apresentada uma proposição de um complexo industrial integrado capaz de suprir plenamente o mercado interno com esses produtos. O complexo utiliza as tecnologias mais adequadas para maximizar o resultado econômico do projeto e atende as condições específicas do mercado brasileiro.

Palavras-chave: Gás natural. Syngas. Metanol. Amônia. Ureia. Simulação. Análise técnico-econômica. Pré-sal.

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LIST OF ABBREVIATIONS

ABIQUIM	Brazilian Chemical Industry Association
ASU	Air Separation Unit
ATR	Autothermal Reforming
BOE	Barrels of Oil Equivalent
C_{5+}	Hydrocarbon fraction from pentane and heavier
COMPERJ	Petrochemical Complex of Rio de Janeiro (*Complexo Petroquímico do Rio de Janeiro*)
GASBOL	Bolivia-Brazil Gas Pipeline (*Gasoduto Bolívia-Brasil*)
GASENE	Southeast-Northeast Integration Gas Pipeline
LPG	Liquefied Petroleum Gas
MAR	Minimum Attractiveness Rate (*Taxa Mínima de Atratividade – TMA*) Definition: corresponds to the minimum that an investor proposes to earn or to the maximum that one proposes to pay when making a financing
MDCI	Ministry of Development, Industry and Foreign Trade (*Ministério do Desenvolvimento, Indústria e Comércio Exterior)*
MF	Ministry of Finance (*Ministério da Fazenda*)
MMBtu	Million British Thermal Units (unit of English energy meter)
MME	Ministry of Mines and Energy (*Ministério de Minas e Energia*)
NG	Natural Gas
NPV	Net Present Value (*Valor Presente Líquido – VPL*);
POX	Partial Oxidation of Methane
PPT	Thermoelectric Priority Program (*Programa Prioritário de Termoeletricidade*)
PSA	Pressure Swing Adsorption
SMR	Steam Methane Reforming
SYNGAS	Synthesis Gas
TCM	Trillion Cubic Meters
TEFS	Technical-Economic Feasibility Study (*Estudo de Viabilidade Técnico-Econômica - EVTE*)
NGPU	Natural Gas Processing Unit (*Unidade de Processamento de Gás Natural – UPGN*)
WGS	Water-Gas-Shift Conversion (conversion reaction of CO to CO_2)

CONTENTS

INTRODUCTION

Natural gas has been pointed by many as a bridge to a future of low-carbon energy (Kerr, 2010; Cole *et al.*, 2016; Gur, 2016). Recent discoveries of vast reserves of shale gas, mainly in the United States, have sharply increased their base and considerably reduced their cost (Gur, 2016). This reduction allowed the expansion on a world scale of the use of natural gas as raw material in several processes of chemical transformation. The use of natural gas as a source of raw material in transformation processes for the production of important commodities in the chemical industry is now considered as the noblest use of natural gas (Dong *et al.,* 2013).

Thus, the use of methane of natural gas as raw material in the chemical industry along with coal or biomass; to coproduce electric energy, but mainly as the preferred basis to obtain methanol, ammonia and urea in several countries (Jukic, 2013). Studies carried out by Lurgi Company indicate that about 5% of the natural gas consumed in the world is applied in processes known as the methane chemistry (Gerosa, 2008). A large number of authors have ratified this approach in their technical works (Galadima and Muraza, 2015, Xiang *et al.,* 2015, Gao *et al.,* 2008).

In terms of volume, the consumption of natural gas for the production of chemical products is dominated by the production of ammonia and its derivatives for the fertilizer market and by methanol for the market of organic chemistry products. These products are bulk traded chemicals that offer producers little opportunity to differentiate themselves in terms of competitive advantage and require large-scale production to become economically viable. The access to technology for the production of gasochemicals is straightforward, with a number of technology licensors offering competing packages (JMPT, 2015) for plants that are typically lower cost per ton of production than the petroleum based chemical industry units (Haldor Topsoe, 2015).

In general, there are few entry barriers for new entrants. It follows that the competitive advantage in the ammonia and methanol industries derives almost entirely from a profitable supply position. This led to two particular trends, which were evident in the methanol industry but also to a lesser extent in ammonia production: there was a dramatic increase in the scale of production plants, with producers seeking to reduce the unit cost per ton produced and the fixed operating costs (CAPEX) of production plants (Jacobs, 2010).

To ensure greater competitiveness, the gasochemical industry has progressively moved to regions where natural gas is available at low cost. Typically, where there is a limited infrastructure to allow its use for industrial or domestic purposes, thus avoiding competition for the raw material. Companies that set up gas-based chemical production facilities in areas with large gas reserves but without a local market sufficiently developed to consume it as fuel have been able to negotiate very attractive deals with respect to the price of the raw material of gas. These prices are usually invariant with oil prices. While gas prices in the developed world increased in line with other fuels, these producers have access to lower price raw materials (Jacobs, 2010).

The world scenario of the natural gas market

In recent years, the use of natural gas has proved to be a very attractive alternative for obtaining cleaner energy on a large scale (Chong *et al.* 2016). The comparison with other fossil fuels unequivocally shows that natural gas has lower rates of greenhouse gas emissions and its massive use can contribute to reduce the environmental degradation of cities with high human concentration (Bai and Li, 2016). The use of natural gas as fuel for electric and thermal energy generation has shown great growth worldwide, emphasizing increasingly the natural ability of gas at being an important source of primary energy (Cole *et al.,* 2016).

Technically, the use of gas as a raw material allows obtaining various basic chemicals such as hydrogen, methanol, ammonia, urea, olefins, carboxylic acids, formaldehyde, among many others (Gur, 2016). All these products have production routes from the synthesis gas, which is generated through conversion reactions of methane into carbon monoxide and hydrogen. The production processes of these chemicals from gas are inherently less polluting and more energy efficient, with the added benefit of generating fewer contaminants and by-products (Ren and Patel, 2009). This simplifies and makes the steps of product purification and waste treatment generated cheaper (Galadima and Muraza, 2015).

The dynamics of gas prices in different regions of the world is established according to specific local characteristics, depending, among other factors, on the scale and logistics of production and distribution, in addition to the international prices of the feedstock. Ultimately, it is this price dynamics that allows the economic viability of the use of natural gas as a raw material for the production of basic chemical products.

Countries with lower natural gas prices have a great competitive advantage in the installation of industrial complexes that use gas as raw material (Jacobs, 2010). Several gas-producing countries have made large investments in the production of chemicals from natural gas as a way to benefit their entire industrial chain.

The United States and countries holding large reserves of gas in the Middle East are using their domestic production, whether conventional or unconventional, to encourage the use of gas as a raw material and the expansion of their basic chemical industries, generating great economic value.

The Brazilian market

The Brazilian gas market began with the importation of Bolivian gas, which significantly increased its availability in the country. Another factor of leverage in the gas market was the implementation of the Priority Thermoelectric Program (PPT), with the installation of several thermoelectric plants powered by natural gas (Valle *et al.*, 2008).

According to MME/BEN (2016), current Brazilian market data show that natural gas increasingly participates in the Brazilian energy matrix, currently serving as a kind of "rainfall insurance". Another important factor for the Brazilian natural gas market was the introduction of LNG terminals, which allowed a greater diversity in the natural gas offering, giving greater robustness and safety to the Brazilian market. However, despite the great expansion of the Brazilian natural gas market in the last two decades, confirming the role of gas as a reliable and available source of energy, almost all of the gas available for the Brazilian market has its use as fuel in industrial processes and thermoelectric generation. The noblest use of gas as raw material in industrial processes is practically not exploited in the country. The current diagnosis of the sector is that Brazil has not followed the world trend of expansion of the noblest use of gas, as raw material in industrial processes for the production of gasochemicals.

In 2014, the Brazilian trade deficit of chemical products reached US$ 28 billion (ABIQUIM, 2015). In the period from March 2015 to March 2016, this deficit reached US$ 24.2 billion (ABIQUIM, 2017), showing a small reduction in relation to the previous year. This data presented evidences that the Brazilian chemical industry is yet very dependent on the importation of several basic chemicals of strategic value, such as methanol, ammonia and urea. In addition to the large disbursement of foreign exchange, the risk of the shortage of these basic products of the industry may jeopardize the performance of the entire industrial chain of the country. Brazil, with part of its pre-salt gas reserves already proven, has the possibility of aligning with the more developed economies and favoring the expansion of its chemical industry from the use of gas as a raw material, in order to reduce the high dependence on imports of strategic products for the Brazilian economy.

The most important simultaneous production processes that use natural gas as a raw material are those involving the coproduction of ammonia, urea and methanol simultaneously, due to the possibility of synergistic gains in this combined production and to the vast use of these basic products as raw material in important processes in the chemical industry generally.

Methanol

Methanol is one of the most important chemicals, and its main production route is from natural gas (NG) due availability and efficiency in conversion (Riaz *et al.*, 2013). Its major importance is that methanol is a chemical intermediate in a large number of synthesis routes of essential products to modern life. Methanol is the main feedstock for the production of several important organic chemical compounds, such as acetic acid, formic acid, formaldehyde, methyl methacrylate and its derivatives (Saade, 2011). On the other hand, we cannot forget the recent acquired function of methanol as a promising energy carrier (Peter *et al.,* 2012), nor the environmental benefits of processes still under study that use the reduction of CO_2 captured from other processes to methanol production (Riaz *et al.*, 2013).

Methanol has multiple applications to supply different markets, evidencing the high level of complexity of the production chain of this strategic feedstock of the world chemical industry. Recent developments have made the use of methanol as fuel for automotive engines a very interesting option for the transportation industry (Luyben, 2010).

Methanol is easy to store and distribute, and can be mixed with gasoline (prohibited in Brazil) and also used in methanol fuel cells (Masih *et al.,* 2010). The methanol market is at a transitional stage in which some products derived from methanol tend to have their output reduced, such as methyl terc-butyl ether (MTBE), while others are experiencing an increase, such as biodiesel, gasoline, dimethyl ether and light olefin production (Riaz *et al.,* 2013). The potential demand for these new markets is highly dependent on the cost competitiveness of methanol over traditional alternatives such as naphtha and heavy gasoline fractions.

According to data from the Brazilian Ministry of Development, Industry and Foreign Trade - MDIC/Aliceweb system (2016), the Brazilian market for methanol has shown a steady evolution in recent years. Only in 2015, more than 840,000 tons of methanol were imported, generating an expenditure of foreign exchange in the order of US$ 290 million. The data presented demonstrate the strong dependence of the Brazilian market on the importation of the methanol, characterizing a relevant strategic fragility given that methanol is one of the main basic feedstock of the chemical industry.

With such great quantities imported, the entire chain of the Brazilian chemical industry that uses methanol as a feedstock is held hostage by the natural oscillations of international prices of this alcohol. This large dependence on imported methanol is expected to deepen from 2016, as the major national producer of the product, COPENOR, stopped producing methanol for economic reasons and decided to import the entire methanol used as feedstock in its methanol derivatives production plants.

Ammonia

Ammonia is an essential chemical for the supply of nitrogen to soils, being the second most limiting product in food production, only behind water (Allman and Daoutidis, 2016). The synthesis of ammonia is considered by any authors as the most important technical discovery of the twentieth century (Kyriakou *et al.,* 2016; Hellman *et al.,* 2013, Shancham and Brauner, 2015), since it allowed the production of fertilizers on a large scale, and consequently increased productivity in the field on a previously unimaginable scale. The expected population growth rate indicates that the world will reach 9.7 billion people by 2050, and the demand for ammonia and fertilizers is expected to accompany this growth. It would be incomprehensible, within present standards, such demographic expansion without the worldwide development of ammonia production (Erisman *et al.,* 2008).

The United States is currently the largest importer of ammonia, accounting for around 40% of world trade, while Europe accounts for approximately 25% of this trade, even at a higher cost of production (Bicer *et al.* 2016). In the near future, further growth in Asian imports is expected, mainly because of industrial development and the increased use of fertilizer products (Potashcorp, 2016). The worldwide ammonia production is up to 200 million tons per year (Kyriakou *et al.*, 2016; Giddey *et al.*, 2013), with 80% to fertilizers production (Klinsrisuk *et al.*, 2015). Another important use of ammonia include industrial refrigeration cycles, besides uses in plastic, pharmaceutical and explosives industries (Edrisi *et al*, 2014).

In Brazil, more than 60% of the ammonia consumption comes from importation (Florez-Orrego and Oliveira Júnior, 2016), mainly because the Brazilian ammonia production has not follow the increase in consumption, generating the need to import large volumes to meet domestic demand (Florez-Orrego and Oliveira Júnior, 2016), which makes the country vulnerable to international market price variations and logistical problems of Brazilian ports (Hernandez and Torero, 2011). According to data from the Brazilian Ministry of Development, Industry and Foreign Trade - MDIC/Aliceweb (2016), the Brazilian ammonia market remains a major importer of the product. In the year 2015 alone, more than 350,000 tons of ammonia was imported, generating an expenditure of foreign exchange in the order of US$ 156 million.

Urea

The use of nitrogen fertilizers, especially compounds highly concentrated in nitrogen, such as urea, is closely related to increased productivity in the field of the main food exporting countries (Aragaw and Disney, 1977). Urea is considered one of the most important chemicals for humanity. It is widely produced by ammonia producing countries. Urea is very stable chemically and has no toxicity in handling and is therefore easy to transport and store. On a global scale, urea has become an indispensable commodity, fostering the development of a very robust market around the world-wide fertilizer industry (Hernandez and Torero, 2011).

Although more than 90% of the worldwide produced urea is destined for the production of chemical nitrogen fertilizers, urea is also used as a raw material in manufacturing processes for various products, such as the production of melamine resin, food supplement for cattle and adhesives manufacturing (Edrisi *et al.*, 2016).

The urea market is of extreme importance for Brazil, since the agribusiness is one of the most important sectors of the Brazilian economy, accounting for about 43% of the country's exports and contributing more than US$ 110 billion in 2014 to the national gross domestic product according to the Ministry of agriculture, Livestock and Supply (*Ministério da Agricultura, Pecuária e Abastecimento - MAPA,* 2015). According to the same Ministry, only in January 2017, Brazil reached US$ 5.87 billion in agribusiness exports, showing an increase of 17.9% in relation to January 2016 (MAPA, 2018).

But this success in the field does not occur free of cost. According to MME/Alice web (2018), the Brazilian disbursement with urea imports reached US$ 1.24 billion in 2017. According to data from the National Association of Fertilizer Diffusion (*Associação Nacional da difusão de Adubos – ANDA*, 2015), Brazil is the fourth greater consumer of fertilizers of the word, responsible for 6% of worldwide fertilizer production. The Brazilian capacity of urea production is around 1.65 million tons per year, while the consumption is up to 5.5 million tons per year (ANDA, 2017).

Objectives of the work

The basic motivation underlying this work is based on two distinct aspects: the first concerns the probable availability of natural gas produced in the Brazilian pre-salt and the second concerns the need to reduce the importation of large quantities of chemical products to the national chemical industry. The combination of these two factors establishes the set of basic assumptions used to prepare the studies presented in this work, as described below.

Based on the scenario described, this work proposes a technical and economically viable solution for the more noble use of part of the natural gas produced in the Brazilian pre-salt that is being made available to the domestic market, in the form of an industrial complex integrated, capable of produce all the ammonia, urea and methanol needed to supply the domestic market. This complex could completely replace the current import of these three methane derivatives. A part of the natural gas from the pre-salt would be used as the only basic raw material for the entire complex. Thus, the project is capable of reducing dependence on imports of strategic chemicals and of reducing the impact on the Brazilian trade balance with the importation of these three products. As secondary objectives, the project aims to give greater strength to the national chemical industry and obviously, expanding the Brazilian natural gas market, making it more competitive and diversified.

In order to meet these objectives, this work presents a critical analysis of the potential of using natural gas as raw material in Brazil, reflecting on the economic benefits that the production of these gasochemicals can bring to the national economy. Technical characteristics of the productive processes studied and factors influencing the market of these gasochemicals are discussed, aiming to support the internal production decision of these products from the gas produced by the pre-salt and made available to the Brazilian market.

The determinants factors that affect the dynamics of the evolution of the prices of natural gas and its derivatives in the domestic market are also considered in the proposed analysis. Production units of methanol, ammonia and urea from natural gas were simulated in a commercial simulator, in accordance with good engineering practices, in order to allow the calculation of the CAPEX of these units and to analyze the correlation between production costs of these chemicals and the expected revenue from the commercialization of the produced gasochemicals.

Structure of the thesis

Chapter 1 provides a critical analysis of the country's real capacity to supply the domestic natural gas market in the short, medium and long term, through the exploitation of its conventional and unconventional gas sources, including importation of natural gas by pipelines and LNG.

Chapter 2 consists of an article that presents a general review on the patented processes of simultaneous production of natural gas derived chemicals, such as ammonia, urea and methanol, presenting a critical analysis of the most suitable technologies for Brazilian context.

Chapter 3 consists of an article that presents a technical-economic analysis on the production of methanol from natural gas, considering the reality of prices of the raw material in the Brazilian market, and using processes chosen from those present in Chapter 2. The article presents economic results of a study on the nominal capacities of a production unit that would be economically viable, considering the Brazilian market scenario, and scaling these capacities by the available supply presented in Chapter 1.

Chapter 4 consists of an article that presents a technical-economic analysis on the production of ammonia from natural gas, expanding the study presented in Chapter 3 to ammonia.

Chapter 5 consists of an article that presents a study on the economic benefits of the production of strategic chemicals for Brazil from the use of the natural gas of the pre-salt as raw material, instead of conventional use as fuel, taking into consideration the natural gas supply capacity presented in Chapter 1, and the results on the production of methane derivatives presented in Chapters 3 and 4.

Chapter 6 consists of an article presenting a technical proposal for the production of gasochemicals from natural gas as a way of supplying the Brazilian internal market and replacing the importation of these products. The article proposed the technologies that should be most appropriate to the national scenario for use in the chemical engineering unit operations in the industrial complex for the production of these gasochemicals. Finally, the General Conclusions provides a brief analysis of all the work conducted and presents the most relevant contributions to the academic community, as well as suggestions for new works.

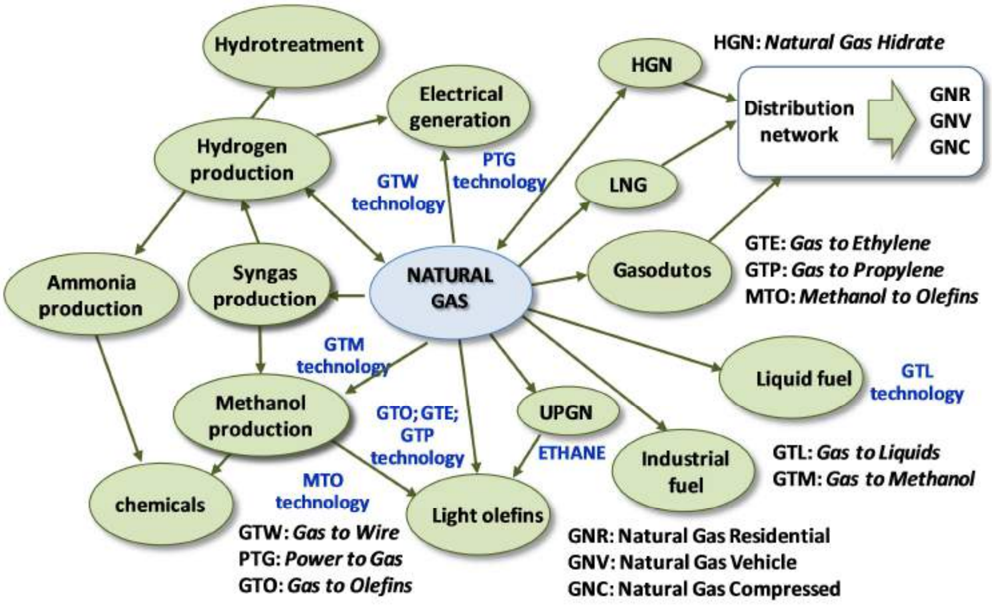
The Appendices inserted at the end of the work have the function of deepening the information presented allowing a better understanding of the scenarios evaluated in the formulation of the proposal of this thesis.

It should be emphasized that all gas flow values indicated in this work are referenced to the PETROBRAS conditions (20 °C and 1 atm). All enthalpy variation presented in this thesis is referenced to the standard enthalpy at 25 °C.

1. AVAILABILITY OF NATURAL GAS IN BRAZIL

Natural gas is considered one of the most important energy sources in the world today, as it is a cleaner and safer fuel than any other fossil fuel (Bai and Li, 2016, Chong *et al.*, 2016). Technically, it is a non-renewable energy resource, consisting of a mixture of light hydrocarbons, including methane, ethane, propane and a small amount of butanes and heavier, usually accompanied by a certain content of light contaminants such as CO_2, H_2S, N_2, Hg and water vapor. It is usually found in deep underground rock formations, pure or associated with liquid hydrocarbons (Viswanathan, 1992), but can also be found in sandy reservoirs, coal beds or in the form of methane hydrate (Carrol, 2010). Figure 01 summarizes the network of the main natural gas products.

Figure 01 - Network of the main products derived from natural gas.



Source: Adapted from UOP, 2012.

One of the main current uses of natural gas is for thermoelectric generation. As a fuel, natural gas has unquestionable environmental advantages, since its combustion is complete and produces much less pollutants harmful to the atmosphere than any liquid fuel of fossil origin (Chong *et al.,* 2006; Santana, 2006).

An important use for the fraction of ethane contained in natural gas is as a raw material for the petrochemical industry, aiming at the production of light olefins, such as ethylene and propylene (Galadima and Muraza, 2015). The fraction of natural gas used in this case is ethane separated from natural gas in natural gas processing units

(UPGNs) and used in pyrolisis process to produce ethene. Methane is used directly in processes such as Gas-To-Olefins (GTO), Gas-To-Ethylene (GTE), Gas-To-Propylene (GTP).

However, it is the use of methane as raw material in industrial processes of chemical transformation that allows valuing the natural gas more significantly. The use of natural gas as raw material for the production of methanol, ammonia, urea, carboxylic acids and a great diversity of other chemicals of great commercial and strategic value is currently the most effective form for the natural gas value appropriation (Gur, 2016).

The present work thus deals with investigating natural gas as the basis for the production of chemical products, and for this purpose it has the following objectives:

i) What is the relationship between gas availability and supply guarantee of the product in Brazil?

ii) ii) How is the production and pricing dynamics of natural gas?

1.1 What is the relationship between gas availability and supply guarantee of the product in Brazil?

A very critical issue for the formulation of any proposal for the use of natural gas in Brazil is in relation to ensuring the continuity of supply of the product. There is no gain in proposing projects for the use of natural gas if there are no guarantees of long-term product supply, at prices that are appropriate to the market, especially in the case of high investment projects and heavily dependent on the scale gain for their feasibility economic, as is the case of projects for the use of gas as raw material in chemical transformation processes.

The diversification of sources of supply of the natural gas is fundamental to generate the confidence that the market needs to decide invest in the expansion of the production of natural gas and thus guarantee its full supply in the long term. Thus, the sources of natural gas will be presented whose reserves and projections of exploration allow the evaluation of gas availability for the production of gasochemicals of interest in the medium and long term.

1.1.1 Brazilian sedimentary basins producing hydrocarbons

Brazil has large sedimentary basins, with areas still little known geologically, with considerable potential for producing hydrocarbons not yet explored (Souto Maior *et al.,* 2009).

Campos Basin is currently the main Brazilian oil area, with an area of about 100,000 km^2, extending from Espírito Santo to the north coast of Rio de Janeiro. The first field with commercial volume discovered in the Campos Basin was Garoupa in 1974. The following year the field of Namorado was discovered, and in 1976, that of Enchova. This was the beginning of a long series of important hydrocarbon discoveries on the Brazilian continental shelf (PETROBRAS, 2013).

In 1985, Petrobras discovered the first giant field in the Campos Basin, named Albacora. Later, other giant fields appeared in deeper waters, such as Marimbá and Marlim in 1985, Marlim Sul in 1987, Barracuda in 1989, Caratinga in 1989 and Roncador in 1996 (PETROBRAS, 2013).

Santos Basin is located in an area of approximately 352,000 km^2 (PETROBRAS, 2013) and extends along the south coast of Rio de Janeiro, all along the coast of São Paulo and Paraná, reaching the coast of Santa Catarina.

In the Espírito Santo Basin, the first oil reserve on the continental shelf was discovered at the Golfinho field in 2002. Since the start of the Southeast-Northeast gas integration pipeline (GASENE) in 2010, the production of non-associated natural gas of the Espírito Santo basin has the function of adjusting supply and demand of natural gas. The non-associated gas fields of Camarupim, Canapu, Cangoá and Peroá have their daily flow modulated to meet the demand of the Brazilian market. Together, the Espírito Santo Basin fields have the potential to produce about 20 million cubic meters per day of natural gas, between associated gas and non-associated gas (PETROBRAS, 2013).

The discovery of the Manati Field in the Camamu Basin in 2000 on the coast of Bahia was of great importance due to the need to meet gas demand in the Northeast region. This field is situated about 10 km from the coast, with total gas reserves of about 24 billion cubic meters (PETROBRAS, 2013).

Potiguar Basin has an area of 119,000 km^2. The first field discovered in this basin was that of Ubarana, on the coast of Guamaré, in operation since 1976. The Potiguar basin was a pioneer in the use of steam to stimulate the production of the terrestrial wells, with an approximate extension of 30 km (PETROBRAS, 2013).

Solimões Basin, which produces oil, condensate and gas, is located in the northern region of Brazil, in the Amazon. The Basin has about 950,000 km^2; of which 480,000 km^2 correspond to the prospecting area (PETROBRAS, 2013). The Solimões Basin is the largest onshore production basin currently in the country. Natural gas is produced in the middle of the Amazon rainforest. The province of Urucu has the capacity to produce about 12 million cubic meters per day, part of which is sent for use in Manaus and part is reinjected, after the removal of heavy fractions for the production of LPG and C_{5+} (PETROBRAS, 2016).

Several other Brazilian sedimentary basins have not been duly tested until now, remaining until then as potential areas for future hydrocarbon production. The large number of basins with natural gas production potential allows us to affirm that Brazil still can to discover many gas reserves in its subsoil, and can therefore maintain the supply capacity of its natural gas market. Figure 02 shows the map of the main Brazilian sedimentary basins.

Figure 02 - Brazilian sedimentary basins.

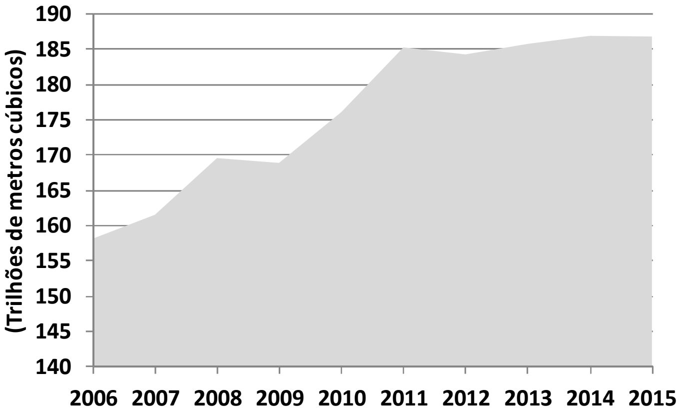
Source: Adapted from Phoenix Paleontology Foundation, 2003.

1.1.2 Conventional sources of natural gas

The conventional sources of natural gas are formed by deep reservoirs, with presence of large amount of light hydrocarbons. These reservoirs consist of conventional reserves of natural gas. Almost 80% of the global demand for natural gas is currently supplied by conventional gas reserves.

Reserves are understood to be the commercially exploitable resources already discovered of natural gas, as of a reference date. The estimation of these values incorporates a certain degree of uncertainty regarding the geological information of the accumulations of hydrocarbons, reservoir engineering and of economic nature. In 2015, proven world natural gas reserves totaled 186.9 trillion cubic meters (ANP, 2016). Figure 03 shows the evolution of the world's reserves of natural gas in the last decade, and shows that the discoveries of new gas accumulations have been able to restore the annually consumed volume.

Figure 03 - Evolution of the world reserves of conventional natural gas.



Source: Brazilian Statistical Yearbook - ANP, 2016.

1.1.3 Unconventional sources of natural gas

In addition to conventional sources, some sources of unconventional gas can be exploited, such as shale gas, tight gas, sand gas, synthetic natural gas (GNS), coal bed gas, deep-water gas , natural gas hydrates (HGN) and biogas (produced from organic waste). These unconventional sources have been gaining ground in recent years, especially in countries with high gas demand, such as China and the United States (IEA, 2015).

Unconventional natural gas is the gas present in rock formations of low porosity and difficult to access, requiring special technologies for extraction and exploitation. Among the unconventional gas forms, shale gas is currently the most prominent in the world gas community, mainly because it caused a sharp reduction in prices in the American natural gas market, with repercussions on the world economy (Gomes, 2011; EIA, 2015).

Shale gas production is possible by the use of the hydraulic fracturing technique in producing regions. Hydraulic fracturing is the propagation of fractures in a rock layer, caused by the injection of a fluid in a high pressure into the reservoir. The technology is based on the vertical drilling of a well, complemented by one (or more) horizontal drilling inside the reservoir. Then, the next step is applied, when controlled small explosions are conducted inside the well (scattered in the horizontal region), allowing the injection of chemical products at very high pressure, with the objective of creating cracks or fractures in the reservoir rocks (EIA, 2013). Production of shale gas can be said to be one of the most important energy revolutions of our time and is transforming the global energy market (Wang and Li, 2016).

Shale gas has had an important share in the global energy supply (Hughes, 2013). Currently, more than 25% of the gas available in the US market is from shale gas reservoirs (EIA, 2017). An effect caused by this new world gas source can be seen in the American market, where the great supply of gas at low prices has provided massive investments in petrochemicals production on American soil, generating strong competition in the international market of chemicals and bringing serious difficulties for the petrochemical industry of countries like Brazil.

A preliminary survey in South America suggests that the region's largest shale gas reservoirs are in Argentina, Brazil and Colombia (EIA, 2015). However, Argentina is the only South American country that is currently investing in the production of these reserves. Despite presenting itself as an abundant source in some countries, shale gas has faced resistance in some regions of the world to obtain proper extraction permits (KPMG, 2011; EIA, 2015). Recent surveys list environmental risks during the hydraulic fracturing process. The risk of contamination of groundwater has left rulers in several countries afraid to release the exploitation of shale gas reserves (Wang and Li, 2016). Table 01 shows the world's largest reserves of technically recoverable unconventional gas.

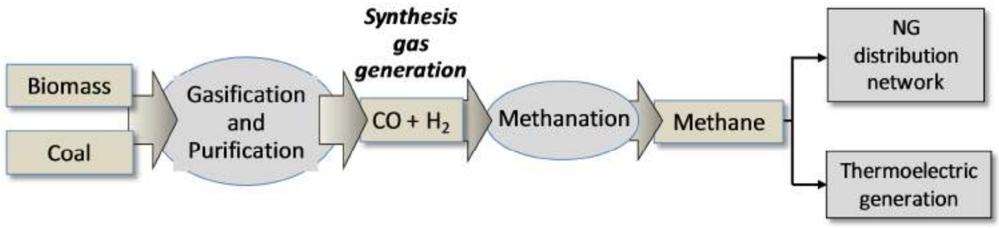
Table 01 - Largest reserves of shale gas.

Position	Country	Technically recoverable unconventional gas reserves (m^3*10^9)
1	China	31.577
2	Argentina	22.713
3	Algeria	20.022
4	U.S.	18.833
5	Canada	16.227
6	Mexico	15.434
7	South Africa	13.735
8	Australia	12.376
9	Russia	8.071
10	Brazil	6.938

Source: EIA, 2013.

In another line of research for new alternative sources of unconventional gas, the production of synthetic natural gas from less noble raw materials has attracted much attention (Ronsch *et al.*, 2016). The most used route for the production of GNS involves the gasification of coal and biomass (agricultural residues) to obtain synthesis gas (mixture of H_2 and CO). After purification, the catalytic reaction of methane gas synthesis is conducted, with methane production (Heidenreich and Foscolo, 2015). The GNS produced is injected into the existing natural gas network for the supply of final customers. Chein *et al.* (2016) investigated the production of GNS from this technique and concluded that conversion of carbon monoxide to methane increases considerably with increasing reactor temperature from 300 °C to 380 °C. The same happens with the increase of the pressure of the reactor. Figure 4 shows a schematic diagram of the production and use of GNS.

Figure 04 - Schematic diagram of GNS production.



Source: Adapted from Chein, 2016.

According to Jean *et al.* (2014), the methanation reaction of the carbon monoxide also allows the storage of electricity produced from renewable sources, based on the concept Power-To-Gas (PTG). This concept envisages the use of electric energy produced from renewable sources as a source of energy for the gasification step of a low cost hydrocarbon source, purification of the generated gases and methanation reaction. It should be noted that the production of methane from more polluting sources, such as coal, through the synthesis gas seems at first to make no sense, but in a scenario where the substitution of more polluting fuels is fundamental for become viable the industrial and electrical production of places with strong environmental restrictions, this model may allow the use of very cheap and available energy sources, such as coal from China, even requiring an additional cost share referring to the methanation stage.

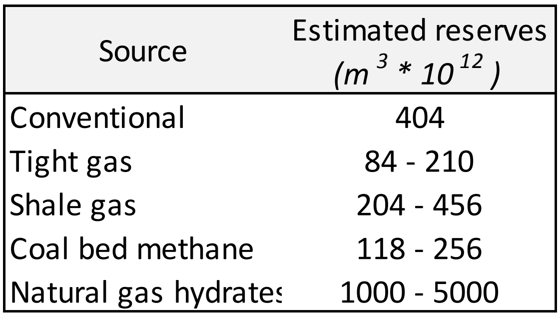
Recently, a source of unconventional methane has caught the attention of the global scientific community. Accumulations of natural gas hydrate (HGN) have been formed in nature for millions of years. These accumulations are found in marine environments (seabed sediments and deep lake sediments) and terrestrial deposits in polar regions under the frozen ground, called permafrost (Li *et al.,* 2016). Hydrate formations of natural gas may become very important considering the huge amount of methane in these structures. In 2001, a work published on the census of ocean natural gas hydrate reserves showed an estimated methane quantity of about twice the known reserves of natural gas, oil and coal together (Clennell, 2001).

Chemically, gaseous hydrates belong to the class of clathrates, which are crystalline compounds in which water molecules, linked to one another by hydrogen bonds, encapsulate gas molecules like methane. Tests conducted in Nankai Trough, southeast Japan and the Mallik field in northwestern Canada, point out that natural gas production from hydrate reserves can supply natural gas continuously to small and large customers (Miller *et al.,* 2015).

Several authors have studied the use of natural gas hydrates as a source of methane for energy supply. Collet and Kuuskraa (1998) studied the physicochemical characteristics of HGN accumulations, while Chen *et al.* (2014) and Wang *et al.* (2013) conducted experiments to understand the mechanism of gas production from these accumulations to develop more efficient methane regasification methods. These authors concluded that it is possible to convert HGN to methane in an economically viable way. The natural gas recovery (regasification step) is done by simple melting of the hydrate. The hydrate melts through direct contact with hot water, resulting in the dissociation of the clathrate structure, with the separation of gas and water. The gas is compressed and dehydrated and then delivered to the distribution.

Chong *et al.* (2016) indicate that in the medium term a significant share of natural gas will be supplied by unconventional sources, notably shale gas, tight gas and coal bed gas. On the other hand, considering the huge quantities of methane in the form of HGN, in the long term it is expected that natural gas hydrate reserves will meet a large part of mankind's fuel needs (Chong *et al.,* 2016). Table 2 presents estimated natural gas reserves from known sources that corroborate with these projections.

Table 02 - Estimated world reserves of unconventional gas.



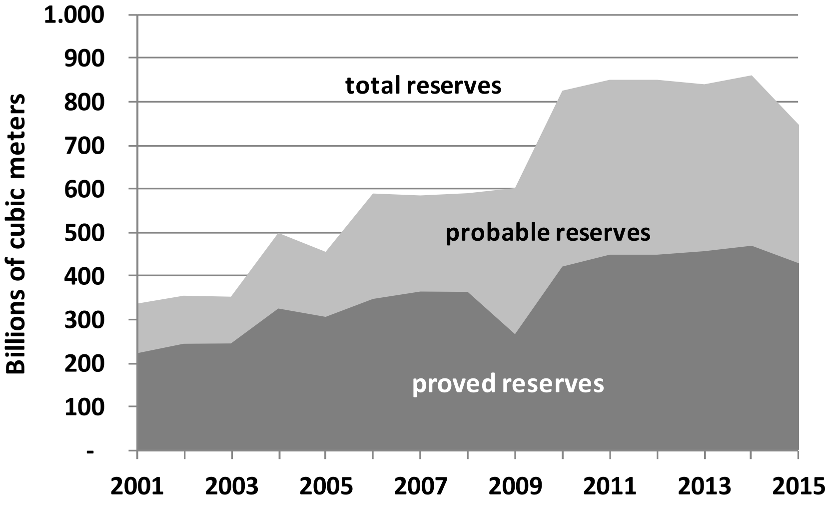
Source	Estimated reserves $(m^3 * 10^{12})$
Conventional	404
Tight gas	84 - 210
Shale gas	204 - 456
Coal bed methane	118 - 256
Natural gas hydrates	1000 - 5000

Source: Chong *et al.,* 2016.

1.1.4 Brazilian reserves of conventional natural gas

Brazilian proved reserves totaled 430 billion cubic meters in 2015 (ANP, 2016). Total reserves, including proved and probable reserves, reached 746 billion cubic meters. Most of the reserves (85%) are located at sea. Brazil remained in the thirty-sixth position in the world ranking of the largest proven natural gas reserves in 2015. Figure 05 shows the evolution of proven and probable reserves in Brazil in recent years.

Figure 05 - Evolution of Brazilian natural gas reserves



Source: Brazilian Statistical Yearbook - ANP, 2016.

1.1.5 Brazilian reserves and pre-salt natural gas flow capacity

The term pre-salt is used to designate the hydrocarbon reserves in located beneath layers of salt between five and seven thousand meters deep below sea level. The pre-salt production area has a extension of approximately 800 km long by 200 km wide, which runs from the coast of Santa Catarina to the coast of Espírito Santo (PETROBRAS/Site pre-salt, 2011).

The known oil and gas reserves of the Brazilian pre-salt cover three important sedimentary basins of the continental shelf (Santos Basin, Campos Basin and Espírito Santo Basin). According to the ANP (2014), these potential pre-salt reserves are currently estimated to be between 70 billion and 100 billion barrels of oil equivalent (BOE). Estimates made by the Energy Economics Group (GEE, 2011) point out that the net supply potential of natural gas coming from the pre-salt alone can reach between 70 million cubic meters per day and 120 million cubic meters per day by 2030.

Petrobras has foreseen the installation of three natural gas flow routes from the main pre-salt production fields already mapped: Lula (old Tupí), Sapinhoá (old Guará), Bem-te-vi, Carioca, Jupiter, Parati, Caramba and Iara. These fields were interconnected by pipelines (ring-shaped) and will be able to flow gas through any of the three defined routes (PETROBRAS/Site pre-salt, 2011).

Route-1 interconnects the production fields with the Caraguatatuba gas processing complex, with the nominal capacity to flow 10 million cubic meters per day of gas. Route-2 will interconnect the production fields with the Cabiúnas processing complex, with a nominal capacity to flow 13 million cubic meters per day of gas. Route-3 will interconnect the production fields with the COMPERJ gas processing complex, with a nominal capacity to flow 21 million cubic meters per day of gas (PETROBRAS/Site pre-salt, 2011). These three routes together make up a flow capacity of 44 million cubic meters per day of gas.

It should be noted that the already mapped fields that will be produced by these three routes have a maximum production capacity higher than the nominal flow capacity of the flow pipelines system (PETROBRAS, 2011). Due to the uncertainties inherent in the reservoirs of the Pre-salt, it has opted for a step-by-step investment strategy for the gas pipelines implantation. As the level of confidence on reservoirs behavior increases, new phases of the pipelines infrastructure deployment will be gradually designed and built.

1.1.6 Brazilian shale gas reserves

According to studies by the Energy Information Administration (EIA, 2013), Brazil occupies the tenth position among the largest shale gas reserves in the world, with an estimated volume of 7.0 trillion cubic meters. This figure is about nine times greater than the sum of proven and probable Brazilian natural gas reserves.

1.1.7 Brazilian reserves of natural gas hydrates (HGN)

Miller *et. al.* (2015), suggest the presence of gas hydrate in the Rio Grande cone area on the continental slope of the Pelotas Basin (RS). Proven by scientific study, this would be the first Brazilian province with gas hydrates recovered in the Brazilian coast.

1.1.8 Brazilian imports of natural gas

Brazil is currently able to import natural gas through two different modes, in order to complement its market needs: the importation of gas via GASBOL and the import of LNG via ships. Brazilian natural gas imports totaled 16.5 billion cubic meters in 2015.

Import of natural gas via GASBOL

The total volume of imported gas from Bolivia in 2015 was 11.9 billion cubic meters. This volume was made available to the Brazilian market through the Bolivia-Brazil Gas Pipeline (GASBOL). The current gas purchase contract provides for the delivery of up to 30 million cubic meters per day, with a take or pay clause, which obliges the importer to pay at least 80% of the maximum contract quantity, even if not using all the gas.

Import of natural gas via LNG

The volume of natural gas imported in 2015 in the form of Liquefied Natural Gas (LNG) reached 7.3 billion cubic meters (ANP, 2016). Most of this gas was imported from Trinidad and Tobago, Nigeria and Qatar, via transport by ships (ANP, 2016). The main function of natural gas imported by Brazil in the form of LNG continues to be the supply of gas to thermoelectric generation. The thermal market has a characteristic of the interruptive consumption. Most of the thermals are only dispatched when the country goes through periods of low rainfall.

That is why LNG should only be purchased in the short-term market (*Spot*) to complement the gas supply in the domestic market, in case of any increase of necessity of thermoelectricity. It would not be economically advantageous for the country to have long-term firm contracts for the purchase of LNG.

Brazilian LNG receive terminals

Brazil has adopted a LNG receiving and regasification terminal project known as flexible, which differs from conventional terminals. The Brazilian terminals have a pioneering engineering project in the world, where a ship equipped with a LNG revaporization plant on the deck remains stopped in a protected marine port and receives the product of a second LNG transport ship that is positioned beside the first ship and transfers the product to the tanks of the fixed vessel, which revaporizes the LNG at the necessary flow to complement the needs of the gas market. There are currently three LNG receiving terminals operating in Brazil, one in Rio de Janeiro, another in Ceará and a third one in Bahia, with a total regasification capacity of 41.0 million cubic meters per day of natural gas (ANP, 2014).

With the adoption of flexible terminals, Brazil has achieved a much robust situation in relation to the guarantee of supply of natural gas to its domestic market, regardless of the level of thermal utilization adopted by the national electric system's managing body. It should be noted that, in addition to serving the thermal market, LNG is currently a guarantee of supply in relation to the lack of Bolivian gas.

1.2 How is the production and pricing dynamics of natural gas?

Due to pressures from society for greater environmental preservation and also by increasing energy generation need, especially in developing countries, natural gas consumption has expanded strongly in recent years. The following will be highlighting the global and Brazilian scenarios.

1.2.1 In the world

World production in 2015 was 3.5 trillion cubic meters (tcm), with output in the United States, Russia, China and Iran totaling 1.7 tcm, representing 47.7% of the world total. Worldwide consumption was 3.5 tcm, with the same four countries consuming 1.6 tcm, representing 44.5% of the world total (ANP, 2016).

Natural gas has been pointed by many as a bridge to a future of low-carbon energy (Kerr, 2010; Cole *et al.,* 2016; Gur, 2016). Recent discoveries of vast reserves of shale gas, mainly in the United States, have sharply increased their abundance, which has considerably reduced their cost (Gur, 2016). Mason and Wilmot (2014) postulated that the use of hydraulic fracturing in the production of American shale gas is an event capable of affecting the world natural gas market. The development of the production of American shale gas reserves is considered today as the most transformative and important event in the world market for natural gas (Medlock and Hartley, 2015).

In 2015, for the first time, natural gas surpassed coal as the largest source of energy in the United States (Gur, 2016) and is now the second most widely used energy source in the industry. Another important fact is that, currently, about 27% of the electricity generated in the United States uses natural gas as a source of thermal energy in thermoelectric plants (Gur, 2016). Market experts believe that US LNG exports will intensify soon (Cole *et al.,* 2016).

A recent research by Wilkerson *et al.* (2014) on plans to invest in energy resources in the United States, points out that 89% of the projects to install new generation units till 2030 will use natural or renewable energy sources (wind, solar, geothermal, tidal or hydroelectric). A large number of studies have been published, arguing for the great potential of natural gas to reduce CO_2 emissions from the energy sector (Mcjeon *et al.,* 2014; Shearer *et al.,* 2014; Shawhan *et al.*, 2015). These studies indicate in general that the abundance of natural gas can lead to important structural changes in electric generation (Logan *et al.*, 2013, Sullivan *et al.,* 2015). Cochran *et al.* (2014) proposed the development of more effective planning of the power generation system in order to identify the circumstances in which natural gas and renewable energy could be complementary.

As in the United States, the demand for less environmentally friendly fuels has increased significantly in China. However, China's shale gas reserves are not yet developed like the American ones, so that Chinese domestic gas production cannot fully meet demand. As a result, China began to import liquefied natural gas (LNG) in 2006 (Kong *et al.,* 2016).

China is already the third largest consumer of natural gas, behind only the United States and Russia (BP, 2015a). According to the prospects of BP Energy presented in Outlook 2035 (BP, 2015b), the Chinese natural gas market will experience a deficit increase of 254 billion cubic meters annually till 2035.

The use of abundant reserves of coal as raw material to produce synthetic natural gas (GNS) has been an option of the Chinese government to ease market pressure on the need to increase LNG imports and prevent natural gas shortages. The Chinese government approved as of 2013, ten major GNS generation projects from coal with an annual nominal capacity of 67.1 billion cubic meters (Li *et al.,* 2014; Yang, 2015).

Projections of the Henry Hub index

The dynamics of production and pricing are connected to each other, depending on the demand of the consumer market and the cost of obtaining the gas. There is no single world price; the price has variations, which historically have almost always accompanied the price of oil (Mokhatab *et al.,* 2006). Despite this, the price of gas in the American market is usually a indicator of world price trends, mainly due to the size of the domestic market of the product. The projection of Henry Hub's value (the main reference for natural gas prices in the American market) has been used as one of the most influential factors in projecting price trends in other markets. The study conducted by the US energy agency Energy Information Administration (EIA) in 2016 projects the annual average value of the Henry Hub in five distinct scenarios (1 to 5) by the year 2040.

In all scenarios studied, Henry Hub's average annual price for natural gas in 2040 (Figure 06) ranges from US$ 2.40 to US$ 9.20/Million British Thermal Units (MMBtu). In the *Reference scenario* (3), the average annual prices of natural gas in the US market remain around US$ 5.00/MMBtu from 2015 to 2040. Oil prices affect natural gas prices through changes in consumption and in exports, as well as increased production of gas associated with oil (EIA, 2016).

In the *High Oil Price (2)* scenario, US exports of liquefied natural gas (LNG) begin to exceed the Reference Scenario by 2024 and by 2030 the exports total 240 billion cubic meters. In response, the Henry Hub spot price begins to rise above benchmark levels from US$ 5.40/MMBtu in 2025 to about US$ 7.90/MMBtu in 2030.

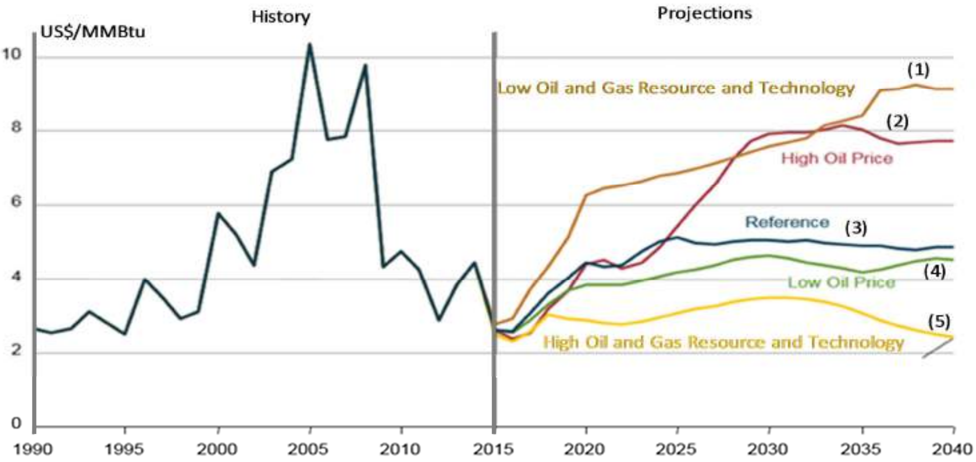
Higher prices are sustained by increased consumption in the transportation sector (EIA, 2016). A high price differential between oil and natural gas favors the use of natural gas over diesel. The consumption of natural gas by GTL (Gas-to-Liquids) units also increases over the projection period (EIA, 2016).

In the *Low Oil Price (4)* scenario, the Henry Hub spot price is on average about US$ 0.50/MMBtu lower than the Reference Scenario throughout the projection. Due to the relatively small price differential between crude oil and natural gas in the Low Oil Price scenario, US LNG exports from 2025 to 2040 are about 50% lower in the Low Oil Price scenario than in the Reference scenario and consumption is lower in both the industrial and transport sectors. Natural gas prices are affected by resource recovery rates from oil and natural gas wells and by technological improvements that affect total natural gas production and associated costs (EIA, 2016).

In the scenario *High Oil and Gas Resource and Technology (5),* with estimated initial recovery per well and faster technological improvements, total dry natural gas production in 2040 is 32% higher than in the Reference scenario (EIA, 2016).

In the scenario *Low Oil and Gas Resource and Technology (1),* with slower rates of resource recovery and technological improvement, total dry natural gas production in 2040 is 37% lower than in the Reference scenario. As a result, US natural gas prices are the lowest in the High Oil and Gas Resource and Technology scenario, ranging from approximately US$ 2.45 to $ 3.50/MMBtu during the projection period and higher on the scenario Low Oil and Gas Resource and Technology, where prices are rapidly rising to more than US$ 6.25/MMBtu in 2020 and to about US$ 9.20/MMBtu in 2040 (EIA, 2016). Figure 6 shows the results obtained in each scenario studied.

Figure 06 - Projection of Henry Hub's annual average price of natural gas in the spot market in five scenarios.

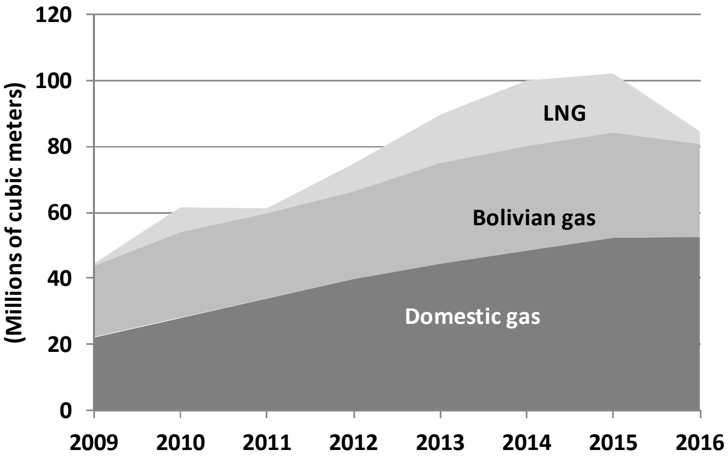


Source: EIA - AEO2016 Market trends, 2016.

1.2.2 In Brazil

The growth of the Brazilian natural gas market was mainly due to the import of Bolivian gas from 1999 onwards, motivating the federal government to encourage its use through lower prices than its direct competitors in order to leverage a market still very incipient. Another reason for leverage was the energy crisis of 2001, which led the federal government to launch the Thermoelectricity Priority Program (PPT), with the implementation of several thermoelectric plants operated by natural gas (Valle *et al.*, 2008). Figure 07 shows the consolidated annual average composition of the natural gas volume offered to the Brazilian market.

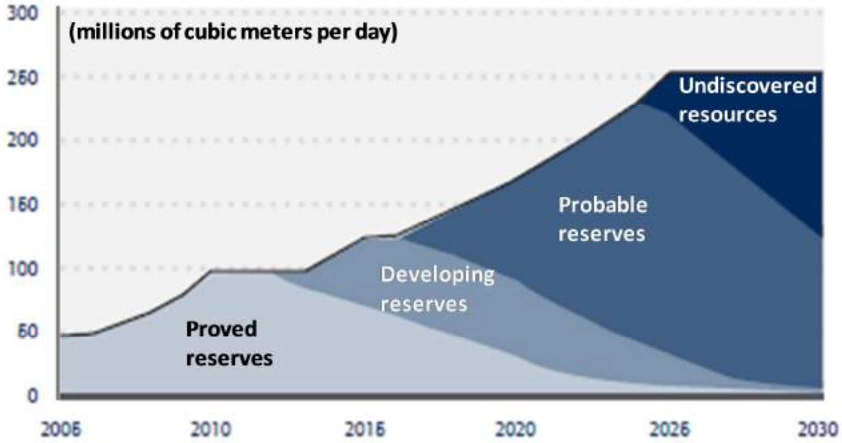
Figure 07 - Composition of the national natural gas supply.



Source: MME, 2017.

The domestic natural gas supply has a consistent growth expectation for the coming years, in accordance with the plans for the development of new reserves, mainly in the pre-salt production area. Figure 08 shows the scenario projected for domestic gas production by the year 2030, according EPE (2007). It should be noted that production derived from resources not yet discovered is partially supported by the good results obtained so far in the development of Brazilian pre-salt fields.

Figure 08 - Scenario for Brazilian natural gas production up to 2030.

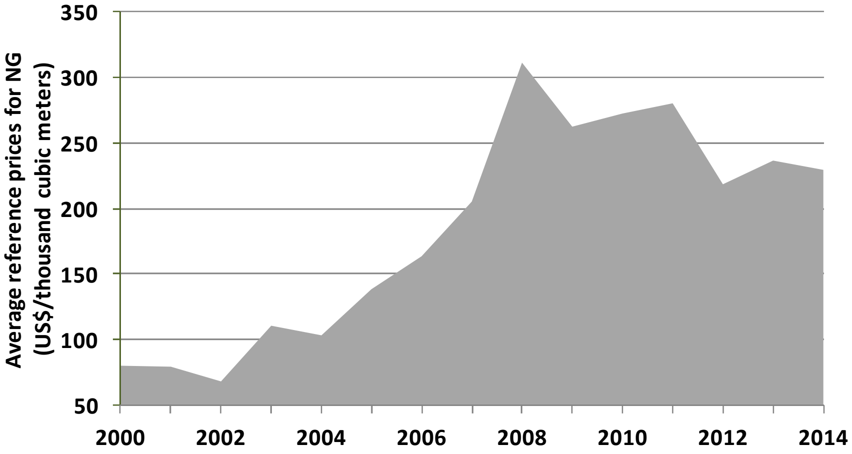


Source: EPE - National Energy Plan - 2030, 2007.

The reference price for natural gas is equal to the weighted average of the sales prices without taxes agreed in the product supply contracts, less the transport tariffs. It should be noted that there is no minimum price for gas. In the absence of sales, the reference price will be equivalent to the price at the entrance of the transportation pipeline, established by Ministry Order MF/MME n° 3/2000, which is indexed to the international price of fuel oil (MME, 2015).

In 2015, the reference price of natural gas dropped by 21.6% in reals (R$) and a reduction of 33.0% in dollars, reaching US$ 145.20/thousand cubic meters. The average reference price of natural gas was R$ 493.41/thousand cubic meters (ANP, 2016). It is important to note that the reference price does not include the share of the remuneration of the natural gas distribution companies. Each distribution company has a policy of defining the tariff for the distribution of natural gas in its operating states. Figure 09 shows the evolution of the reference price of natural gas in the country.

Figure 09 - Evolution of the reference price of natural gas in the Brazilian market.



Source: ANP, 2016.

1.3 The "key" for the expansion of the Brazilian natural gas market

The Brazilian market for natural gas is restricted to the country's coast, where transport gas pipelines are located (TRANSPETRO, 2015). The "key" to the expansion of the Brazilian market would be the possibility of expanding the existing gas transport network. It occurs that this expansion is very expensive and it hinders the economic feasibility of new gas pipelines. An alternative that can contribute to the economic solution of the great challenge of expanding the Brazilian gas pipeline network is the insertion of large-scale gas projects in the country. Projects that can guarantee large consumptions generate enough revenue to reimburse the construction of gas pipelines that can economically make possible the continuous expansion of the gas pipeline network.

1.4 Concluding analysis on the guarantee of supply of natural gas to the Brazilian market

The Brazilian capacity for receiving and revaporizing LNG reached 41 million cubic meters per day, and currently the country uses only about 40% of this maximum capacity (TRANSPETRO, 2018). The country's maximum capacity of supply natural gas already reaches the mark of 120 million cubic meters per day and the total demand is remaining at 100 million cubic meters per day. The non-associated gas fields of the Espírito Santo Basin, used to adjust gas supply to domestic consumption, have been demanded at only 7.0 million cubic meters per day (ANP, 2016).

The conclusion of the expansion of the processing units of Route-1 of the gas produced in the pre-salt (Caraguatatuba-SP) allowed an increase of 10 million cubic meters per day of national gas availability to the market. In 2016, the start-up of gas exports from Route-2 provided an additional capacity of 13 million cubic meters per day to the national supply system. In complement, Route-3 should provide an additional 21 million cubic meters per day by the year 2020.

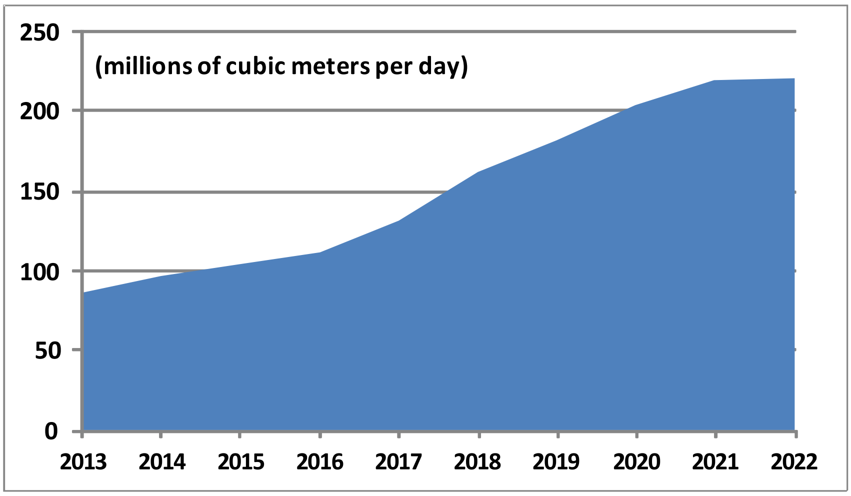
Considering that a large part of this extra gas quantity does not yet have a defined consumer, it would be a good time to propose a project that could be a major consumer of gas. Information released at the 16th Natural Gas Seminar (2015), shows that Brazil will have two more LNG regasification terminals in the next decade (2020), both of which are designed to receive up to 14.0 million cubic meters per day. In the same event, EPE (*Empresa de Pesquisa Energética*, 2015) announced the expectation of gross national natural gas production, showing that the country will have about 200 million cubic meters per day of natural gas available in 2020. This volume is double the amount currently consumed.

With total natural gas reserves of around 750 billion cubic meters, an average daily consumption of around 100 million cubic meters (ANP, 2016) and the current capacity of importing natural gas consolidated in the country, it is possible to conclude that Brazil has a comfortable position in guaranteeing the supply of future natural gas for structuring projects that consume natural gas as raw material for the production of chemicals of economic interest. Although the country's official reserves/production (R/P) ratio in 2015 is 12.2 (ANP, 2016), this number has not yet incorporated the giant pre-salt reserves or the Brazilian potential for unconventional gas production.

The future scenario of natural gas production allows predicting that the different types of Brazilian gas reserves will be able to supply the country at different times. The large reserves of the pre-salt already allow supplying of the market in the short term, the reserves of unconventional gas (shale gas and tight gas) allow guaranteeing the supply in the medium term and the reserves of hydrates of methane give expectation of attendance in the long term. Gas imports from LNG terminals allow the supply of gas to interruptible segments of the market and can complement firm domestic demand, if necessary.

Figure 10 shows the volumes expected for the coming years of gross national production of natural gas.

Figure 10 - Estimation of gross national natural gas production.



Source: MME / EPE - 16th Natural Gas Seminar - IBP, 2015.

2. SIMULTANEOUS PRODUCTION OF METHANOL, AMMONIA AND UREA FROM NATURAL GAS: A REVIEW OF PATENTED PROCESSES

Abstract

This work presents an overall review of the patented gasochemical production processes that avail synergies between the processes and the technologies available, for the simultaneous production of methanol, ammonia and urea, in the same industrial site. General trends and superstructure are elaborated. Such studies are helpful for understanding processes integration and as a basis for future optimization studies.

Keywords: natural gas, syngas, ammonia, methanol, urea, combined production.

Introduction

Natural gas (NG) has been pointed as a bridge to a future of low-carbon energy (Cole; Medlock; Jani, 2016; Gur, 2016; Kerr, 2010). Recent discoveries of vast reserves of shale gas, mainly in the United States, have sharply increased their base and considerably reduced their cost (Gur, 2016). This reduction allowed the expansion on a world scale of the use of NG as raw material in several processes. The noblest use of NG is as raw material for the production of important commodities, such as methanol, ammonia and urea (Backhaus, 2017; Bermúdez *et al.*, 2013; Han; Christensen, 2007; Kralj, 2014; Tock; Maréchal; Perrenoud, 2015). However, only about 5% of the natural gas consumed in the world is applied in processes known as the methane chemistry (Galadima and Muraza, 2015; Gao *et al.*, 2008; Gerosa, 2007; Xiang *et al.,* 2015).

The importance of the main three products from natural gas becomes clear as follows:

i. *Methanol*: The main route of methanol production is from natural gas, due its availability and conversion efficiency (Riaz; Zahedi; Klemes, 2013). Methanol is a raw material of several products essential to modern life, such as acetic acid, formic acid, formaldehyde, methyl methacrylate and its derivatives (Bertau *et al.*, 2014; Hader; Wallace; Mckinney, 1952; Olah; Goeppert; Prakash, 2006; Waters; O’Hair; Wedd, 2003). Methanol also has an important role as an energy source (Bertau *et al.,* 2014; Olah; Goeppert; Prakash, 2006; Peter *et al.,* 2012), besides presenting potential environmental benefits of processes that use the reduction of CO_2 captured from other processes to methanol production. It becomes clear why methanol has been in the center of attention of the scientific community in recent years (Riaz; Zahedi; Klemes, 2013).

ii. *Ammonia*: an essential chemical for the supply of nitrogen to soils, being the second most limiting product in food production, only behind water (Andrew; Allman; Daoutidis, 2016). Its synthesis is considered by many authors as the most important technical discovery of the twentieth century (Hellman *et al.,* 2013; Kyriakou *et al.,* 2017; Shacham; Brauner, 2015), since it allowed the production of fertilizers on a large-scale, and consequently increased productivity in the field on a previously unimaginable scale. The expected population growth rate indicates that the world will reach 9.7 billion people by 2050, and the demand for ammonia and fertilizers is expected to accompany this growth. It would be incomprehensible, within present standards, such demographic expansion without the worldwide development of ammonia production (Erisman *et al.*, 2008).

iii. *Urea*: Nitrogen fertilizer, especially compounds highly concentrated in nitrogen, such as urea, is closely related to increased productivity in the field of the main food exporting countries (Disney and Aragaw, 1977). Urea is considered one of the most important chemicals for humanity.

NG consumption for the production of chemical products is dominated by the production of ammonia and its derivatives for the fertilizer market and by methanol for the market of organic chemistry products. The most important simultaneous production processes that use natural gas as a raw material are those involving the coproduction of ammonia, urea and methanol simultaneously, due to the possibility of synergistic gains in this combined production and to the vast use of these basic products as raw material in important processes in the chemical industry generally. Literature present several studies investigating traditional or new processes for the synthesis of syngas (Aasberg-Petersen *et al.,* 2011), methanol (Blumberg; Morosuk; Tsatsaronis, 2017; Canete; Gigola; Briginole, 2014; Luu; Milani; Abbas, 2016; Rasmussen; Glarborg, 2008), ammonia (Malmali *et al.,* 2016; Martínez *et al.,* 2017; Song e*t al.*, 2017), urea (Hao *et al.,* 2001; Meesen, 2014; Wang; Li, 2017) or integrated processes (Flórez-Orrego;

Oliveira Júnior, 2016; Milani *et al.,* 2015; Taghdisian; Farhadi; Pishvaie, 2012). Such studies are not described in this work, which focus on patented processes.

2.1 Integration among the production processes of methane derivatives

In general, the combined production of ammonia and urea brings, among other advantages, the elimination of the necessity to move ammonia produced in one place to serve as a raw material for the production of urea in another site, main due the transport of ammonia is considered a high-cost special transportation. The use of CO_2 in the purification step of the synthesis gas used for the production of ammonia greatly increases the overall efficiency of the process, giving a use to the CO_2 more attractive than simply throwing it into the atmosphere.

The integration between the ammonia and urea production processes, where the carbon dioxide produced in the synthesis gas and the ammonia produced in the conversion reactor are reacted, generates an aqueous solution of carbamate. This is send to the synthesis reactor of urea, and implies, on one hand, a great simplification of the plant, with special reference to the sections of elimination of CO_2 and separation of ammonia from CO_2. On the other hand, this combined production generates an accentuated overload of the sections correlated with urea production, essentially due to the lack of heat formation and the excess molar ratio H_2O/CO_2 in the urea synthesis reactor, generating a lower conversion and higher energy consumption. As a consequence, in the field of combined ammonia and urea production, there is a growing necessity to provide processes that increase the conversion efficiency of urea in a simple manner with low cost production and lower initial investment (Cook and Mavrovic, 1967b).

In another direction, the combined production of methanol and ammonia in the same site allows a good flexibility in the distribution of the synthesis gas produced for feeding the two plants simultaneously. On the other hand, this combination increases the restrictions in terms of possibility of variation of the quality and composition of the synthesis gas used as raw material, because in order to optimize the composition of the syngas for one unit, the opposite effect will occur for the other (Davey and Wurzel, 2007). It should be noted that another important issue is that the production of methanol and ammonia in combined units requires different systems of storage and production flow.

In this background scenario, several patents describing processes of coproduction of methane derivatives in one place have been and are being developed to make these coproduction processes increasingly efficient, more profitable and more interesting from the perspective of environmental preservation. Some of the most important patents on coproduction of methane derivatives in a same site are described as follows.

2.2 Investigated patents

Firstly, several patents were investigated. Then, it was performed an overall analysis of patents, identifying general trends and proposing a superstructure for the flowsheet of the integrated process. Some of the most relevant associated to the scope of this study were selected for detailed analyzes, as follows:

P1. US 1967/3310376-A: Process for combined production of ammonia and urea (Cook; Mavrovic, 1967b);
P2. US 1968/3371115-A: Process for combined production of ammonia and urea (Cook; Mavrovic, 1968);
P3. US 1971/3598527-A: Ammonia and methanol production (Quartulli; Kandall, 1971);
P4. US 1987/4690812-A: Integrated production of ammonia and urea (Ranke; Schrader, 1987);
P5. US 1991/4988491-A: Flexible integration of the production of ammonia and urea (Vandijk; Fraley, 1991);
P6. US 1993/5180570-A: Integrated process for making methanol and ammonia (Lee; Leblanc, 1993);
P7. US 1993/4869887-A: Integrated ammonia-urea process (Dijk, 1989);
P8. US 2001/6333014-B1: Process for ammonia and methanol coproduction (Filippi, 2001);
P9. US 2001/6231827-B1: Process for combined production of ammonia and urea (Pagani; Zardi, 2001);

P10. US 2002/6448441-B1: Gasification process for ammonia/urea production (Wing-Chiu; Reich, 2002);
P11. US 2004/6696026-B2: Process for combined production of ammonia and urea (Pagani; Zardi, 2004);
P12. US 2007/0299144-A1: Of Methanol And Ammonia From NG (Davey; Wurzel, 2007);
P13. US 2010/7674932 B2: Method for the Production of Urea from NG (Davey; Wurzel, 2010);
P14. US 2012/0148472-A1: Process for methanol and ammonia coproduction (Ahmed; Basshir, 2012);
P15. US 2014/8692034-B2: Coproduction of methanol and ammonia (Han, 2014);
P16. US 2016/0083260-A1: A process for coproduction of ammonia, urea and methanol (Dahl, 2016a);

Many other patents were also investigated (Axel; Russell, 1961; Barry; Williams, 1958; Bishop; Viramontes-Brown, 1977; Bonetti, 1977; Bongiorno; Oradell, [s.d.]; Cook; Mavrovic, 1967a; Dahl, 2016b; Eiji; Toyoyasu, 1967; Friedman, 1973; Guadalupi *et al.,* 1977; Henry; Jaeschke, 1967; Kurpit; Ivo; Saffian, 1965; Kurpit; Mavrovic; Saffian, 1964; Luke, 1989; Marion; Reynolds, 1976; Mavrovic, 1964; Pagani, 1982; Schmid, 1979; Steimberg, 2010; Thiebaut; Vidalin, 2002). However, they have only minor differences in relation to the processes reported here. Other patents reporting specific processes such as catalytic hydrocarbon reforming, synthesis gas purification, hydrogen generation, configuration of catalytic reactors, among other subjects of interest, were also verified to allow a better theoretical basis.

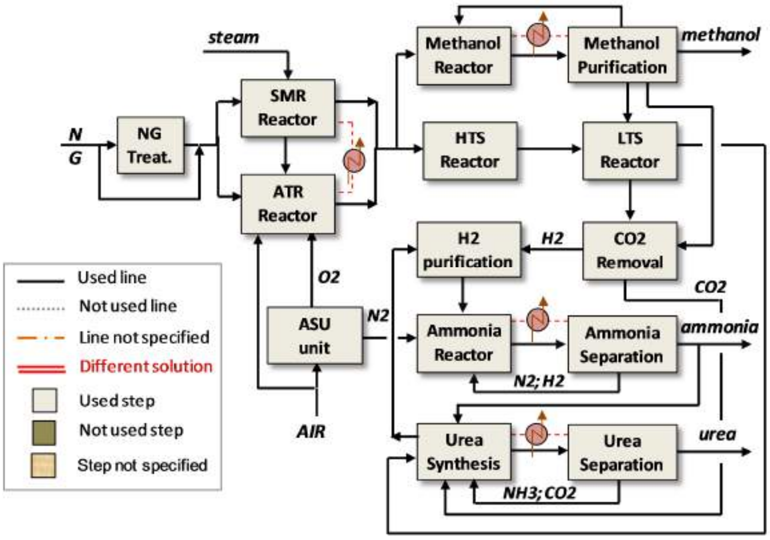
In order to compare the processes described in the patents studied and to facilitate the identification of similarities and discrepancies between the processes, a standard general superstructure was developed for signaling the described technologies and the process flow sequence of each patent studied. It is possible to visually verify the most common technologies chosen by the inventors, as well as those used only to meet a specific objective in the process of each patent studied, following a pattern of identification of the technologies employed in each of them. In next section we decided to first present the general trends and the superstructure, reducing them for each patent investigated.

2.3 Analysis of the patents

For the sake of clarity, the proposed superstructure will be presented for the first time, encompassing the entire patent proposal studied in this thesis. For each patent, it is performed its description and the superstructure is then simplified to the authors proposition. It is possible to visually verify the most common technologies chosen by the inventors, as well as those used only to meet a specific objective in the process of each patent studied, following a pattern of identification of the technologies employed in each of them.

Therefore, Figure 11 shows the superstructure of each patent evaluated. The caption defines the active process steps (continuous line) and non-active steps (dotted line). They also present eventual different solutions that were used by the inventors (in red). It should be noted that some steps have not been described by the inventors, who only report that such steps are fully known to the scientific community and have already been detailed in previous patents.

Figure 11 – Superstructure of patens evaluated.



Source: The Author, 2017.

Main stages of the process

i) NG Treatment: load treatment step, normally used for the removal of sulfur compounds.

- Main reaction: $ZnO + H2S \rightarrow ZnS + H2O$ (Reaction 01)

ii) SMR reactor: Steam Methane Reforming; first step of syngas generation

- Main reaction: $CH4 + H2O \leftrightarrow CO + 3H2$ (Reaction 02)

iii) ATR reactor: Autothermical Reforming; second step of syngas generation.

- Main reaction: $CH4 + \frac{1}{2}O2 \leftrightarrow CO + 2H2$ (Reaction 03)

iv) Methanol reactor: methanol conversion step.

- Main reactions: $CO + 2H2 \leftrightarrow CH3OH$ (Reaction 04)

  $CO2 + 3H2 \leftrightarrow CH3OH + H2O$ (Reaction 05)

v) HTS/LTS reactors: CO conversion into CO_2 step (water-gas-shift reaction)

- Main reaction: $CO + H2O \leftrightarrow CO2 + H2$ (Reaction 06)

vi) Methanator reactor (Hydrogen purification)

- Main reactions: $CO + 3H2 \leftrightarrow CH4 + H2O$ (Reaction 07)

  $CO2 + 4H2 \leftrightarrow CH4 + 2H2O$ (Reaction 08)

vii) Ammonia reactor: ammonia conversion step.

- Main reaction: $N2 + 3H2 \leftrightarrow 2NH3$ (Reaction 09)

viii) Urea reactor: urea conversion step.

- Main reactions: $3NH3 + CO2 \leftrightarrow NH2COONH4$ (Reaction 10)

  $NH2COONH4 \leftrightarrow (NH2)2CO + H20$ (Reaction 11)

Heat integrations appear only in units associated to the pairs of processes SMR-ATR, Methanol Synthesis-Methanol Purification, Ammonia Synthesis–Ammonia Purification, and Urea Synthesis-Urea Purification. On other hand, material integrations appear between several units, however, in many possibilities, according to each patent specification. Bellow it is presented each patent and its description, together with superstructure simplification.

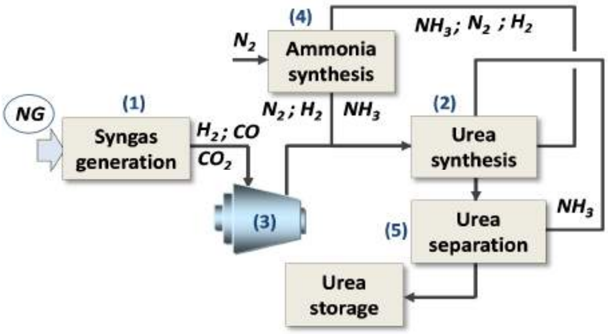
2.3.1 Patent US 1967/3310376-A: Process for combined production of ammonia and urea (Cook; Mavrovic, 1967b)

The process for the combined production of ammonia and urea presented in Patent U.S. 1967/3310376-A, assigned to inventors Lucien Cook and Ivo Mavrovic, having as original assignee the Chemical Construction group, relates to a process wherein the ammonia synthesis and the synthesis of urea are combined in a different way. In this process, the synthesis gas generated in the syngas reactor (1) and consisting of CO, CO_2 and H_2 is mixed with ammonia and unreacted gases exiting the high pressure ammonia synthesis reactor. This mixture feeds the urea synthesis reactor (2), where urea formation occurs, with consumption and complete extinction of the CO_2 present in the gas stream. Urea synthesis is employed to remove carbon dioxide from the synthesis gas used for the production of ammonia. Thus, the synthesis gas is compressed (3) and combined with liquid ammonia from ammonia synthesis. This mixture is submitted to the urea synthesis reactor (2).

Carbon dioxide originally contained in the synthesis gas is converted to water and starch, generating a residual gas phase containing only hydrogen, nitrogen and ammonia, which is separated from the liquid phase containing a urea. The residual gas phase is recycled to the ammonia reactor (4), while the liquid phase produced, consisting of an aqueous solution of urea, ammonium carbamate and excess ammonia, is separated in a separator vessel (5).

A solution of ammonium carbamate and excess ammonia which is separated from the urea produced and recycled to the urea synthesis reactor. This process has as main advantage the reduction of the investment related to the step of CO_2 removal of the synthesis gas and the subsequent regeneration of the absorber (usually monoethanolamine - MEA). It is worth noting that this process only has the objective of producing urea as the final product. Figure 12 shows the schematic diagram proposed in this patent.

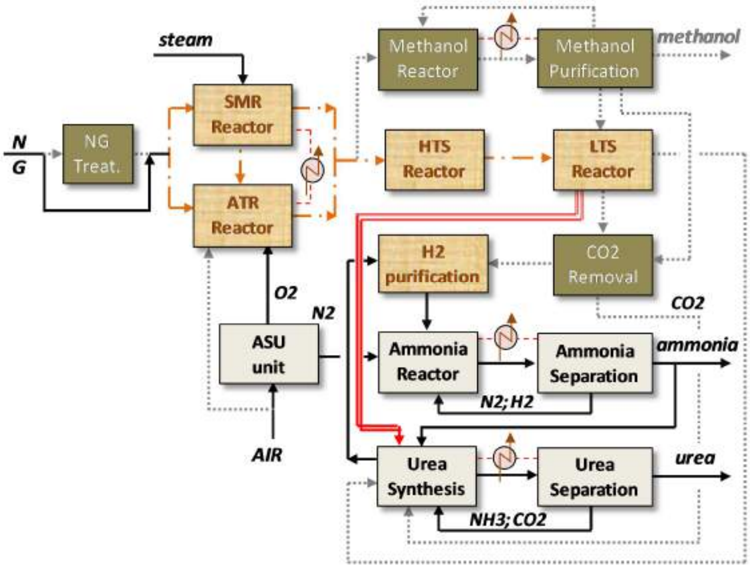
Figure 12 – Block diagram of the conceptual design of the patent US 3310376-A.



Source: Based on patent US 3310376-A, 1967.

Figure 13 shows the superstructure simplified to this patent. Syngas is send to ammonia and urea synthesis. An outlet stream from ammonia separation is also send to urea synthesis, as usual.

Figure 13 - Superstructure of patent US 1967/3310376-A.



Source: The Author, 2017.

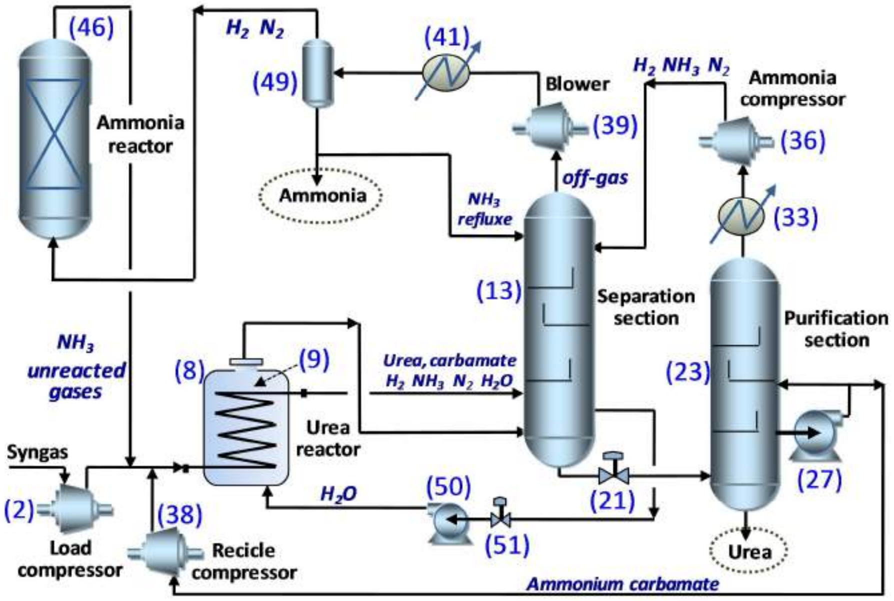
2.3.2 Patent US 1968/3371115-A: Process for combined production of ammonia and urea (Cook; Mavrovic,1968)

The process presented in patent U.S. 1968/3371115-A, assigned to inventors Cook Lucien H. and Ivo Mavrovic, and has as original assignee the Chemical Construction Corp. This patent relates to a combined process for ammonia and urea production from synthesis gas.

The main object of the present invention is to produce ammonia and urea in a combined process using the step of synthesizing urea as a means of removing carbon dioxide from the ammonia synthesis gas. An additional object is to reduce the capital investment and cost of operating utilities of an ammonia plant by combining the synthesis of urea with ammonia synthesis in the same production site.

The process reported here carries out the reaction of the feed gas of the complex containing a substantial proportion of carbon dioxide with effluent gas from the ammonia synthesis reactor and a solution of recycled aqueous ammonium carbamate. The resulting mixed process stream is reacted under optimum conditions for the urea synthesis. Carbon dioxide is consumed in the formation of urea. The residual CO_2-free gas from the urea reactor is then sent to the ammonia synthesis reactor to form more ammonia. Ammonia is produced by the catalytic combination of hydrogen and nitrogen at high pressure and temperature. Hydrogen is produced from hydrocarbons by steam catalytic reforming or partial oxidation. Figure 14 shows a schematic of the patented process.

Figure 14 – Block diagram of the conceptual design of the patent US 3371115-A.



Source: Based on patent US 3371115-A, 1968.

A crude synthesis gas stream containing hydrogen, nitrogen and carbon dioxide is generated from hydrocarbons in a steam reforming section, followed by a catalytic oxidation step to promote complete extinction of the CO present in the remaining gas.

The CO-free gas is compressed in the compressor (2) so that the pressure is raised to the range from 17.24 MPa to 41.37 MPa (required for urea synthesis and ammonia synthesis).

The compressed gas stream is combined with the effluent stream from the ammonia synthesis reactor. The mixed gas is then further combined with the recycled aqueous ammonium carbamate solution. The resulting process stream from these two blends is then sent to the urea synthesis reactor (8). The urea reactor contains a high pressure coil (9) through which the process stream passes exchanging heat with condensed water.

The carbon dioxide originally contained in syngas feedstock combines with ammonia from reactor (46) to form ammonium carbamate as the process stream passes through coil (9). This exothermic reaction generates heat and the process stream within the coil (9) is cooled and maintained at a temperature typically in the range of 150 °C to 200 °C by exchanging heat with the liquid water in the reactor (8). The liquid water is vaporized and the steam generated is withdrawn through the upper of the urea reactor (8) at a pressure in the range of 0.28 MPa to 1.17 MPa. A part of the ammonium carbamate is further converted to urea as the process stream passes through the coil (9).

The process stream is removed from the coil (9) and consists of a gas-liquid mixture containing mainly urea, ammonium carbamate, ammonia, water, hydrogen and nitrogen. This stream deriving from urea reactor is send to the high pressure gas separation section (13). This section is formed basically by a separator column. In this column, the input stream is then divided into a gas phase carbon dioxide-free and consisting of hydrogen, nitrogen and ammonia that goes up by the column, while a liquid phase containing mainly urea, water and ammonium carbamate descends through the column.

The separation column (13) has a top reflux section consisting of a set of bubbler trays. A temperature gradient is maintained in the upper reflux section by means of cold liquid ammonia which is injected into the separator column (13) above the upper tray as top reflux. The upper tray temperature is usually kept below 130 °C to avoid the critical point of ammonia at high operating pressure. Because of the temperature gradient and the refluxing ammonia, any carbon dioxide originally present in the gas phase is converted to liquid ammonium carbamate and down the separation column. A gas phase purified without carbon dioxide and consisting of hydrogen, nitrogen and ammonia is removed at the top of the separation column.

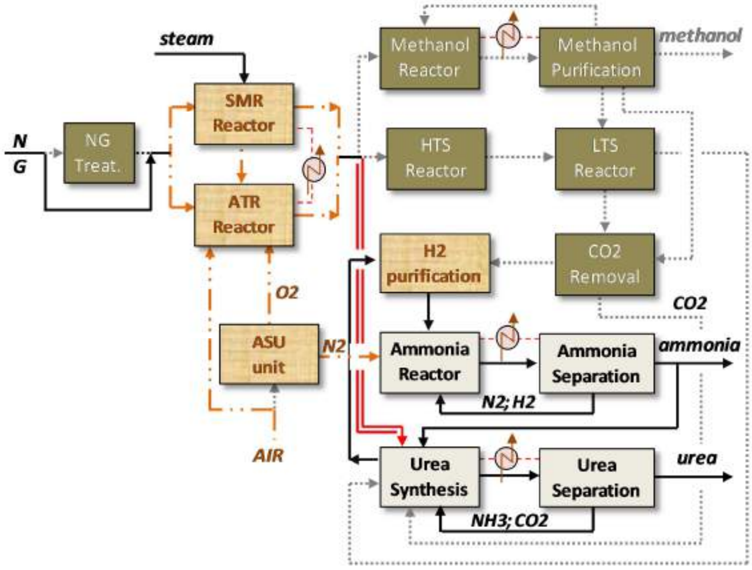
The liquid phase at the bottom of the separator column is heated by the gaseous stream from the top of the urea reactor. The condensed water is removed from the bottom of the column and is recycled to the urea reactor. A condensate water pump (50) and a pressure control valve (51) are required to allow recycling of the condensed water at the bottom of the separator column.

As the liquid phase is heated in passing downward through the lower section of separator column, further conversion of ammonium carbamate to urea takes place. The resulting liquid containing urea is removed from the high pressure separator column and passed through the pressure reducing valve (21). The liquid, now typically at a pressure below about 2.76 MPa, is injected into the purification section (23). This liquid is heated at the bottom of the purification section, causing the decomposition of ammonium carbamate and the generation of an off-gas consisting of a mixture of ammonia and carbon dioxide. This process can occur in several stages. The residual liquid phase is extracted from the purification section. The upward off-gas flow through the filling section of the unit (23) is partially condensed by the circulating ammonium carbamate solution which is withdrawn of column. This stream is then pumped by the pump (27) and recycled to the column, after cooling.

The residual gas stream, which now consists mainly of ammonia, is further purified in the upper reflux section of the purifying column (23), and finally a stream of carbon dioxide-free ammonia gas is drawn through the upper of the purifying column. The ammonia vapor plus nitrogen and hydrogen stream is cooled in the cooler (33) and is then compressed in the compressor (36) at a pressure between 17.24 MPa and 41.37 MPa. After compression, the ammonia vapor is recycled to the separation section (13). The discharge stream of the pump (27) containing an aqueous solution of ammonium carbamate is divided. Part of the flow returns to the purifying section (13) and part is send as a recycle stream to the urea reactor after compression in the recycle compressor (38) till the urea synthesis pressure level (between 17.24 MPa and 41.37 MPa).

The off-gas from the top of the separation section (13) is composed of hydrogen, nitrogen and ammonia and is passed first through the blower (39), which compensates for the drop in pressure of the circulating gas phase. The gas stream discharged by the blower (39) is send to the cooler (41), where part of the gas stream is condensed as liquid ammonia and is separated in a separator vessel (49). The liquid ammonia is partially recycled to the unit (13) to provide ammonia reflux. The remaining ammonia forms the ammonia flow product. The remaining gaseous phase is withdrawn from a separator vessel (49) and send to the ammonia catalytic converter (46). The ammonia reactor effluent stream consisting of ammonia and unconverted hydrogen and nitrogen mixture is send to the urea synthesis unit (8). Figure 15 shows the superstructure simplified to this patent. Syngas is send to urea synthesis, which outlet stream returns to ammonia synthesis. Ammonia is send to urea synthesis too.

Figure 15 - Superstructure of patent US 1968/3371115-A.



Source: The Author, 2017.

2.3.3 Patent US 1971/3598527-A: Ammonia and methanol production (Quartulli; Kandall, 1971)

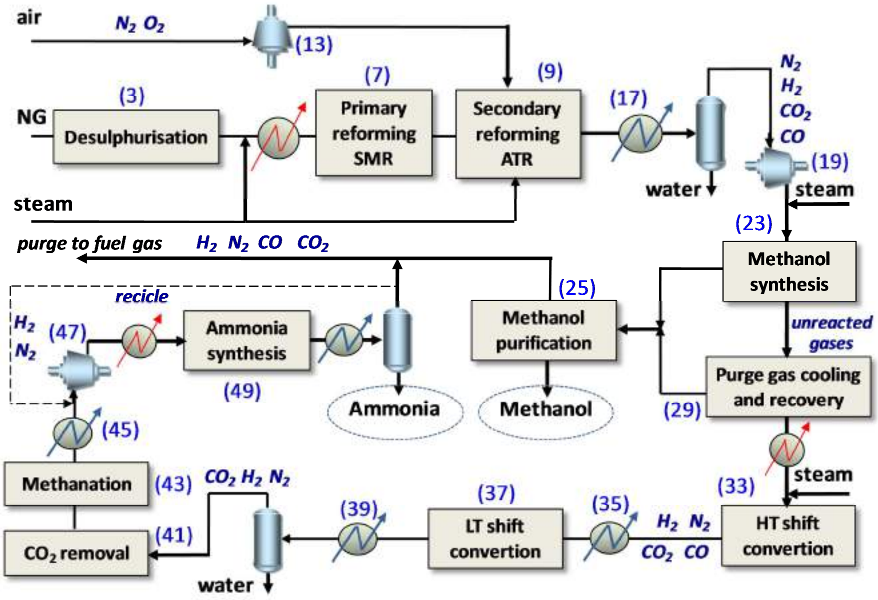
The process presented in patent U.S. 1971/US3598527-A, assigned to inventors Robert Jay Kandall and Orlando J. Quartulli, and has as original assignee the M. W. KELLOGG group. This patent relates to an integrated process for low capacity methanol and ammonia production.

Until the 1960s, it was considered non-economic to build low-capacity methanol plants based on the use of alternative compressors. However, the development of a low pressure process for the production of methanol using centrifugal compressors has made the construction and operation of low capacity methanol plants economically viable. Although this low pressure methanol production process was a major breakthrough in that time, even greater benefits were incorporated into the process through the integrated production of methanol and ammonia at the same site, in terms of reduced capital investment and reduced operating costs. The main purpose of this invention therefore is to provide a process for integrating methanol and ammonia production, reducing the initial investment required for the construction of the low capacity process plants and the operating costs of the complex.

In simple methanol plants, an external source of carbon dioxide is usually required in order to maximize the production of methanol. Normally used feedstock (natural gas), when reformed, does not contain enough carbon oxides to maximize methanol production, as predicted by equilibrium thermodynamic. Imports from other units can be used to supplement the CO_2 supply and the carbon dioxide compressors are needed to ensure an adequate arrival pressure for the injection of CO_2 into the methanol synthesis reactor at a high cost in terms of energy.

During the synthesis of ammonia in a simple plant, carbon dioxide is discarded into the atmosphere without any use unless there is a methanol production plant or other facility capable of consuming carbon dioxide nearby. The carbon dioxide would then be compressed and delivered to this consumer, through the use of powerful CO_2 compressors. Thus, there is a doubling of equipment and manpower required in both separate ammonia and methanol production facilities. The methanol production unit remains dependent on the ammonia production unit for a stable supply of carbon dioxide in the synthesis of methanol. When a problem occurs in the ammonia unit, this problem adversely affects the supply of carbon dioxide to the methanol unit, often causing a reduction in production or total shutdown of the methanol unit. Figure 16 shows a schematic representation of the patented process.

Figure 16 – Block diagram of the conceptual design of the patent US 3598527-A.



Source: Based on patent US 3598527-A.

A hydrocarbon feedstock (natural gas) is conducted into a desulfurization chamber (3) containing the activated carbon as the desulfurization agent wherein, at room temperature, substantially all of the sulfur compounds are removed from the feed-stream in order to avoid poisoning the reform catalysts. After desulphurisation, steam is introduced into the feedstock at a predetermined molar ratio of steam/carbon of 3:1. The steam-hydrocarbon mixture, after preheating to 524 °C, flows to a primary reformer (7) containing a nickel oxide catalyst. Under the influence of the catalyst, an inlet temperature of 524 °C and an outlet temperature of 871 °C, a large part of the gases is converted into hydrogen and carbon oxides. An inlet pressure of 3.44 MPa (35.18 kgf/cm^2) and an outlet pressure of 3.10 MPa (31.66 kgf/cm^2) are employed for the primary reform.

This first conversion is not complete, so that the gases are then sent to a secondary reformer (9) where the air is introduced through an air compressor (13) in an amount sufficient to satisfy the nitrogen requirement for a given ammonia production rate. The inlet temperature of the reactor rises from 871 °C to an outlet temperature of 1,260 °C to complete the hydrocarbon reforming. During secondary reforming, more steam is introduced into the reactor to adjust the optimal vapor/carbon molar ratio. The reformed gases are then fed into the heat exchanger (17), where the temperature of the reformed gases is reduced to 38 °C. The recovered heat can be used to produce steam, preheat boiler feed water and heat the supply process. The cooled reformed gases, after removal of the condensed vapor, are passed to a compressor (19) which compresses the gases to a required pressure for methanol synthesis (5.17 MPa or 52.8 kgf/cm^2).

After compression, the reformed gases receive more steam to adjust the optimum vapor/carbon molar ratio and proceed to the methanol synthesis reactor (23), where the methanol is catalytically synthesized, at temperatures in the range of 251 °C to 270 °C and a pressure around 5.17 MPa (52.8 kgf/cm^2) from the synthesis gas. After separation of the crude methanol from the gas stream, the crude methanol flows into a methanol purification system (25), where high boiling and low boiling impurities are removed and water and refined methanol is removed of the system.

The unreacted gases from the methanol synthesis converter (23) are separated and passed through the cooling and recovery section (29) to remove methanol and impurities. The liquid-free gas stream is heated to a temperature of 371 °C, combined with more steam and conducted to a high temperature CO converter (33). In the shift converter (33), additional hydrogen is produced by reacting with the present carbon monoxide with steam to produce carbon dioxide and hydrogen.

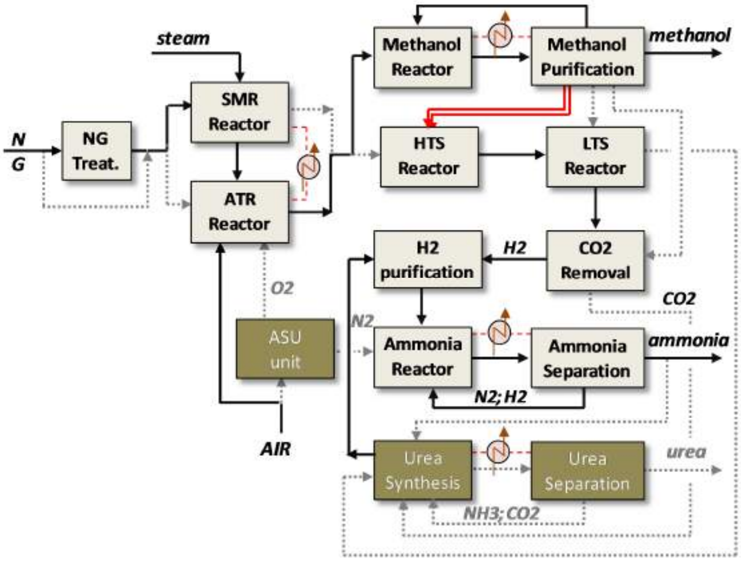
The amount of total hydrogen in the reformed gases is sufficient to satisfy the stoichiometry for the production of ammonia and the requirement of hydrogen for the methanation of residual carbon oxides. The gases then leave the high temperature CO converter (33) at a temperature of 413 °C and enter a heat recovery system (35), where the gases are cooled and the heat recovered is used to produce steam. The gases now enter a low temperature converter (37), at a temperature of 239 °C, completing the conversion of carbon monoxide in carbon dioxide. After the gases leave the low temperature CO converter (37) at a temperature of 254 °C, they are introduced into additional heat recovery equipment (39), where the gases are cooled. After this step of cooling, the condensed vapor is removed of the gaseous stream.

The gases are then sent to a carbon dioxide removal system which includes a column (41) provided with a regenerative solvent suitable for removing the carbon dioxide. After the removal of all carbon dioxide, the gases flow into a methanator reactor (43) where the residual carbon oxides are converted to methane by the catalytic reaction of the residual carbon oxides with the hydrogen contained in the gas stream. Removal of residual carbon oxides is necessary to prevent poisoning of the ammonia synthesis catalyst.

Upon further recovery of heat in the exchanger (45), the gases flow to the synthesis gas compressor (47), for raises the gas pressure to 14.48 MPa (147.7 kgf/cm^2). The compressed gases are then preheated to 410 °C and are introduced into the ammonia synthesis converter (49) where, under the influence of elevated temperature and pressure, the ammonia is catalytically synthesized. The gases leave the converter at 454 °C. The inert methane and argon present in the ammonia synthesis gas are continuously purged out of the ammonia synthesis circuit. The purged gas is used to provide a part of the fuel necessary for the operation of the primary reform.

Figure 17 shows the superstructure simplified to this patent. Methanol is fed with syngas stream. An outlet stream from methanol systems go to HTS and LTS reactor, which follows to CO_2 removal, H_2 purification and ammonia synthesis.

Figure 17 - Superstructure of patent US 1971/3598527-A.

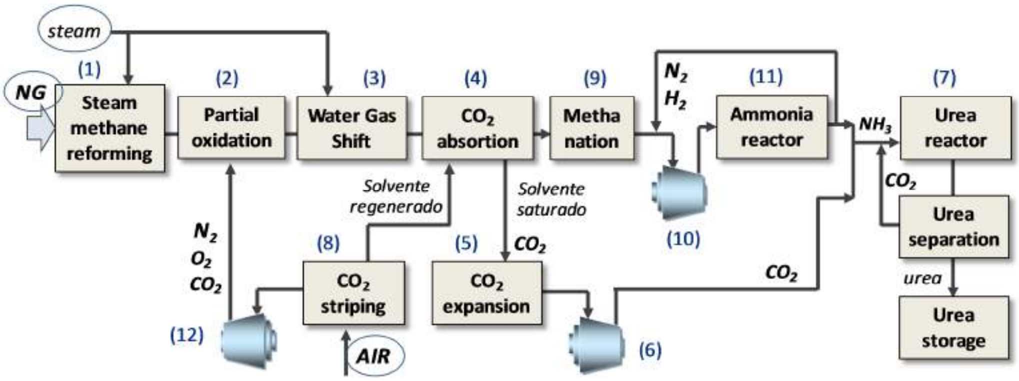


Source: The Author, 2017.

2.3.4 Patent US 1987/4690812-A: Integrated production of ammonia and urea (Ranke; Schrader, 1987)

The process for the combined production of ammonia and urea presented in the patent U.S. 1987/4690812-A, assigned to the inventors Gerhard Ranke and Ulrich Schrader, having as original assignee the Linde group, refers to an industrial unit which can be described as follows: a load of natural gas is fed into a steam reformer (1), operated at a pressure range of 1.47 MPa to 3.43 MPa (15.0 kgf/cm^2 to 30.0 kgf/cm^2). Figure 18 shows a simplified schematic of the process steps.

Figure 18 – Block diagram of the conceptual design of the patent US 4690812-A.



Source: Based on patent US 4690812-A, 1987.

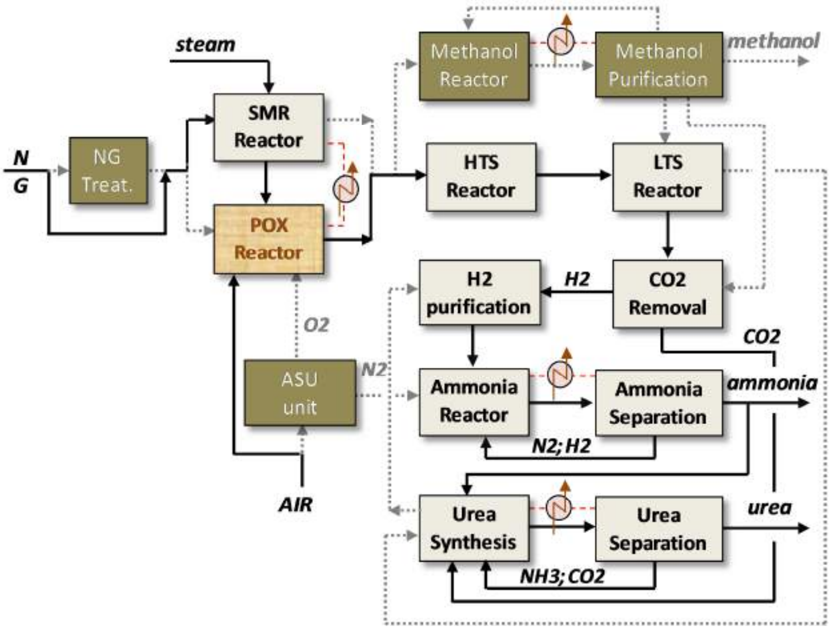
The catalytic reaction of steam reforming of natural gas occurs, producing a mixture of H_2 and CO (syngas). The reformed gas then proceeds to a secondary reformer (2), operated at a pressure range of 1.37 MPa to 3.33 MPa (14 kgf/cm^2 to 34 kgf/cm^2). In this reactor, the residual methane present in the gas leaving the primary reformer is extinguished by incomplete combustion with the injected air. The amount of air is sufficient to produce a gaseous mixture at a ratio of 3 moles of H_2 to each mole of N_2. The gas from the secondary reformer is treated in a water gas shift reactor (3), operated between 1.37 MPa to 3.33 MPa, to convert CO to CO_2. Typically, the residual CO content in the treated syngas is about 0.3%.

The CO_2 present in the syngas is separated into an absorption column (4) operated at high pressure in the range of 1.47 MPa and 6.86 MPa (15 kgf/cm^2 to 70 kgf/cm^2) 15. The residual CO_2 content in the syngas after this step is in the order of 100 ppm. The CO_2 solvent is conducted to an expansion stage (5) optionally performed in several stages. After this step, the CO_2 separated from the solvent is compressed in the load compressor (6) and feeds the urea synthesis reactor (7). The solvent still with some CO_2 from the expansion phase is destined to the regeneration column (8), where the final separation of CO_2 from the liquid phase occurs. In this step, atmospheric air is mixed to the solvent, facilitating the removal of CO_2. The regenerated solvent returns to the absorption column (4) in a closed cycle. The residual CO_2 separated from the solvent, together with the atmospheric air, is compressed in the air load compressor (12). Then, the CO_2 compressed is fed into the secondary reformer (2).

The CO_2-free syngas at the outlet of the absorber is conveyed to the methanation stage (9), where the CO and the CO_2 residuals react catalytically with H_2 to form methane and water, ensuring the complete extinction of oxygenated compounds. At the methanation exit, the syngas is compressed in the load compressor (10) of the ammonia synthesis reactor (11). Finally, the compressed CO_2 in step 6 is fed together with the ammonia resulting from the synthesis reactor (11) in the urea synthesis reactor (7). The urea produced is stored. The final product of the complex is urea, and the production of ammonia surplus is not predicted continuously.

Figure 19 shows the superstructure simplified to this patent. A series of SMR and POX reactor is used, follows the sequence HTS, LTS, CO_2 removal. CO_2 from last unit is send to urea synthesis, while H_2 rich stream is send to hydrogen purification and ammonia synthesis.

Figure 19 - Superstructure of patent US 1987/4690812-A.



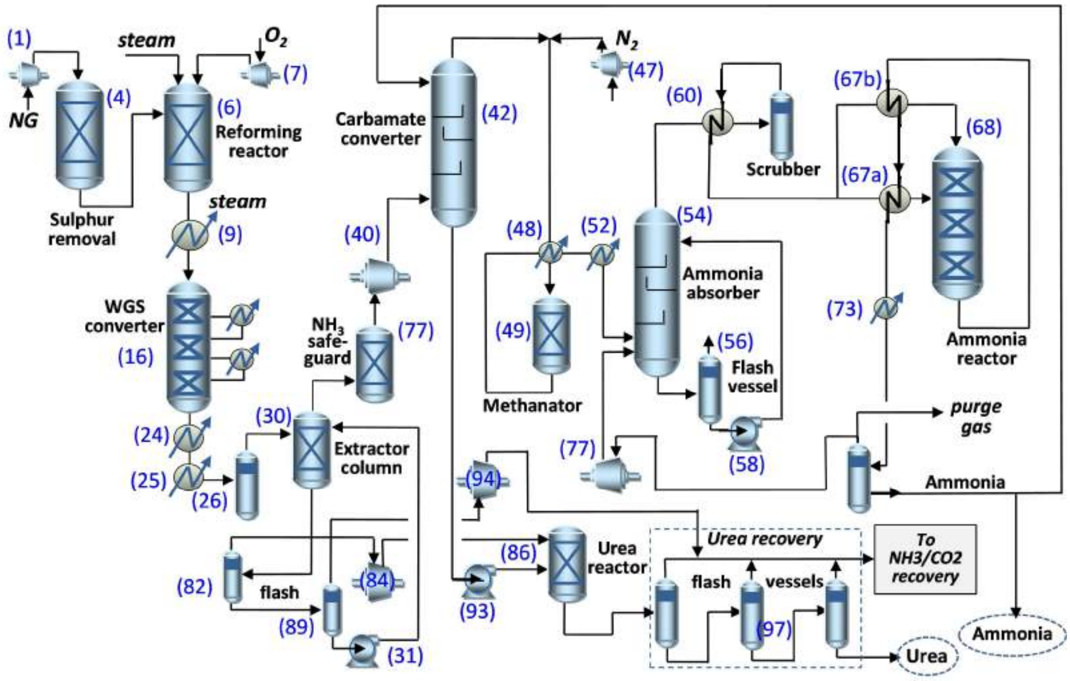
Source: The Author, 2017.

2.3.5 Patent US 1991/4988491-A: Flexible integration of the production of ammonia and urea (Van Dijk; Fraley, 1991)

The process presented in patent U.S. 1991/US4988491-A, assigned to inventors Christiaan Van Dijk and Lowell D. Fraley, has as the original assignee the same inventors. This patent relates to a process that produces ammonia and urea in a flexible and integrated way on a same production site. The process uses adiabatic reforming of the hydrocarbons such as natural gas. With adiabatic reforming of natural gas, a surplus of carbon dioxide is produced and also substantially pure oxygen and nitrogen may be used which minimizes circulating inert gases such as argon in the system.

More importantly, adiabatic reforming allows operation at much higher pressure than standard primary reforming, namely, between 4.82 MPa and 20.68 MPa (49 kgf/cm^2 to 211 kgf/cm^2). When these pressures are used, the process includes a recycle of the methane and hydrogen from the ammonia synthesis loop to the adiabatic reformer. The process here related uniquely removes the carbon dioxide which is produced by the reforming of the hydrocarbons. The treatment by the water gas shift reaction in two independent stages convert CO into CO_2. After the water gas shift, treatment of the ammonia synthesis gases is carried out with a physical solvent, which removes at low cost most part of the carbon dioxide. The remaining carbon dioxide is removed by reaction with ammonia, either hot or cold, leading to the production of ammonium carbamate. Figure 20 presents a simplified block diagram of the process.

Figure 20 – Block diagram of the conceptual design of the patent US 4988491-A.



Source: The Author, 2017.

The natural gas is compressed in the compressor (1) at a pressure between 4.83 MPa and 20.68 MPa. A small amount of hydrogen-containing gas, available from the purge stream, is mixed with the natural gas. A small amount of steam can also be added to the gas stream. The stream of gas mixed with steam enters the vessel (4) for cleaning traces of sulfur compounds in the natural gas. The vessel 4 contains a bed of zinc oxide to remove the sulfur compounds. The cleaned gas stream is then preheated and fed into an adiabatic reforming reactor (6). A gas stream containing oxygen is also fed into the reformer reactor 6 which is compressed by the compressor (7). This gas containing oxygen can be pure oxygen or atmospheric air with nitrogen. In the reforming reactor 6 a temperature between 1,150 °C and 1,480 °C can be achieved. The outlet effluent gas from the reformer reactor (6) is introduced into the heat exchanger (9). The cooling water used in the heat exchanger (9) is vaporized, generating high pressure steam for use in the plant.

The cooled gas is then mixed with water. Steam is generated adiabatically and the gas mixture is fed to a three-stage water-gas conversion unit (16), which operates at three different temperature levels. The gases are introduced into a first bed of shifting catalyst at the top of the unit 16 and are then passed to the cooler (18). Thereafter the gases are passed to the next stage of the unit 16 containing a second bed of shifting catalyst. The change reaction, which is the reaction of CO and H_2O to form CO_2 and H_2, is repeated in the second bed. Then, the gases are removed from the converter and cooled in the cooler (21) and reintroduced into a third bed of shifting catalyst. The gases are then removed from the water gas shifting unit (16). The gases are then cooled by passing through a first heat exchanger (24) and a second heat exchanger (25). Medium pressure vapor is produced in the heat exchanger (24). The cooled gases are then introduced into a separator vessel (26), where the condensed water is removed by the bottom of the vessel (26).

In processes of integrating ammonia plant and urea plant so far, all carbon dioxide is removed as it is made in ammonia production or absorbed to convert carbon dioxide and ammonia into ammonium carbamate. But, in the process of the present invention, however, it is advisable to remove any excess CO_2 (the excess means the amount of CO_2 in excess of the stoichiometric amount which will combine with ammonia to form urea). In addition, at least 50% of the CO_2 required for the production of urea by solvent extraction and remove the remaining CO_2 by reaction with ammonia to produce ammonium carbamate.

The gas stream from the separator vessel (26) is then fed in a solvent extraction column (30). Removal of the excess carbon dioxide occurs in the contacting column (30). Extraction is preferably performed with a physical solvent such as Selexol® which is fed by the pump (31).

The amount of CO_2 removed by solvent extraction will depend on the pressure used in the reforming step. The gas outlet stream from contactor column (30) is fed to an ammonia safe-guard chamber (34). This chamber is a multi-stage vessel with water in each tray. When the ammonium carbonate concentration in the lower tray increases above a predetermined level, additional water is added and the solution is withdrawn through the valve (37). The gas after this contact with water to remove any residual ammonia present is fed into the row synthesis gas compressor (40).

The pressurized gas is fed to a contactor column (42), where carbon dioxide still remaining in the gases is reacted with ammonia, which is also fed to the top of this column as aqueous solution. During normal operation, when both the ammonia plant and urea synthesis sections are operative, most of the water present in the aqueous ammonia solution is derived from the water recovered from the urea synthesis section.

Thereafter carbon dioxide is converted into ammonium carbamate solution in a contactor column (42). The temperatures in the converter (42) vary with the pressure. If there are high pressures approaching the pressures used in the urea sector, the carbamate produced in the converter (42) will be close to the urea reaction temperatures, which are between 170 °C and 200 °C. However, at the pressure level recommended in the present process, which is essentially the ammonia production pressure level, the temperatures will not exceed 104 °C to 138 °C.

The raw ammonia synthesis gas exiting unit (42) may contain ammonia and possibly some water taken from the absorption unit (42). Pure nitrogen compressed to the pressure of the gas by compressor (47) is added. The combined gases are fed to exchanger (48), where the combined gases are heated to methanation temperature of about 343 °C and contacted with a methanation catalyst in converter (49). The effluent gas, is warmed up by the methanation reaction, is then fed to the other side of the above mentioned heat-exchanger. The gas is then ready to be fed into ammonia absorber (54). Here the gas may be combined with the ammonia recycle stream and contacted with an aqueous stream of ammonia.

In vessel (54) cooling is provided by pre-cooled cooling water which is cooled by evaporation, induced by steam jet. Very low pressure steam can be used for this cooling of cooling water. The ammonia solution is removed from vessel (54) and concentrated by flashing at reduced pressure in a flash tank (56). A concentrated solution containing less than 3% water is obtained. This solution exits from the top of the flash tank. The remaining liquid is removed from the bottom of the flash tank and cooled and pumped by the pump (58) to the top of the vessel for contacting the combined gas streams. Additional water may be added to the flash loop in the line between vessel (54) and (56). The ammonia-free gas stream effluent from the top of the vessel (54) is cooled by exchanging heat with cold gas in the exchanger (60).

The cooled gas is then introduced into a scrubber vessel (62), where the gas is washed with liquid ammonia. This washing removes all residual water present in the gases. The aqueous ammonia formed in vessel (62) is removed from the bottom thereof.

The temperature of the washed gases is now less than about -12 °C. The outlet stream from the vessel (62) is send to the heat exchanger (60), where the gases are heated.

After the exchanger (60), the stream of ammonia synthesis gases is divided into two. The first part of the gas exchanges heat in the exchanger (67A) and enters the ammonia reactor (68) at the top. This gas is then reacted in contact with the ammonia catalyst in the first bed of the ammonia reactor. The remainder of the gas exchanges heat at an intermediate temperature in the exchanger (67B) and is introduced into the ammonia reactor (68) below the first catalyst bed to reduce the temperature and allow an additional reaction on the second and third catalyst beds in the ammonia reactor.

Finally, the gas stream, which now contains 10% to 15% ammonia, depending on the conditions, is fed back as recycle stream to the heat exchanger (67A) and (67B) to exchange heat with the inlet gases. The effluent gas from the ammonia reactor is then fed into the heat exchanger (73), where it is cooled by cold cooling water, obtained by evaporation induced by a jet of steam. The condensed liquid ammonia is then withdrawn as product. This liquid ammonia can be used in a number of ways, one of which is like the liquid ammonia introduced into the vessel (62) to remove water from the ammonia synthesis gas. The cooled gas follows to a point, where a small gas flow is removed from the process as purge gas stream. After withdrawal of the purge stream, this cooled gas is send to the compressor (77) and them, is injected into the vessel (54) as a recycle stream.

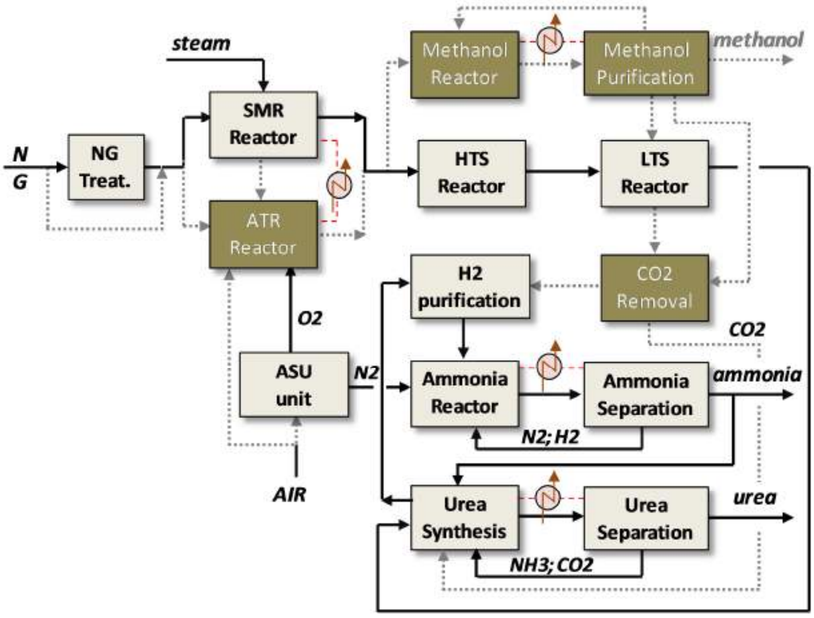
The description of the integrated ammonia-urea plant and the process proposed in this invention presents various details of the interfaces between the ammonia production section and the urea production section. The first interface with the urea section is the removal of CO_2 from the reformed gases. The first CO_2 removal is with the solvent extraction in the extractor column (30). The CO_2 enriched solvent which is removed from the extractor column (30) feeds the flash vessel (82), where a part of the carbon dioxide in solution is released and feeds the compressor of CO_2 (84) and thence to the urea reactor (86).

The liquid from the flash vessel (82) is fed into a second flash vessel (89), where more CO_2 is removed and the remaining liquid is then introduced into the pump (31). The CO_2 separated from the flash vessel (89) is compressed in the compressor 94, and fed into the urea recovery section (pressures in the range of 1.89 MPa to 2.76 MPa). The liquid generated in the contactor column (42) is pumped by pump (93) to the urea reactor (86). The urea reactor (86) is maintained at a temperature between about 182 °C and 202 °C by indirect heating with vapor.

After reaction of the ammonium carbamate at about 20.68 MPa to 31.03 MPa, the concentrated urea liquid is passed through a series of pressure reducing valves (96) and introduced into a series of flash vessels (97). The gases from the urea flash vessels are sent to the gas recovery section (NH_3/CO_2). The concentrated urea solution is evaporated and is grainy.

Figure 21 shows the superstructure simplified to this patent. HTS and LTS are fed with syngas stream, which feeds Urea Synthesis. This unit generates streams that are sending to H_2 purification and posteriorly to ammonia synthesis.

Figure 21 - Superstructure of patent US 1991/4988491-A.



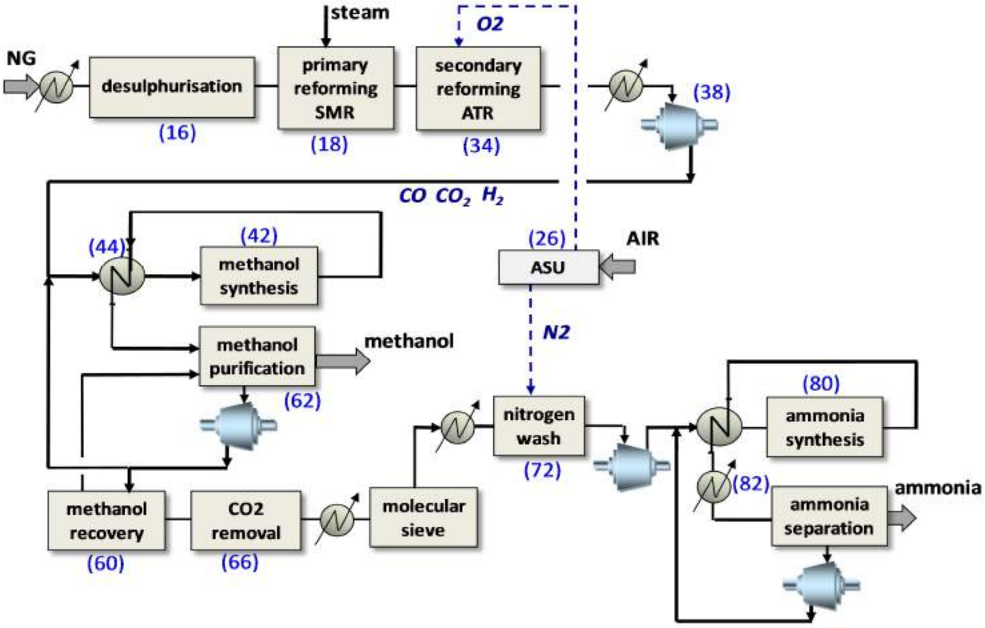
Source: The Author, 2017.

2.3.6 Patent US 1993/5180570-A: Integrated process for making methanol and ammonia (Lee; Leblanc, 1993)

The process presented in patent U.S. 1993/US5180570-A, assigned to inventors Jing M. Lee and Joseph R. Leblanc, has the original assignee the same inventors. This patent relates to an integrated process for making methanol and ammonia from a hydrocarbon feed stock and air is disclosed. An air separation unit is used to produce substantially pure oxygen and nitrogen gas streams. The oxygen gas is used in the secondary reformer to increase the operating pressure of the reformers so that the previous compression to the methanol synthesis reactor may be done by a single stage compressor. The nitrogen is used to remove carbon oxides impurities from the ammonia synthesis feed stream in a nitrogen wash unit in addition to supplying the reactant nitrogen in the ammonia synthesis. Use of nitrogen wash obviates the need for water gas shift reactions and methanation reactions used in conventional processes.

The integrated methanol and ammonia production plant showed in the present invention utilizes substantially pure oxygen and nitrogen streams separated in an Air Separation Unit (ASU). The process described reduced the demand for energy and capital costs, in addition to presenting greater flexibility of production. Pure oxygen flow is used to improve the operational efficiency of the reforming step in generating a more efficiently synthesis gas for the production of methanol. The pure nitrogen stream is used to remove carbon monoxide, carbon dioxide and methane undesirable from the methanol synthesis reactor output gas, as well as provide nitrogen for ammonia synthesis. Figure 22 presents a simplified block diagram about the process.

Figure 22– Block diagram of the conceptual design of the patent US 5180570-A.



Source: Based on patent US 5180570-A, 1993.

As determined by the process described herein, a gaseous hydrocarbon feed stream under pressure is heated to a temperature on the order of 370 °C by a pre-heater (14) and is then introduced into the primary reformer reactor along with steam. When the feed stream contains sulfur, this component must be removed in the sulfur removal unit (16), consisting of a catalytic hydrotreatment to convert sulfur to hydrogen sulfide through the hydrogenation reaction and later absorption of the hydrogenated sulfides formed. The feed stream should be free of sulfur components to avoid poisoning of the various catalysts used in the reforming steps, methanol synthesis and ammonia synthesis.

The desulphurized gas is mixed with steam and heated by the pre-heater (14) at an inlet temperature of the primary reformer (18) of the order of 620 °C. The vapor/methane molar ratio should be 2.5:1.0 to 3.5:1.0. Much of the methane is converted in the primary reformer (18) at H_2, CO and CO_2. The primary reformer is operated in a pressure range of 2.7 MPa to 5.2 MPa and a temperature in the range of 750 °C to 900 °C. The primary reformer contains a conventional nickel based catalyst. A secondary reformer (34) is used to provide an additional conversion. The hot effluent gas from the primary reformer containing unreacted methane is mixed with pure oxygen and heated by the pre-heater (14) at temperature of the order of 450 °C.

Oxygen is produced from an air separation unit (26) and fed into the secondary reformer, where the unreacted methane in the primary reformer is reacted with the oxygen. After the secondary reformer, the residual methane contained in the synthesis gas is less than 1% (molar). The secondary reformer has an operating pressure of 2.7 MPa at 5.2 MPa and an operating temperature of 900 °C at 1,050 °C. The conversion rate of hydrocarbons into synthesis gas of the primary reformer is about 80% to 70% of the total conversion, while the conversion rate of the secondary reformer is in the range of 20% to 30% of the total conversion. The output synthesis gas of the secondary reformer (34) is send to the heat recovery exchanger (36), where the sensible heat of the gas is used to heat the boiler feed water, vaporize crude methanol, among other uses.

The countercurrent heat transfer occurring in the heat recovery exchanger (36) cools the synthesis gas to a temperature of about 38 °C. Condensation and vapor withdrawal are carried out in a conventional separation vessel. The synthesis gas cooled and dehydrated for the production of methanol is compressed by a compressor (38) at a pressure of about 6.2 MPa to 10.3 MPa.

After compression, the synthesis gas is mixed with the recycle of unreacted gases and is heated by heat exchange with the effluent gases of the methanol synthesis step. Then, the gas is directed to the inlet of the methanol synthesis reactor (42), where the methanol is produced in the presence of a copper catalyst at a temperature of about 210 °C to 270 °C. Since the conversion to methanol is still incomplete, an effluent from the methanol synthesis unit (42) containing methanol and unreacted synthesis gas is send to the cooler (44) to effect the condensation of liquid (crude methanol) which is separated from the gases unreacted. The crude methanol is directed to the methanol purification section (62), where the impurities are removed by distillation.

The unreacted synthesis gas is compressed to compensate for pressure losses in the methanol synthesis unit (42) and then is combined with the fresh gas charge for new passage in the methanol synthesis unit. A part of the unreacted synthesis gas is withdrawn as a purge gas stream, so as to avoid accumulation of methane, nitrogen and other inert substances in the reaction medium of the synthesis reactor. The purge gas is formed by 70% to 90% mol of hydrogen, 1% to 7% mol of CO, 1% to 7% mol of CO_2, 0.5% to 1% mol of CH_4, 0.5% a 5% mol of methanol and 0% to 6% mol of N_2. The hydrogen in the purge gas stream is separated and used as feedstock for ammonia synthesis. The purge gas is send to a methanol recovery unit (60), consisting of a water wash column. The methanol is then removed from the purge gas and returned to the purification step.

The effluent gas from the methanol recovery unit (60) is directed to a carbon dioxide removal unit (66), consisting of an absorption column employing an absorbent such as monoethanolamine. An acid gas removal column (CO_2) regenerates the used amine. The effluent gas from the absorption column of the carbon dioxide removal unit (66) is cooled in a condenser by thermal exchange with a coolant at a temperature of the order of 10°C to remove water by condensation. A molecular sieve bed is typically used to absorb CO_2 and residual H_2O still present in gas and complete the treatment. The dehydrated gas is cooled in a cold box type heat exchanger to bring the temperature down to about -180°C. Thereafter, the cold gas is fed into a nitrogen scrubbing unit (72) to remove carbon monoxide and other residual components inert or detrimental to the ammonia synthesis catalyst.

The nitrogen wash unit (72) comprises a cryogenic fractionation tower operating at a mean temperature of -184°C, where liquid nitrogen of purity greater than 99.5% is used to absorb CO and CH_4 residual from gas. The nitrogen is produced in the air separation unit (26) and is supplied to the process at a rate sufficient to produce a synthesis gas with H_2/N_2 ratio suitable for ammonia synthesis (3:1). The H_2-N_2 mixture is then compressed to the pressure suitable for the operation of the ammonia synthesis reactor (80), combined with the recycle gas from the reactor outlet. The mixture is heated by heat transfer with the hot gases effluent from the ammonia synthesis reactor and then feeds the reactor so that in the presence of an iron catalyst the ammonia is produced. The ammonia synthesis reactor is operated at a temperature of about 230 °C to 480 °C and at a pressure of about 8.3 MPa to 17.2 MPa.

Hot effluent gas exiting the ammonia synthesis unit comprising ammonia in the vapor phase and unreacted gases is conducted through heat exchangers, for heat recovery such as a steam super-heater, steam boiler and exchanger to heat the gas of the reactor. The effluent gas from the reactor is further cooled to allow condensation of the ammonia vapor and separation of the unreacted gas in the refrigeration unit (82). The recycle gas separated from the liquid ammonia is compressed to compensate for the pressure losses and combined with the fresh charge of the unit for new passage through the ammonia synthesis reactor (80). The liquid ammonia is recovered and sent to storage.

The air separation plant (26) utilizes conventional equipment and techniques, such as liquefaction of air, followed by cryogenic distillation, to produce gaseous oxygen, gaseous nitrogen and liquid argon.

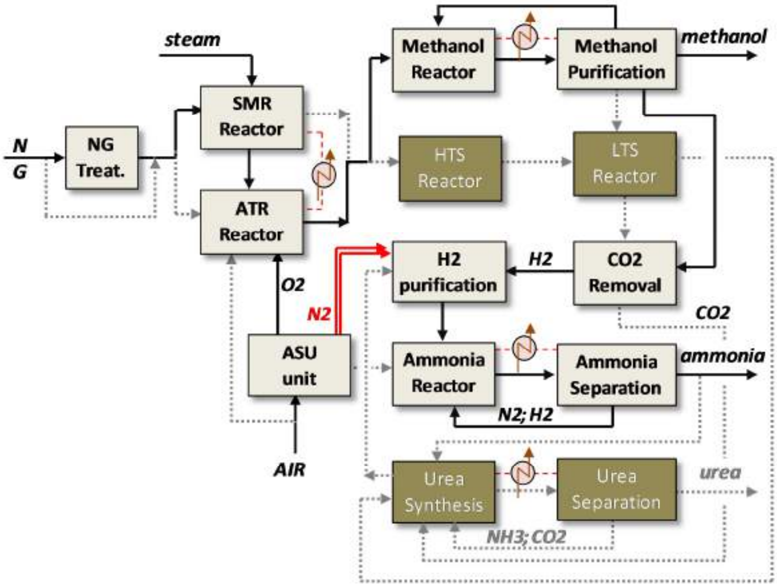
Ammonia production can be increased when the carbon monoxide contained in the purge gas is catalytically reacted with steam in a shift (WGS) reaction. After methanol recovery by washing (60), the purge gas is mixed with steam in a proportion of about 2 to 3 moles of steam per mole of carbon monoxide and then, the gas is heated to a temperature of the order of 210 °C. After, the gas is conducted to a shift converter (92). In the presence of a catalyst, carbon monoxide is converted to carbon dioxide and hydrogen, which is used for ammonia synthesis. The hot effluent from the shift converter reactor (92) is send to heat recovery unit (94) to cool the purge gas prior to the removal of carbon dioxide.

As main features, the process described here utilizes a higher reforming stage operating pressure and this reduces the energy expenditure in the compression required for methanol synthesis. On the other hand, the secondary reformer uses oxygen instead of air to eliminate the accumulation of inert nitrogen in the methanol synthesis circuit. Reduction of inert such as nitrogen or methane into the synthesis gas for methanol production increases conversion of the methanol reactor and reduces compression costs. Additional benefits of the use of oxygen in the secondary reformer are the increase in the overall conversion rate of the reform (hence lower inert methane content in the methanol synthesis circuit) and use of lower catalyst volumes in the reforming reactor. These process innovations result in significant energy and capital savings.

The nitrogen wash unit replaces the shift units (conversion from CO to CO_2) and the methanization unit. The present integrated process has the flexibility to adjust methanol and ammonia production to the needs of the market. For example, the recycle gas stream of the methanol synthesis can be reduced and the purge gas can be increased correspondingly to reduce the rate of methanol production and increase the rate of ammonia production.

Figure 23 shows the superstructure simplified to this patent. ATR is followed by SMS reactor, which follows to methanol, and then to CO_2 removal, H_2 purification and ammonia synthesis and separation. ASU unit separate air, which send O_2 to ATR and N_2 to ammonia synthesis.

Figure 23- Superstructure of patent US 1993/5180570-A.



Source: The Author, 2017.

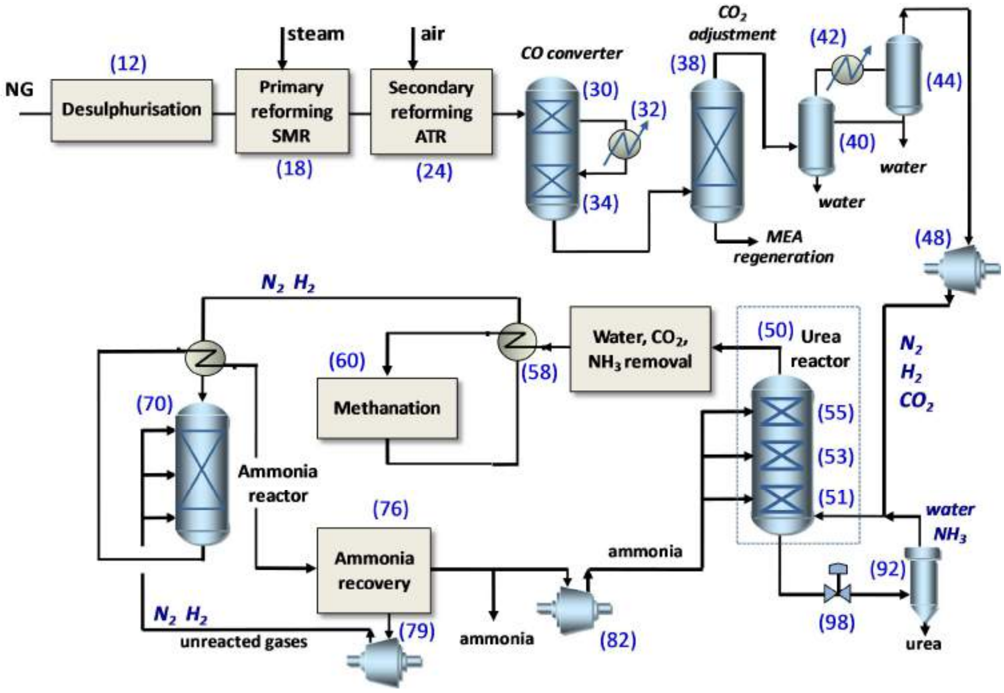
2.3.7 Patent US 1993/4869887-A: Integrated ammonia-urea process (Dijk, 1989)

The process described in patent US 1993/4869887-A, attributed to inventor Christiaan P. Van Dijk, describes an integrated process for the production of ammonia and urea in the same place. More specifically, the invention provides a process for producing urea through the reaction of carbon dioxide and ammonia conducted in a reactor in the presence of synthesis gas, which is the most outstanding feature of this invention.

The described urea reactor has a condensation section, a reaction section with more than one stage and a gas withdrawal section. The crude synthesis gas containing carbon dioxide is introduced into the removal section of the urea reactor at a pressure in the range of 13.79 MPa to 24.13 MPa. The effluent withdrawn from the stripping section is comprised by the synthesis gas, carbon dioxide and ammonia and is introduced into the reaction section of the reactor. Three steps are used in the reaction section. At each step a stream of hot liquid ammonia is introduced. In the process described, the proportions of ammonia in carbon dioxide are of the order of 6:1, while the more conventional process of producing urea has a ratio of the order of 4:1 or less.

The significant and practical distinctions of the present invention are that the operating conditions of the ammonia and urea plants are basically the same and very close to the conditions which minimize the operational costs of the complex. A second advantage of the described process is that it does not require carbamate pumps, which are the main source of corrosion and problems causing the shutdown of the urea production plant. Figure 24 shows a schematic of the patented process.

Figure 24 – Block diagram of the conceptual design of the patent US 4869887-A.



Source: Based on patent US 4869887-A.

A hydrocarbon feed, preferably natural gas, is introduced into a desulfurization vessel (12), where any sulfur compound present is removed from the gas. The desulphurized gas is mixed with steam and sent to a primary reformer (18) containing reforming catalyst. In the primary reformer, methane and steam are heated to temperatures that cause catalytic conversion to form hydrogen, carbon monoxide, and carbon dioxide. The reformed gas stream is send to a secondary reformer (24), also containing reforming catalyst. In the secondary reformer a stream of air is injected. Oxygen burns the unreacted residual methane in the primary reactor, increasing the temperature of the hydrocarbon and vapor mixture to form more hydrogen, carbon monoxide, and carbon dioxide.

The reformed gas is send to the CO conversion reactors. Most of the carbon monoxide is converted to carbon dioxide in two distinct phases. In a first bed of catalyst (30), conversion takes place at high temperature. Thereafter, the gases are cooled in the heat exchanger (32) before being introduced into a second bed of CO conversion catalyst (34).

In a conventional ammonia plant, gases from CO conversion reactors, consisting of hydrogen, nitrogen, carbon dioxide, argon, and small amounts of carbon monoxide and methane are generally introduced into a carbon dioxide removal column (38), which removes completely the CO_2 from the remaining gases. In the process described herein, it is very important to note that the CO_2 withdrawal step is only necessary if there is excess of CO2 in the reformed gas stream. In this case, only the excess part of CO_2 will be removed. The removal of CO_2 is done by extractions with chemical solvents, such as ethanolamine. It should also be emphasized that this removal step is a low-cost, low-power operation. After adjusting the CO_2 content, the dehydration of the gas occurs, for the elimination of traces of water, through the passage of the gas in a countercurrent condenser (40). The gas is again cooled and sent to a phase separator vessel, where the liquid formed is separated from the gas stream. The gas stream from the separator is introduced into a compressor (48). The compressed gas is composed by synthesis gas, nitrogen and carbon dioxide, besides very small amounts of carbon monoxide, argon and methane. The molar ratio of hydrogen and nitrogen present in the gas is such that there are approximately three moles of hydrogen per mol of nitrogen.

After the compression step, the synthesis gas and the carbon dioxide are injected into the urea reactor (50). In the process described herein, the operating pressure of the urea reactor is in the range of 13.79 MPa and 24.13 MPa. This pressure level is the optimum range for both ammonia and urea production. The urea reactor is comprised of a withdrawal section (51) at the bottom, a condensation section (55) at the top and a reaction section (53) in the middle of the reactor. Synthesis gas and carbon dioxide are introduced into the withdrawal section (51) of the reactor.

The reaction section (53) consists of three or more equilibrium stages (each stage constitutes a reactor tray). The temperature of the first stage of the reaction section is close to 160 °C, so as to allow the urea formation to proceed at acceptable rates. The reaction of 2 moles of ammonia with 1 mol of carbon dioxide is a heterogeneous and highly exothermic reaction (formation of ammonia carbamate).

On the other hand, the urea formation reaction (carbamate dehydration) is a slow endothermic equilibrium reaction that proceeds in the liquid phase where the carbamate is in equilibrium with urea and water. It should be noted that the reactions of formation of carbamate and urea occur to a lesser or greater degree, in all three stages of the reaction section. The heat generated by the ammonia carbamate formation reaction serves to volatilize the ammonia and water, both present in the liquid phase of the reaction medium. In the condensation section of the urea reactor (55), water, carbon dioxide and ammonia are condensed so as to allow their separation from the gas stream. After carbon dioxide removal, the gas stream contains ammonia and water, which is condensed. The water can be removed from the process in the condensation section by distillation, thus separating from the ammonia.

The process can be performed with total or partial reflux (30% and 90% of the total flow). Removal of the water from the reaction medium in the condensation section allows a substantial increase in the conversion of carbamate. As a significant advantage, it reduces the thermal load consumption in the stripping section. With the removal of carbon dioxide, ammonia and substantial amounts of water, the synthesis gas stream is produced which is passed through a heat exchanger (58) and, in turn, feeds the methanator reactor (60).

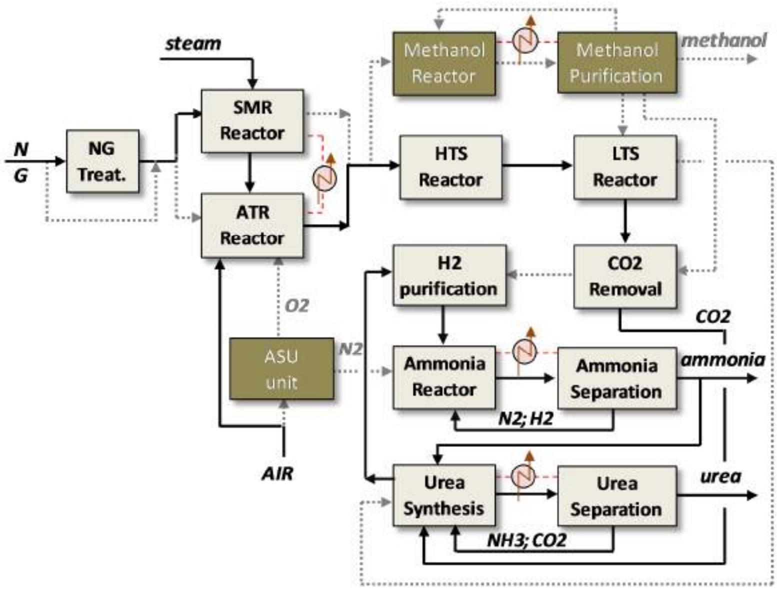
The methanation step converts the small amounts of carbon monoxide and carbon dioxide present in the gas stream into methane through hydrogenation reactions. This is necessary, since carbon monoxide and carbon dioxide are considered poisons of the ammonia catalyst, while methane is simply an inert. The synthesis gas leaving the methanator exchanges heat with the inlet gas through the heat exchanger (58). The gas then enters a condensation zone (63) which comprises a series of heat exchangers to cool the gas and remove condensates (mainly ammonia and water) to obtain a suitably dry synthesis gas. This dry gas exchanges heat in the exchanger (66) and is injected into the ammonia reactor (70).

In the ammonia synthesis reactor, hydrogen and nitrogen react to form ammonia. The ammonia reactor effluent exchanges heat with the reactor inlet gas in the heat exchanger (66) and then moves to the ammonia recovery section (76) where, by means of cooling, the ammonia is condensed at the temperature of about -10 °C. The unreacted gases (hydrogen, nitrogen and argon) are again compressed in the compressor (79) to be recycled to the ammonia reactor (70). Most of the produced ammonia is compressed in the compressor (82) and is injected into the urea reactor (50).

The treatment of liquid urea can be carried out conventionally to obtain the urea as a solid in both pellets and flakes. The stream is generally passed through a pressure relief valve (98) and separated into a separation vessel (92). The incondensable gases, composed by water and ammonia, can be recompressed for reintroduction into the urea reactor (50). It is noted that the only compression required in the process of the present invention is an ammonia or ammonia-water stream, thereby eliminating the carbamate pumps. In comparison with conventional urea production processes, the process described herein utilizes a large excess of ammonia which is injected into the urea reactor. Most of this ammonia is in the gaseous phase.

Figure 25 shows the simplified superstructure to this patent. Again, in terms of material integration, it is similar to previous patents, where CO_2 unit is fed with syngas, and CO_2 goes to urea synthesis, while H_2 rich stream is send to ammonia synthesis. There is a recycle from urea synthesis to ammonia synthesis.

Figure 25 - Superstructure of patent US 1993/4869887-A.

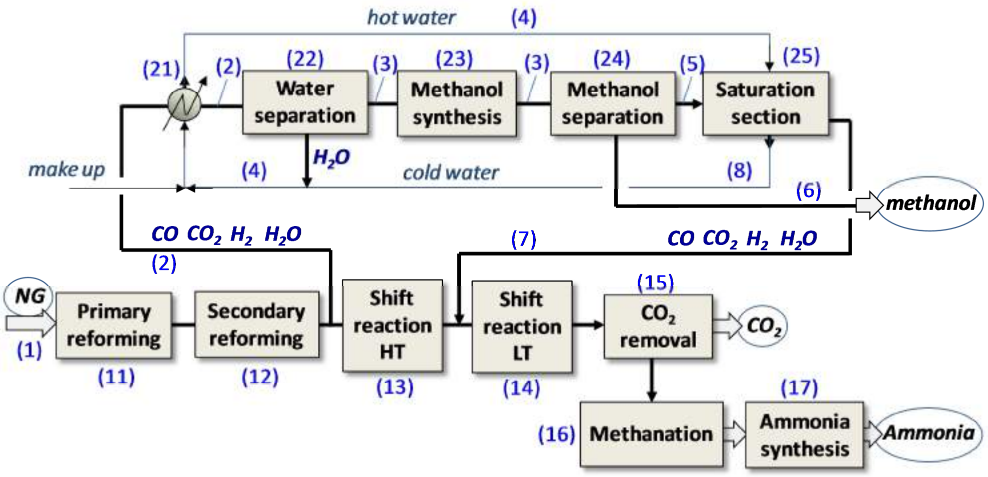


Source: The Author, 2017.

2.3.8 Patent US 2001/6333014-B1: Process for ammonia and methanol coproduction (Filippi, 2001)

The process presented in patent U.S. 2001/6333014-B1, assigned to inventor Ermanno Filippi, has the original assignee the Methanol Casale group. This patent relates to a process for ammonia and methanol coproduction in a plant comprising a secondary reformer section, a high-temperature CO conversion section and a low-temperature CO conversion section. Such equipment are arranged in series, and an ammonia synthesis section, is distinguished by the fact that the unreacted gas flow coming from a methanol synthesis, before being fed to the low-temperature CO conversion section, is advantageously saturated with a liquid flow comprising H_2O appropriately heated by indirect heat exchange with a gaseous flow coming from the secondary reformer section. Figure 26 presents a simplified block diagram about the process.

Figure 26 – Block diagram of the conceptual design of the patent US 6333014-B1.



Source: Based on patent US 6333014-B1, 2001.

In Figure 26, blocks 11 through 17 respectively indicate a primary reformer section, a secondary reformer section, a high temperature CO conversion section, a low temperature CO conversion section, a CO_2 separation section, a section of methanation and an ammonia synthesis section. At the entrance to the primary reformer section indicated by block 11, the gas flow line (line 1) is composed substantially of methane or natural gas, while at the outlet of the ammonia synthesis section, represented by block 17, the flow is composed mainly of ammonia formed in the synthesis reactor. The operational conditions of the ammonia production process, as well as the type of reactions that occur during the passage of the gaseous flow through the various sections, are conventional of a high pressure and temperature ammonia plant.

Blocks 21-25 indicate, respectively, a cooling section, a water separation section, a methanol synthesis section, a methanol separation section and a water saturation section of unreacted gases. The flow line (2) represents a gaseous stream from the secondary reformer section (block 12) consisting of CO, CO_2, H_2 and water. This flow crosses the cooling section (block 21), where most of the vapor contained in the stream condenses and feeds the H_2O separation section (block 22). The outgoing gas stream from block 22 is composed primarily of CO, CO_2 and H_2. This flow then passes only once through the methanol synthesis section (block 23), where a part of the reactants contained in the gaseous stream reacts to produce methanol and is fed into separation section indicated by block 24, separating the unreacted gas stream composed of CO, CO_2 and H_2 from methanol.

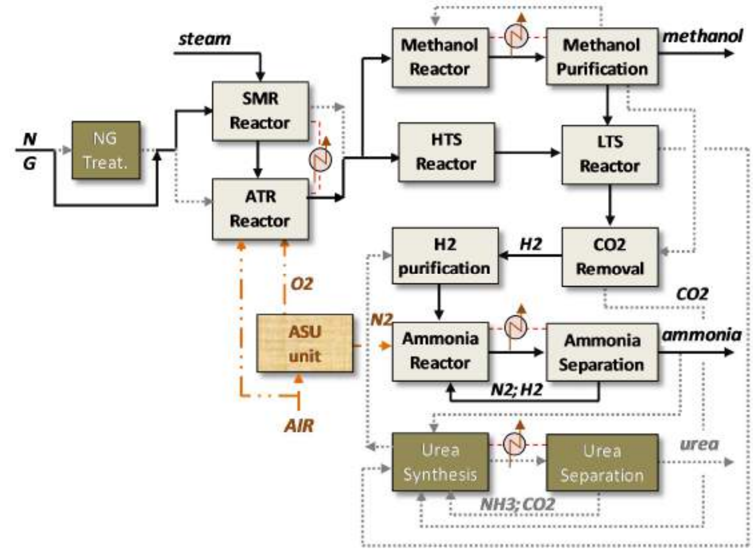
The flow line (6) indicates the methanol flow produced, while the flow line (5) represents the outgoing unreacted gaseous stream from the synthesis reactor, which is fed to the water saturation section (block 25). The block 25 is also fed by the flow line (line 4), which is composed of H_2O which has been preheated in the block (21) by indirect heat exchange with the gaseous stream from the secondary reforming section. The flow line (7) exits the water saturation section (block 25). This gaseous stream is composed of CO, CO_2, H_2 and H_2O and returns to the main ammonia synthesis stream upstream of the low temperature CO conversion section indicated by block 14. From block 25, there is also a flow line (8), composed of liquid water, which is returned to join the flow line (4), upstream of the cooling section (block 21).

A gaseous stream composed of CO, CO_2, H_2 and H_2O is withdrawn from the secondary reforming section (block 12) and is fed into the cooling section (block 21). In the water separation section (block 22) the condensed water in the heat exchanger (block 21) is withdrawn from the flow of gases feeding the methanol synthesis reactor. Then, a gaseous stream substantially free of H_2O is then sent to the methanol synthesis section (block 23) where it reacts to be converted to methanol. The gaseous stream from the methanol synthesis section is then sent to the methanol separation section (block 24) for the separation of the methanol produced. The unreacted gas stream (5) from block 24 is composed of CO, CO_2 and H_2. This flow feeds the water saturation section (block 25). After saturation, a stream composed of CO, CO_2, H_2 and H_2O (7) is returned to the low pressure CO conversion section (block 14).

The water stream (4) is heated by indirect heat exchange with the gaseous stream from the secondary reforming section (2) in the exchanger (block 21). This thermal exchange represents one of the main advantages of this patent, which is the high heat recovery rate of the process. By operating in this manner, at least some of the heat from the gaseous stream from the secondary reformer is recovered to aid water saturation and heating of the gaseous stream to be transported to the low temperature CO conversion section. The water stream feeding into the saturation section (block 25) is preheated to a temperature between 150 °C and 280 °C. The water stream from the block 22 is pumped to a pressure between 1.96 MPa and 9.8 MPa and then returned to the process upstream of the exchanger (block 21).It is possible to reuse the H_2O contained in the gaseous stream from the secondary reforming section, suitably condensed and separated upstream of the methanol synthesis section.

The advantage of this invention is that the single passage through the methanol synthesis reactor allows the elimination of all of the equipment associated with the recycling to the synthesis reactor of at least part of the unreacted gaseous reactants, substantially reducing investment costs and energy consumption. Figure 27 shows the superstructure simplified to this patent. Urea synthesis is not performed; besides, ASU unit is not specified. SMR and ATR are sequential steps, and methanol is fed by outlet stream of ATR. LTS is fed by streams from methanol purification.

Figure 27 - Superstructure of patent US 2001/6333014-B1.

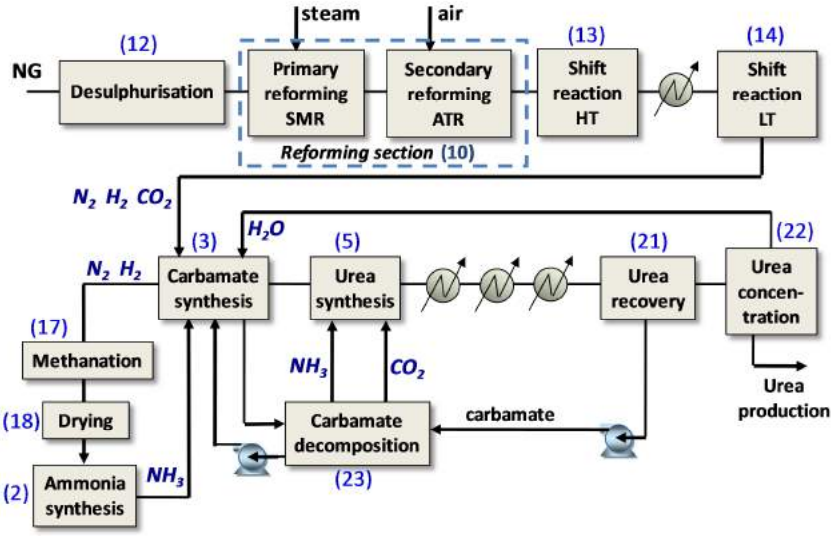


Source: The Author, 2017.

2.3.9 Patent US 2001/6231827-B1: Process for combined production of ammonia and urea (Pagani; Zardi, 2001)

The process presented in patent U.S. 2001/6231827- B1, assigned to inventors Giorgio Pagani and Umberto Zardi, has the original assignee the Urea Casale group. This patent relates to a process for ammonia and urea combined production in a complex composed by: an ammonia synthesis reactor (2); urea synthesis reactor (5); urea recovery section (21); urea concentration section; carbamate synthesis section (3); carbamate decomposition section (23); and a syngas generation section. The syngas section is composed of natural gas treatment for desulfurization, a steam reforming reactor, a autothermal reforming reactor, CO conversion reactors and CO_2 removal section. Figure 28 presents a simplified block diagram about the process.

Figure 28 – Block diagram of the conceptual design of the patent US 6231827-B1.



Source: Based on patent US 6231827-B1, 2001.

The process stands out for the fact of submitting at least a part of a flow composed by carbamate in aqueous solution coming from the urea recovery section (21) to a partial decomposition treatment. To obtain a flow composed by ammonia and carbon dioxide in vapor phase and a flow composed by diluted carbamate in aqueous solution, which is fed together with a gaseous flow comprising hydrogen, nitrogen and carbon dioxide and a flow comprising ammonia coming from the ammonia synthesis reactor (2) to a carbamate synthesis section (3). In this, ammonia and carbon dioxide react to obtain carbamate in aqueous solution and a gas flow composed by hydrogen and nitrogen. The aqueous solution of carbamate is then sent to the urea synthesis reactor (5), while the gas flow composed by hydrogen and nitrogen is send to the ammonia synthesis reactor (2).

The urea synthesis section is formed by a reactor (5) and a high pressure separator (17.64 MPa) for the partial decomposition of carbamate and the separation of the free ammonia in aqueous solution. The process for the combined production of ammonia and urea according to the present invention provides a yield of between 62% and 70% in the synthesis reactor of urea (5). For the proper operation of the urea synthesis reactor, the reagent feed must comply with the molar ratio of NH_3/CO_2 of 3.8 and molar ratio of H_2O/CO_2 of 0.8. The expected conversion yield is 64% at a pressure of 17.64 MPa and a temperature of 190 °C. The part of the plant for the production of urea is of the total recycle type, that is, with the recycling of reagents into the synthesis reactor (5). However, the present invention can also be implemented in plants which operate with partial or "one-way" type of recycle type urea synthesis without reactant recycling.

The carbamate synthesis section is fed by a gas stream composed of hydrogen, nitrogen and carbon dioxide, a stream composed of ammonia, a stream composed of water and a stream comprising carbamate diluted solution. The gas stream comprising hydrogen, nitrogen and carbon dioxide comes from a hydrocarbon vapor reforming section, composed by a natural gas desulfurization section (12), a primary reforming reactor, a secondary reforming reactor and CO high (13) and low temperature (14) converters. After treatment, natural gas and steam are fed into the reforming section (10). Natural gas and steam enter the primary reforming reactor, resulting in the formation of hydrogen, carbon monoxide, and carbon dioxide. Thereafter, this flow is fed into the secondary reformer reactor, which is also fed with atmospheric air.

After the reforming step, the reacted gases are sent to a high temperature CO conversion section (13) and a low temperature CO conversion section (14) for the conversion of carbon monoxide to carbon dioxide. The gas stream composed of hydrogen, nitrogen and carbon dioxide is fed into the carbamate synthesis section (3). This section is fed the ammonia flow into the vapor phase from the ammonia synthesis reactor (2). Ammonia reacts instantaneously with the carbon dioxide present in section 3, facilitating the synthesis of carbamate. A stream of water from the urea concentration section (22) is fed into the carbamate synthesis section (3) to stimulate the uptake of carbon dioxide and its immediate reaction with ammonia. A flow of dilute carbamate solution from the carbamate decomposition section (23) is also injected into the carbamate synthesis section (3), aiming at increasing the conversion of the product. About 30% to 40% of the total amount of water fed into the carbamate synthesis section comes from the urea concentration section (22) and about 60% to 70% comes from the decomposition section of carbamate (23).

Carbamate synthesis section (3) produces a flow of carbamate solution to the urea synthesis reactor (5) and a flow of hydrogen and nitrogen to the ammonia synthesis reactor (2), after methanation and drying steps. A flow of carbamate solution exiting the urea recovery section is pumped to the carbamate decomposition section (23). An anhydrous flow of ammonia and vapor phase carbon dioxide is obtained which is recycled to the urea synthesis reactor (5) and a very dilute stream of carbamate solution, which is recycled to the synthesis section of carbamate (3).

Part of the carbamate stream formed in section (3) is subjected to a partial decomposition treatment, resulting in the production of vapor phase ammonia and carbon dioxide flow and a stream composed by carbamate diluted solution. The flow composed by ammonia and vapor phase carbon dioxide is fed into the urea synthesis reactor (5), while the flow of dilute carbamate solution returns to the carbamate synthesis reactor, along with a flow of hydrogen, nitrogen and carbon dioxide and a flow of ammonia from the ammonia synthesis reactor (2). At the output of the carbamate synthesis reactor, a flow of carbamate solution is then fed into the urea synthesis reactor (5), while the gas stream composed of hydrogen and nitrogen is fed into the ammonia synthesis reactor (2).

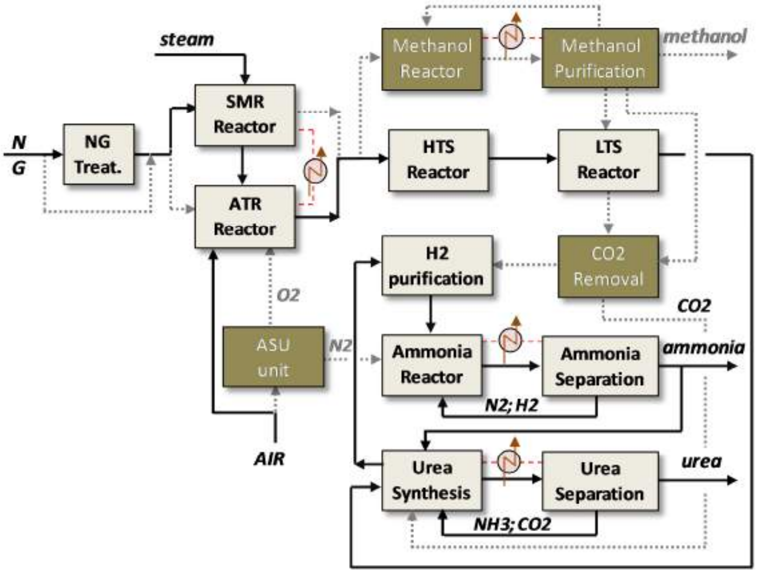
An advantage of the described process in this invention is the possibility of keeping at low levels the amount of water sent to the urea synthesis reactor (5), through recycling of water to the carbamate synthesis section (3), thus allowing simple and effective way, to obtain high yields of urea conversion. On the other hand, the carbamate partial decomposition step allows high process flexibility, since it allows operating even with large amounts of water in the carbamate synthesis section (3), without this adversely affecting the H_2O/CO_2 molar ratio in the urea synthesis reactor (5) and, therefore, the conversion yield. The described process enables the H_2O/CO_2

molar ratio to be further reduced in the urea synthesis reactor (5), thereby increasing the conversion yield, thus by feeding a part of the carbamate solution flow from section 3 directly in the decomposition of carbamate (23). Another striking feature of this process is that the carbamate synthesis section (3) is formed by three chambers separated by two intermediate film absorbers. Chambers and film absorbers are comprised within a single vertical tubular device. The first chamber is located at the lower end of section 3. The second chamber is located in the central part and the third chamber is located at the upper end of the same section. The first film absorber is located between the first and second chambers and the second film absorber is located between the second and third chambers. The optimum pressure and temperature values within the carbamate synthesis section (3) are between 13.72 MPa and 19.60 MPa and between 110 °C and 150 °C, respectively.

Purge gas rich in inert substances such as nitrogen and methane exiting the ammonia synthesis reactor (2) are separated from the reacted gas and washed in a washing section with the water flow fed into the carbamate synthesis section (3). Once washed, the exhaust gas is send to a conventional recovery plant (not shown). The washing allows to recover most of the entrained ammonia by the purge gas, which is then recycled to the carbamate synthesis section (3).

The project further provides for the thermal exchange between the gas stream from the reforming section (10) to provide the heat necessary for the decomposition of the carbamate, without the need to resort to external heat sources, which therefore results in energy savings and operating costs. Figure 29 shows the superstructure simplified to this patent. HTS and LTS are fed with syngas stream, which feeds Urea Synthesis. This unit generates streams that are sending to H_2 purification and posteriorly to ammonia synthesis.

Figure 29 - Superstructure of patent US 2001/6231827-B1.



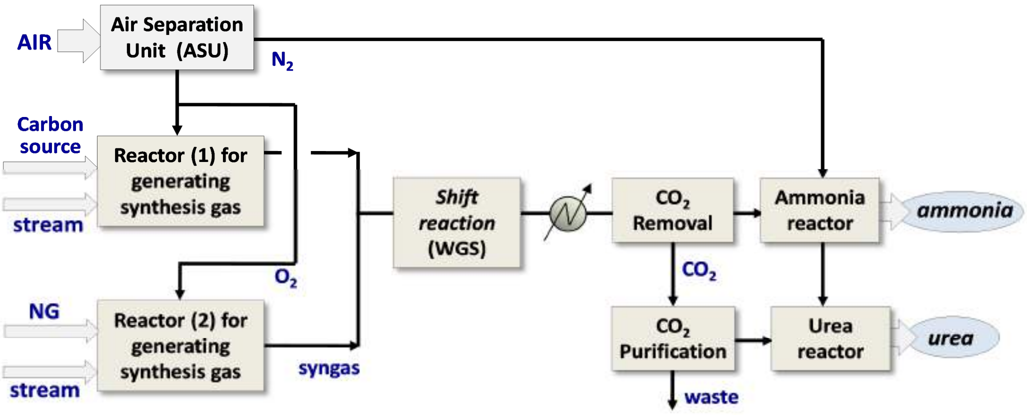
Source: The Author, 2017.

2.3.10 Patent US 2002/6448441-B1: Gasification process for ammonia/urea production (Wing-Chiu; Reich, 2002)

This process describes a process of generating synthesis gas from natural gas for ammonia and urea, in which two parallel gasifiers are used. This configuration seeks to optimize the H_2/CO_2 ratio in the synthesis gas of the combined product, thus maximizing the ammonia and urea production. This patent U.S. 2002/6448441-B1 is assigned to the inventors Francis Fong Wing-Chiu and Erwin A. Reich.

As a distinguishing feature of this patent, the use of two reactors in parallel, where one reactor is fueled with natural gas and the other is fueled with an alternative source of carbon (solid or liquid). In this process, it is planned to produce ammonia surplus to supply the market and the composition of the synthesis gas generated in this process can be flexibilized according to the desired product profile. Figure 30 shows a schematic of the patented process.

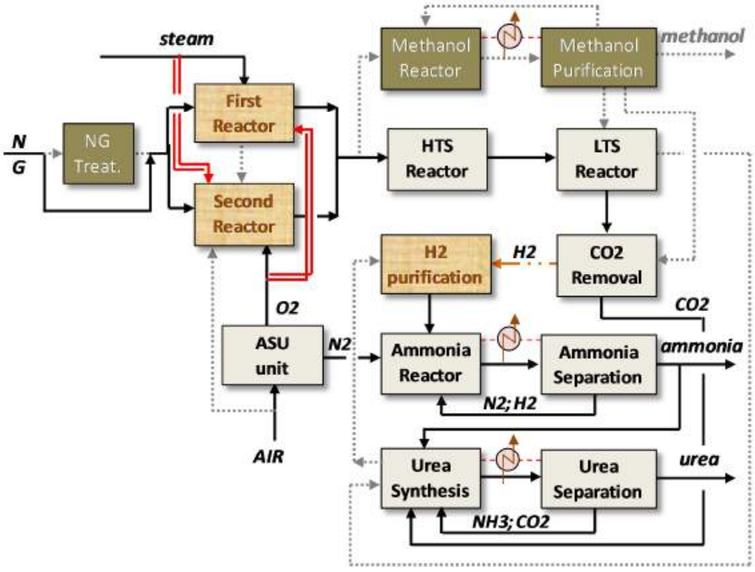
Figure 30 – Block diagram of the conceptual design of the patent US 6448441-B1.



Source: Based on patent US 6448441-B1, 2002.

Figure 31 shows the superstructure simplified to this patent. Two syngas reactors are used. In terms of material integration, it is usual to previous patents described, where CO_2 unit is fed with syngas, and CO_2 goes to urea synthesis, while H_2 rich stream is send to ammonia synthesis.

Figure 31 - Superstructure of patent US 2002/6448441-B1.



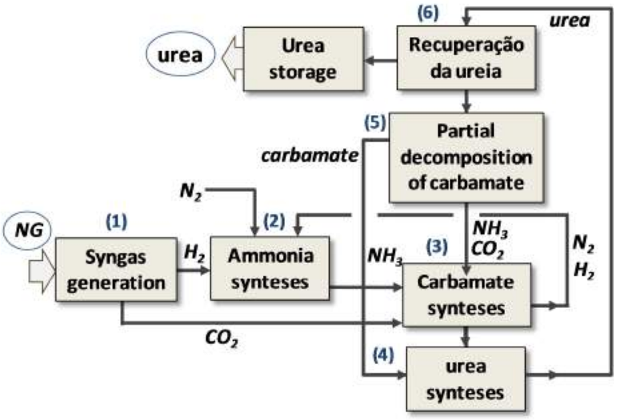
Source: The Author, 2017.

2.3.11 Patent US 2004/6696026-B2: Process for combined production of ammonia and urea (Pagani; Zardi, 2004)

The process presented in patent U.S. 2004/6696026-B2, assigned to inventors Giorgio Pagani and Umberto Zardi, having the original assignee the Urea Casale group.

It relates to a process for the combined production of ammonia and urea through the synthesis of carbamate of ammonium in a plant comprising an ammonia synthesis reactor, a urea synthesis reactor and a urea recovery section, forming a unique process that integrates the ammonia production process with the urea production process. It should be noted that this technology had already been proposed in the patent US 2001/6231827-B1, by the same authors. The differences between the patents are some improvements added in this latest version. Figure 32 shows a schematic of the process diagram.

Figure 32 – Block diagram of the conceptual design of the patent US 6696026-B2.



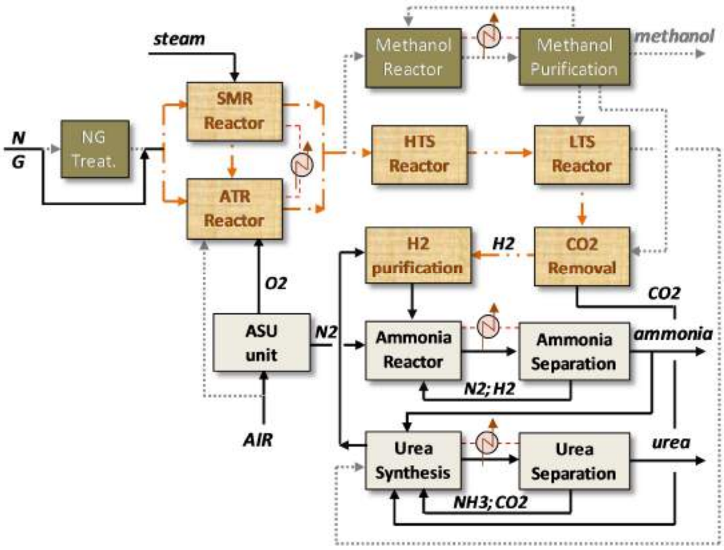
Source: Based on patent US 6696026-B2, 2004.

According to this technology, natural gas is supplied as feedstock for a synthesis gas generation unit, through steam reforming of methane. The synthesis gas is purified and the hydrogen generated is separated, serving to produce ammonia along with a stream of nitrogen. Urea is produced by combining the ammonia produced with the separated carbon dioxide in the preview step of purifying the synthesis gas. Still according to the inventors, the urea conversion yield is higher and the operating and investment costs lower than the previous processes. This improvement of the process is obtained by subjecting part of the carbamate from the urea recovery section to a partial decomposition step, obtaining ammonia and carbon dioxide in the vapor phase and an aqueous solution of carbamate. The processes of this type allow to remarkably reducing the CO_2 withdrawal section present in the synthesis gas unit, besides elimination the ammonia separation section produced in the corresponding synthesis reactor and also the carbon dioxide compression section.

Energy and investment costs resulting from a single integrated system are substantially lower than those resulting from two distinct processes of ammonia and urea production. Such advantages of the integrated process are particularly enhanced in cases where all or most of the ammonia produced is converted to urea by reacting it with the carbon dioxide obtained as a by-product in the purification of the synthesis gas.

The process presents a partial decomposition of carbamate section (5), which comes from the urea recovery section (6). This section decomposes the carbamate and separates the phases formed, obtaining a flow of ammonia and carbon dioxide in the vapor phase and ammonium carbamate diluted in aqueous solution. The carbamate solution is fed together with a residual gas consisting of hydrogen, nitrogen and carbon dioxide obtained by hydrocarbon vapor reforming process (1) and an ammonia flow from the synthesis reactor of the product (2) to a synthesis section of ammonium carbamate (3), where ammonia and carbon dioxide react to form carbamate in aqueous solution. The vapor flow consisting by nitrogen and unreacted hydrogen returns to the ammonia converter. The aqueous solution of carbamate is then sent to the urea synthesis reactor (4), where, by dehydration reaction of the carbamate, the urea is formed. It is worth mentioning that this process has the objective of producing urea as final product. The ammonia produced is considered an intermediate product of the process and is fully utilized for the production of urea. Figure 33 shows the superstructure simplified to this patent. Syngas is send to ammonia synthesis, which follows to urea synthesis.

Figure 33 - Superstructure of patent US 2004/6696026-B2.



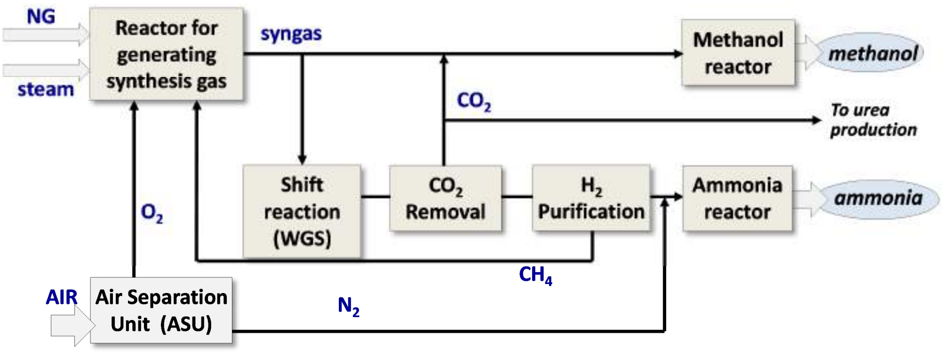
Source: The Author, 2017.

2.3.12 Patent US 2007/0299144-A1: Production of Methanol and Ammonia from Natural Gas (Davey; Wurzel, 2007)

Another patent US 2007/0299144-A1, assigned to the inventors William Davey and Thomas Wurzel describes a method for production of methanol and ammonia from natural gas in a multiphase process. In this process, natural gas, oxygen and water vapor are mixed in a first reactor, in which the natural gas is partially oxidized and additionally catalytically reformed. The gas mixture from the outlet of the first reactor is divided into a stream used for methanol synthesis and another one for the separation of hydrogen. The CO present in the stream destined to hydrogen production is catalytically converted to CO_2 in a water shift conversion (WGS) reactor.

The remaining impurities, such as methane, traces of CO and argon are removed by washing the gas and CO_2 is destined for urea synthesis. The synthesis gas for the production of methanol is converted catalytically into methanol. The required purity of the product is obtained by distillation. Synthesis gas for the production of ammonia is compressed and after, catalytically converted to ammonia in a reactor and then, the ammonia is separated from the unreacted gas mixture by partial condensation. The process described in the patent is for the production of methanol and ammonia, the integration of the complex with a urea synthesis unit is only a contingent alternative. Figure 34 shows a schematic of the patented process.

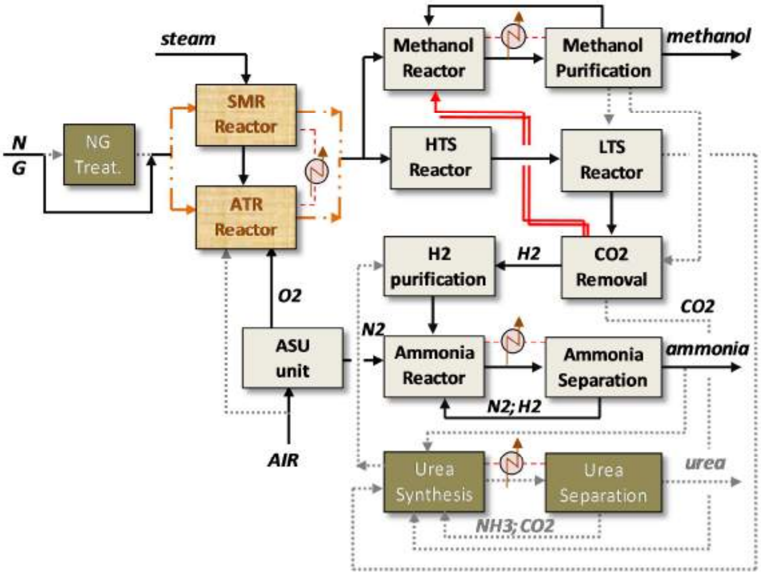
Figure 34 - Block diagram of the conceptual design of the patent US 0299144-A1.



Source: Based on patent US 0299144-A1, 2007.

Figure 35 shows the superstructure simplified to this patent. Neither SMS nor ATR is specified. Methanol is fed with syngas and with a stream that comes from CO_2 removal, which is basic, the main integration of this process.

Figure 35 - Superstructure of patent US 2007/0299144-A1.



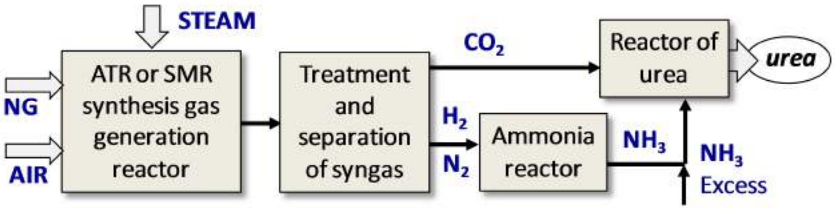
Source: The Author, 2017.

2.3.13 Patent US 2010/7674932 B2: Method for the Production of Urea from Natural Gas (Davey; Wurzel, 2010)

The patent US 2010/7674932 B2, assigned to the inventors William Davey and Thomas Wurzel describes a method for producing urea from natural gas. In this patent, the natural gas is subjected to partial oxidation or autothermal reforming with a gas oxygen-containing in a first step and the synthesis gas resulting, undergoes a second conversion step, now catalytic, for additional H_2 generation.

CO and CH_4 are removed from the syngas in a multi-step purification process. In sequence, the hydrogen is converted to ammonia by reaction with nitrogen. In a next stage of the process, the ammonia is combined in a reactor with CO_2 previously separated in the step of gas purification and totally converted into urea. The main characteristics of this patent are the flexibility of choosing the synthesis gas generation technology, besides the possibility of complementing the ammonia load of the reactor urea with excess ammonia produced in other units. Figure 36 shows a schematic of the patented process.

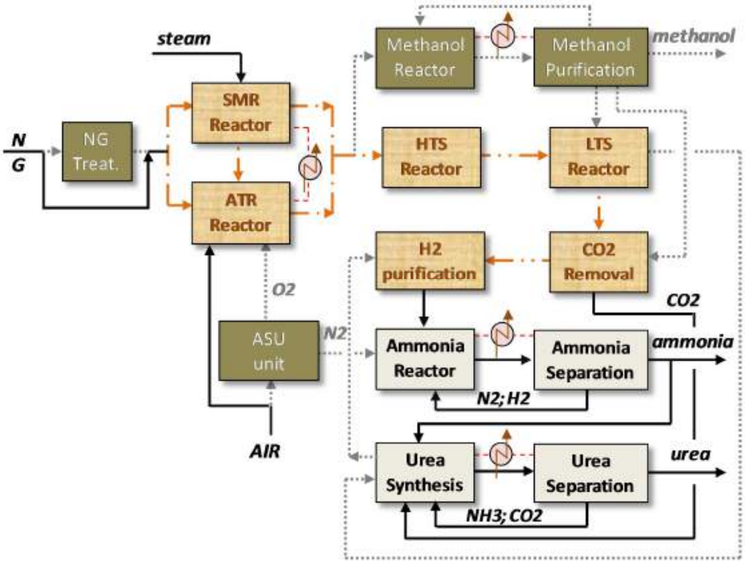
Figure 36 – Block diagram of the conceptual design of the patent US 0207948-A1.



Source: Adapted from patent US 0207948-A1, 2008.

Figure 37 shows the superstructure simplified to this patent. Again, in terms of material integration, it is similar to previous patents, where CO_2 unit is fed with syngas, and CO_2 goes to urea synthesis, while H_2 rich stream is send to ammonia synthesis.

Figure 37 - Superstructure of patent US 2008/0207948-A1.



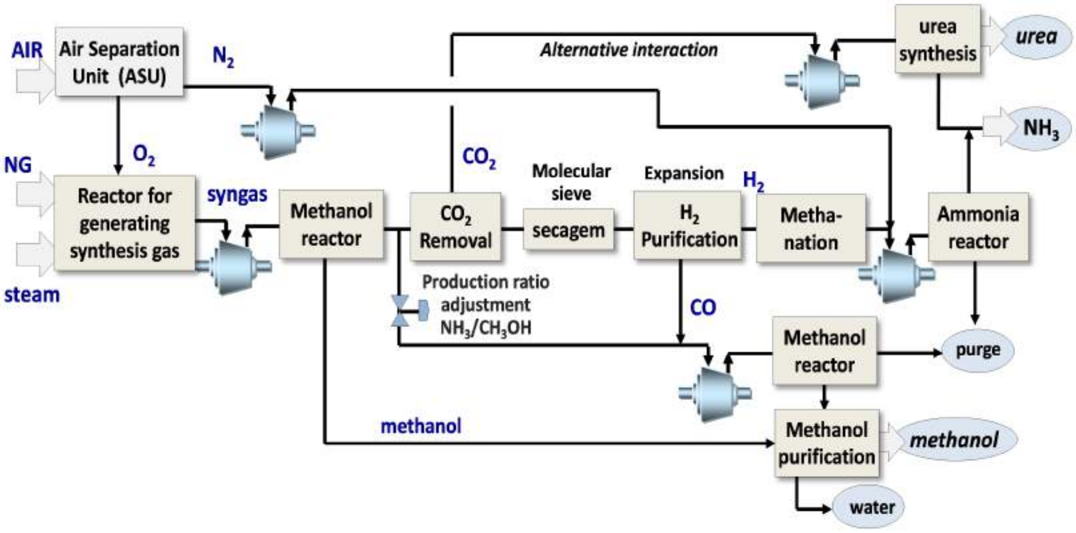
Source: The Author, 2017.

2.3.14 Patent US 2012/0148472-A1: Process for methanol and ammonia coproduction (Ahmed; Bashir, 2012)

The process presented in patent U.S. 2012/0148472-A1, assigned to inventors Ijaz C. Ahmed and Mubarak Bashir, and has as original assignee the Saudi Basic Industries Corporation. This patent describes a process for the of methanol and ammonia in a same site, wherein a synthesis gas consisting essentially of carbon monoxide, carbon dioxide and hydrogen is first made to partially react with a mixture of methanol in only one pass through the reactor. The unreacted synthesis gas is divided into two streams. The first stream is purified and feeds the ammonia synthesis section. The second stream feeds the methanol synthesis reactor and the purification section.

The process allows the production of methanol and ammonia in a single integrated process, from natural gas and air, besides allowing a balanced production of ammonia. The separated carbon dioxide in the purification of the syngas still allows for synergistic gains with the integration of the production of urea in the same site. It is to be noted that the process described in the patent is intended for the production of methanol and ammonia, since the integration of the complex with a urea synthesis unit is only a suggested alternative. Figure 38 shows a schematic of the patented process.

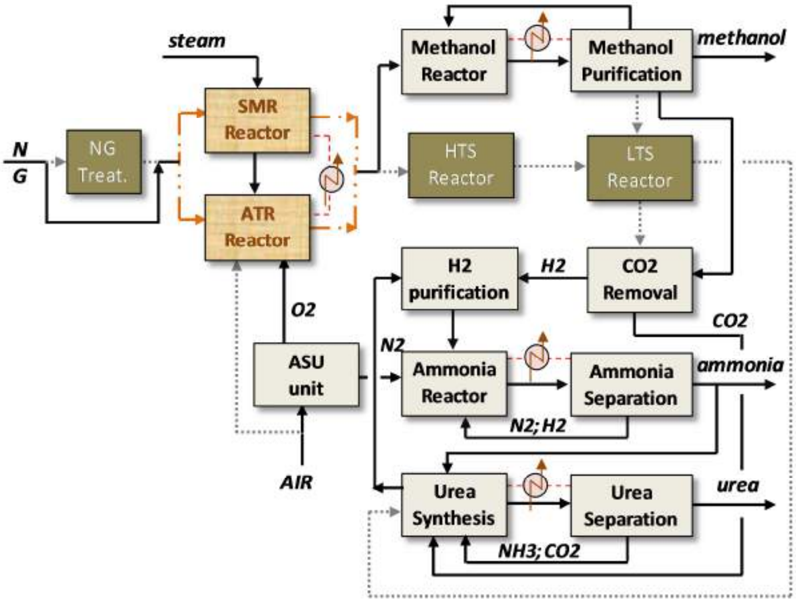
Figure 38 – Block diagram of the conceptual design of the patent US 0148472-A1.



Source: Based on patent US 0148472-A1, 2012.

Figure 39 shows the simplified superstructure to this patent. Neither SMS nor ATR is specified. Methanol is fed with syngas. An outlet stream of methanol feeds a unit of CO_2 removal, which sends CO_2 to Urea unit and H_2 rich system to H_2 purification and posterior ammonia synthesis.

Figure 39 - Superstructure of patent US 0148472-A1, 2012.

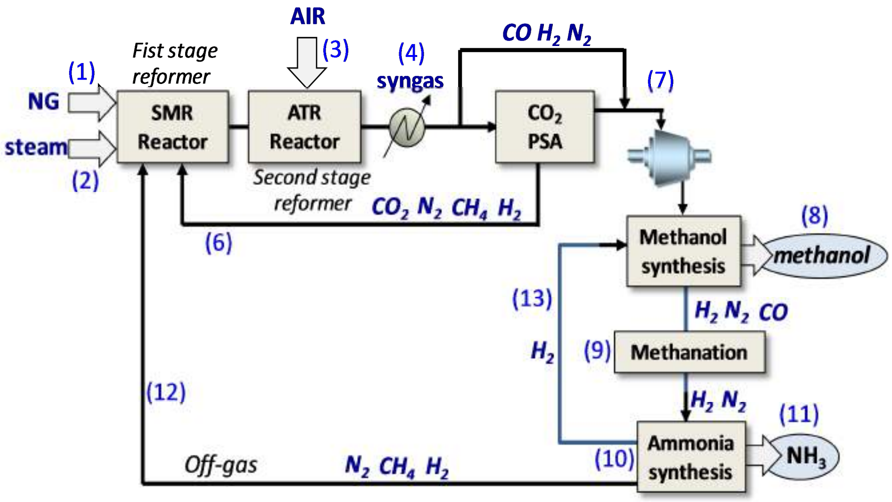


Source: The Author, 2017.

2.3.15 Patent US 2014/8692034-B2: Coproduction of methanol and ammonia (Han, 2014)

The process presented in patent U.S. 2014/8692034-B2, assigned to inventor Pat A. Han, has the original assignee the Haldor Topsoe group. This patent relates to a process for the combined production of ammonia and methanol from a hydrocarbon feed (natural gas - NG or substitute natural gas – SNG) without venting to the atmosphere carbon dioxide captured from the methanol or ammonia synthesis gas and without using expensive air separation units, water gas shift and acid gas wash for removal of carbon. Figure 40 presents a simplified block diagram about the process.

Figure 40– Block diagram of the conceptual design of the patent US 8692034-B2.



Source: Based on US 8692034-B2, 2014.

Current processes for coproduction of methanol and ammonia involve generally parallel processes in which a common reforming section is used to generate a synthesis gas which is split in separate parallel streams, one of which is used for methanol synthesis and the other for ammonia synthesis. The coproduction of methanol and ammonia can also be conducted sequentially or in series, where the synthesis gas produced in the reforming section is first converted to methanol and the unreacted gas containing carbon oxides and hydrogen is subsequently used for ammonia synthesis. Water gas shift and/or carbon dioxide removal steps of the synthesis gas stream are required, thus involving the release of CO_2 to the atmosphere and the investment in highly expensive and complicated units for conducting the shift conversion and carbon dioxide removal.

This invention is concerned with a sequential and once-through (single pass) process for the coproduction of methanol and ammonia without water gas shift and acid gas wash carbon dioxide removal and without air separation unit used in the reforming section of the plant. The great advantage of this described process is that it is able to allow certain flexibility for control of the production ratio between methanol and ammonia. The product ratio between methanol and ammonia is given by the feedstock composition.

According to the inventors, this process is simpler and cheaper than the current processes in terms of both capital costs and operating costs and at the same time allows for a minimum release of carbon dioxide into the atmosphere. The main steps in this process are as follows:

- Synthesis gas generation by hydrocarbons reforming in two stages. The primary reform in a SMR reactor, followed by a second reactor, using the partial oxidation of the residual methane by atmospheric air;
- Division of synthesis gas generated in two streams, a first methanol synthesis gas stream being sent directly to the methanol conversion reactor and a second stream being sent to a pressure swing adsorption stage for retention of part of the CO2 contained in gas stream;
- Conversion of synthesis gas into methanol in a single passage through the reactor;
  Treatment of the synthesis gas used for the production of ammonia without the use of a water-gas-shift reaction and without the step of removing carbon dioxide by removing the unconverted carbon oxides from the gas effluent of the step;
- Extinction of residual oxygenates through catalytic methanation step;
- Synthesis of ammonia in a catalytic reactor.

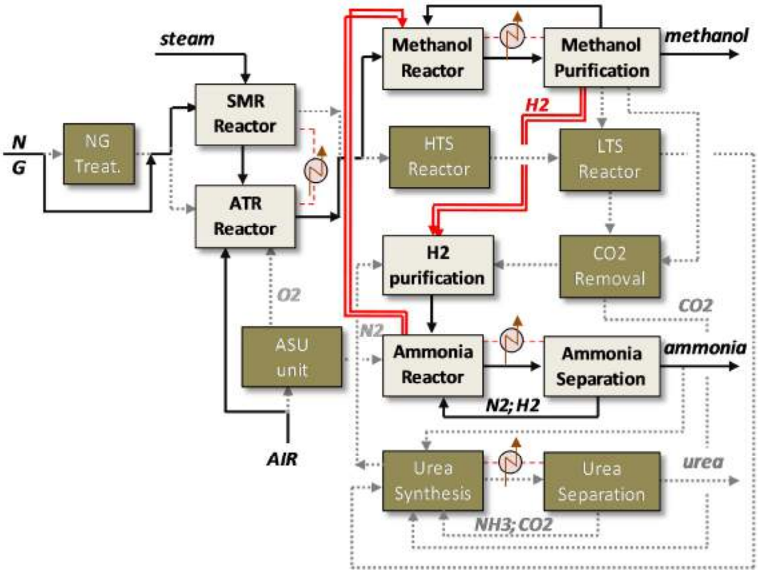
The list of the main steps of the process is: two-stage reforming, CO_2 removal, methanol synthesis, methanation, and ammonia synthesis is presented: natural gas (1) is added to primary reforming (steam methane reformer) under addition of steam (2). The partly reformed gas is then further reformed in air-blown secondary reforming (autothermal reformer) under addition of air (3). The methanol synthesis gas (4) containing hydrogen, carbon oxides and nitrogen is cooled in waste heat boiler(s) under the production of steam. Prior to compression to the methanol synthesis, a split stream of approximately 10 vol% is treated in a CO_2 PSA in order to adsorb carbon dioxide. The treated stream (5), which is rich in hydrogen, carbon monoxide and nitrogen, is mixed with the bypassed synthesis gas to form combined stream (7). This combined stream represents a methanol synthesis gas (make up synthesis gas) having now obtained a higher ratio between carbon monoxide and carbon dioxide, thus resulting in a more reactive synthesis gas for the methanol synthesis.

The CO_2 PSA off-gas stream (6) containing hydrogen, carbon dioxide, carbon monoxide and methane is used as fuel in the reforming stage. The methanol synthesis gas 7 is then compressed to methanol synthesis pressure. In methanol synthesis the methanol synthesis gas (7) is converted in once-through operation (single-pass operation, no recirculation) under the production of liquid effluent (8) containing methanol and gas effluent (9) containing nitrogen, hydrogen and unconverted carbon oxides. Approximately 80 wt % of the total plant capacity goes to the production of methanol of effluent 8. Carbon oxide in gas effluent 9 is hydrogenated to methane in methanation thereby generating an ammonia synthesis gas (10) having a H_2:N_2 molar ratio of 3:1.

The ammonia synthesis gas (10) is then passed through ammonia synthesis under the production of effluent (11) containing ammonia and a recycle stream (12) containing hydrogen, methane and nitrogen which is returned in the form of off-gas fuel stream (12) to the primary reforming. A hydrogen-rich stream (13) (>90 vol% H_2) is also withdrawn from the ammonia synthesis. This stream is added to the methanol synthesis by combining with the methanol synthesis stream 7. Approximately 20 wt% of the total plant capacity goes to the production of ammonia in effluent 11.

Figure 41 shows the superstructure simplified to this patent. Neither LTS, HTS, CO_2 removal, Urea synthesis or ASU unit are employed. Methanol reactor is fed directly from ATR reactor. Non-condensable gases from the methanol purification step feed H_2 purification step, which follows to ammonia reactor. A hydrogen-rich gas from ammonia condensation step feed to methanol reactor. Also a recycle stream from ammonia condensation step, containing hydrogen, methane and nitrogen is returned in the form of off-gas fuel to the primary reforming.

Figure 41- Superstructure of patent US 2014/8692034-B2.



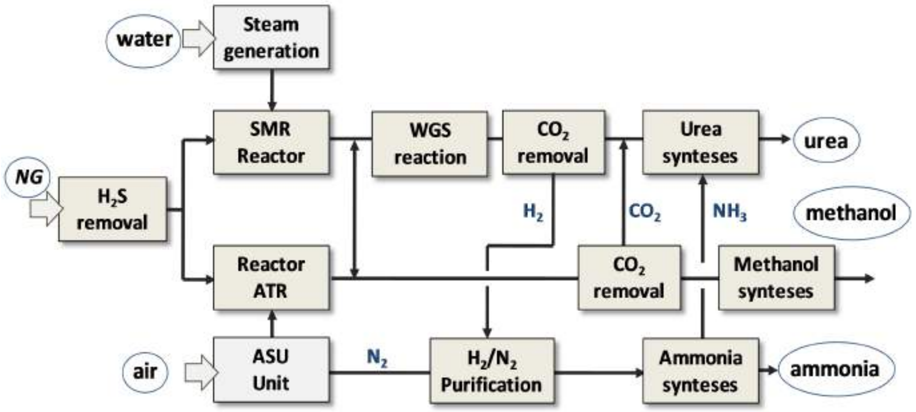
Source: The Author, 2017.

2.3.16 Patent US 2016/0083260-A1: A process for coproduction of ammonia, urea and methanol (Dahl, 2016a)

The patent U.S. 2016/0083260-A1, assigned to the inventor Per Juul Dahl, having the assignee Haldor Topsoe, presents a process for the simultaneous production of ammonia, urea and methanol using natural gas as feedstock. The request of the applicant describes a flexible process for the production of synthesis gas from a hydrocarbon feedstock. Synthesis gas is produced in two stages using two different types of reactors.

Figure 42 shows a block diagram with the basic design of the process described in patent US 0083260-A1.

Figure 42 – Block diagram of the conceptual design of the patent US 0083260-A1.



Source: Based on patent US 0083260-A1, 2016.

The project based on this patent is customized for the integrated production of ammonia, urea and methanol, with great synergy among the steps of the process. The process presents some possibilities of flexibilization among the flows of products of the industrial complex, according to the need of their clients. The original process, according to the patent application publication, can be used for the synthesis of ammonia, methanol, dimethyl ether, liquid hydrocarbons and combinations thereof. The invention describes a process for simultaneous coproduction of ammonia, urea and methanol, process starting from the generation of synthesis gas as an intermediate step. Specifically, the idea behind the invention is to use a combination of an autothermal reforming (ATR) with a methane steam reforming reactor (SMR) to realize the generation of the synthesis gas required for a variety of combinations of production flows ammonia, urea and methanol.

The reactions are conducted in an externally heated primary reactor (SMR). The feedstock of the primary reformer can be desulfurized if the feedstock contains sulphurous contaminants. The vapor is mixed with the hydrocarbon load and fed into the reactor. If the gas used as raw material is very rich, a pre-reform stage can be used from an auxiliary reformer installed upstream of the main reformers. The primary reformer is often of the tubular type, consisting of tubes filled with catalyst installed in a furnace heated by one or more burners. The reactor operates under severe conditions where the outlet temperature of the tubes is relatively high, generally in the range of 650 °C to 950 °C.

The autothermal reforming is a technology used for the production of synthesis gas, in which the conversion of a hydrocarbon feedstock, in this case natural gas, is carried out in a single reactor, through the combination of partial combustion and adiabatic steam reforming of methane. The combustion of hydrocarbons occurs with sub-stoichiometric amounts of air or oxygen-enriched air, in order to prioritize the formation of carbon monoxide in the combustion zone of the burner.

The synthesis gas is produced from natural gas and is then used as raw material for the production of basic chemicals. The following process steps are used:

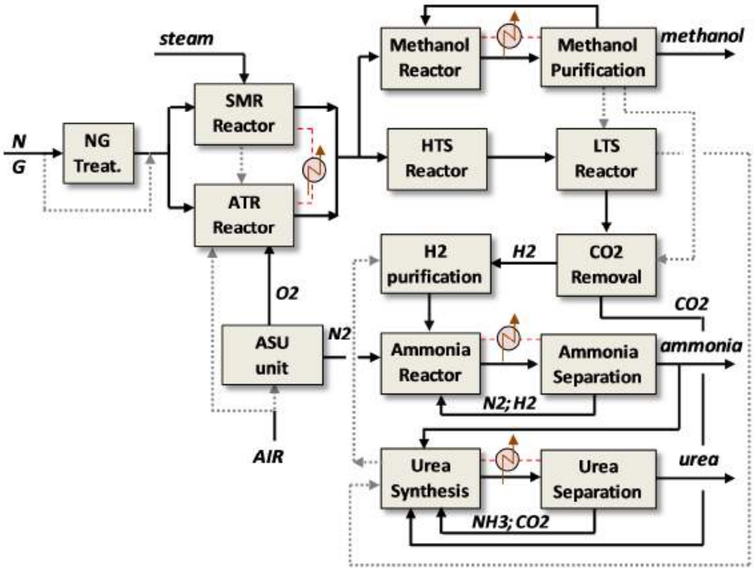
- Synthesis gas generation in the catalytic reforming stage of methane, through two synthesis reactors operating in parallel;
- Separation of atmospheric air in an Air Separation Unit (ASU), for the generation of oxygen for the autothermal and nitrogen reform for the subsequent synthesis of ammonia;
- Conversion of CO to CO_2 through the water-gas-shift reaction (WGS) in catalytic bed reactors constituted by copper and nickel with alumina support;
- Removal of carbon dioxide through absorption with chemical absorbent;
- Removal of impurities (oxygen compounds) from the synthesis gas;
- Synthesis of methanol in the conversion reactor.

The described process presents the flexibility to allow the alteration of the produced flows of ammonia, urea and methanol, according to the specific market demands of each of these products (Dahl, 2016). It should be noted that although the project allows the production of ammonia, urea and methanol, only the last two products are destined to their respective markets, since ammonia is produced only for the internal supply of the process (as intermediate product).

In a general way, by presenting a higher level of energy efficiency and synergy among the production processes, currently, Haldor Topsoe's patents (and its licensed derivations) dominate much of the world-wide joint production market for ammonia and methanol. Especially considering the mega-projects built in countries holding large reserves of natural gas (Peiretti, 2013).

Figure 43 shows the superstructure simplified to this patent. Methanol synthesis receives syngas, and has no integration with other units. As present in previous patents, CO_2 removal is preceded by water gas shift reactors, and CO_2 is send to Urea unit while H_2 is send to ammonia reactor.

Figure 43 - Superstructure of patent US 2016/0083260-A1.



Source: The Author, 2017.

2.4 General considerations about the processes studied

2.4.1 The choice of raw material

The use of natural gas as raw material in virtually all the studied processes is indicated as the best option for gasochemical production projects in terms of product conversion efficiency, amount of contaminants and energy savings. Units that only use natural gas as raw material have the advantage of producing products with less contaminant, thus requiring less disbursement with product purification systems, as well as lower energy consumption per quantity of product generated.

2.4.2 Generated products by the evaluated processes

In relation to the evaluated processes, the great majority of them describe the combined production of ammonia and methanol or the combined production of ammonia and urea. Processes that describe the simultaneous production of the three products with integration between productive units are rare in the specialized literature. Only a few patents describing a combined production process with the objective of generating ammonia, urea and methanol as final products in a single site in a continuous manner and with reasonable integration between the units of the complex were identified by the bibliographic research carried out in this work. A good reason for this is that the commercial and economic interest of the combined production is linked to the supply of specific markets in an advantageous way and to the synergistic gain generated by the integrated production.

The major world producers of ammonia, urea and methanol in general operate only in one of these markets, mainly due to the great complexity of the logistics necessary for the transportation, storage and distribution of these products. The cost of deploying the logistics necessary to operate in all three markets simultaneously is very high and few financial groups are willing to take the economic risk of operating in several large financially demanding markets simultaneously.

2.4.3 Main technical aspects verified in the evaluated processes

Several patents studied present the production of ammonia only as a way of generating the necessary raw material for the production of urea, without pretension of attending to the specific market of ammonia continuously. Each combined production association aims to exploit certain strategic advantages. For example, the integrated production of ammonia and urea eliminates the high cost of transporting ammonia to a urea production plant. Part of the CO_2 removed from the synthesis gas purification for the production of ammonia can be harnessed as raw material in the urea production unit, incorporating added value to the project.

Some technical design options are used by almost all the processes studied. For example, in the case of reforming reactors for the conversion of hydrocarbons to synthesis gas, the use of two stages of reform is practically unanimous. The first stage being the steam reforming of methane, complemented by the second stage of autothermal reform with the injection of a stream of oxidizing gas, composed of atmospheric air or pure oxygen. In this case the use of an atmospheric air distillation unit is preferable by generating an oxygen stream for the autothermal reform and a nitrogen stream for the conversion of ammonia together with the hydrogen current produced by the hydrocarbon reform.

The use of two stages of reform gives the project a large flexibility in relation to the content of oxygenates in the generated synthesis gas. This flexibility allows the operator to change the profile of products generated by the complex more easily. For example, in the integrated production of methanol and ammonia, the major strategic advantage of this coproduction is the great operational flexibility of modifying the proportion of NH_3/methanol generated simply by modifying the amount of the oxidant feed in the auto-thermal reforming reactor (ATR). Thus, production profile adjustment needs of can be more easily solved, reducing the ammonia production and increasing the production of methanol or vise-versa.

Another great advantage of this configuration of reforming reactors is that the self-thermal reactor operates with quite exothermic combustion reactions, so that this generated energy can be used by the steam reforming reactor, which operates with endothermic reactions of generation of hydrogen and carbon monoxide. A well-sized design eliminates virtually the need for additional energy supply at the steam reforming reactor.

An alternative possibility to this configuration is the use of the two reforming reactors (SMR and ATR) in parallel, being fed simultaneously. This alternative configuration allows varying the feed of hydrocarbons between the reactors, increasing or decreasing the flow of one of them with respect to the other. The great advantage of this alternative is the greater flexibility to change the ratio of ammonia/methanol produced.

This study evidenced that virtually all reported processes use steam dilution at the steam/hydrocarbon molar ratio close to 3:1 to feed the reforming reactors. The dilution allows a reactive equilibrium of carbon monoxide and hydrogen generated suitable for most uses of the synthesis gas and still reduces the occurrence of coke generation in the reforming reactor. Much smaller proportions than the one presented here tend to greatly increase the rate of coke formation in the reactors, thus inhibiting the catalyst action and consequently reducing the conversion rate of the reforming reaction.

Another relevant technical aspect is the mention of the use of sulfur compounds removal systems, especially when the project provides for the alternative use of hydrocarbon sources other than natural gas. In terms of syngas conditioning for the ammonia conversion step, the most widely used treatment for the elimination of carbon monoxide is the Water-Gas-Shift reaction, which converts the monoxide to carbon dioxide. In general, this conversion reaction occurs in two steps, one at high temperature and one at low temperature. The shift conversion is complemented by the CO_2 removal step, usually by washing with monoethanolamine (MEA) in an absorber column.

An alternative process for these two purification operations is the passage of the syngas by the methanol synthesis reactor without recycle (a single pass). The methanol formation reaction consumes the oxygenated compounds besides hydrogen. The hydrogen-rich residual gas generated in the methanol conversion reactor is used for the conversion of ammonia after treatment.

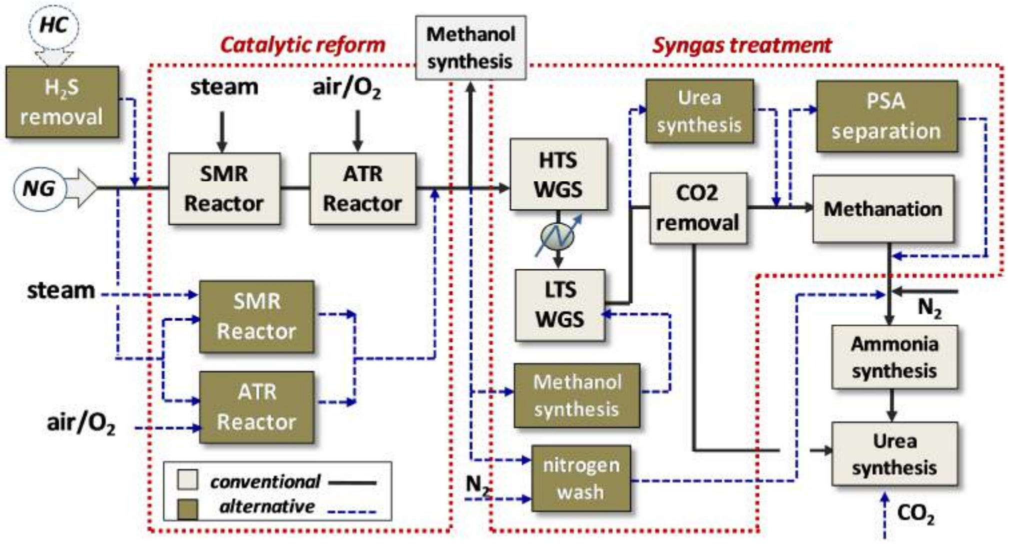
Whether by the traditional or alternative process, the syngas used for the conversion of ammonia needs to undergo a complementary step to extinguish traces of oxygenated compounds. Usually a methanation reactor is used for this step. In this reactor, hydrogen reacts with the carbon oxides to form methane and water.

An alternative technology to the methanation process is the washing of the syngas intended for the conversion of ammonia with a stream of liquid nitrogen. This operation, besides eliminating the oxygenated compounds, still provides all the nitrogen necessary for the ammonia conversion. However, in practice, this technology is not widely used, due to the high costs involved. Another alternative technology for the removal of oxygenates is the Pressure Swing Adsorption (PSA). This technology operates by alternating high and low pressure in separation vessels. Due to the difference in adsorption rate of the different species of gases, the required separation of the oxygenated compounds is achieved.

A few processes propose the alternative use of urea synthesis to remove the CO_2 generated by the shift reactions from synthesis gas intended for the production of ammonia. In this case, there is a strong interaction between the reactors of urea and ammonia, with several intermediate currents between the reactors. It should be noted that this alternative does not eliminate the need for shift conversion reactors to convert the monoxide to carbon dioxide.

Figure 44 shows, in a simplified way, the consolidated block diagram of the conventional processes used, as well as the main alternative technologies for the combined production of methanol, ammonia and urea in the same production site.

Figure 44 - Block diagram of the used processes to ammonia-urea-methanol coproduction.



Source: The Author, 2017.

After treatment to remove oxygenated compounds, the syngas is sent to the ammonia conversion reactor. After separation, usually by condensation at low temperature, the produced ammonia is used as raw material for the production of urea together with the separated CO_2 in the treatment step of the synthesis gas.

In terms of energy efficiency, the combined processes allow the recovery of much of the hot and cold energy of the currents generated, regardless of the configuration used. But there is a limit that should not be exceeded, due to the risk of greatly increasing the possibility of operational stops of the whole complex by the occurrence of an operational problem in only one unit. The unit of greatest energy consumption is the section of reform, but the use of the configuration of two reactors in series practically nullifies this large consumption.

In terms of cold utilities, the refrigeration cycle required for the ammonia condensation is the main consumer. Usually this cycle uses the ammonia produced in the complex as the refrigerant fluid. In economic terms, the great advantage of the combined production of methanol, ammonia and urea on the same site, is the possibility of connection between distinct markets, which makes the economic viability of the project more robust. In moments of low consumption of a certain product, the flexibility of the project allows to reduce the production of this one to increase the production of the other products.

2.5 Conclusions

The general review conducted on the patents for natural gas derivative production processes presented in this chapter identifies the technical and economic advantages of the main technologies used in the unitary operations of chemical engineering of the combined production plants of the gasochemicals. The study allows a direct comparison between the processes involved, regardless of the period in which they were proposed. Some relatively old processes are still used today, with few modifications implemented.

The use of natural gas as a raw material in industrial complexes for the production of gasochemicals is practically unanimous in the evaluated processes, emphasizing the great technical and economic advantage of the use of the gas for this purpose.

It is evident that some engineering solutions are consecrated and used by the great majority of the processes presented. As an example, the use of two stages of natural gas reform is used by all processes, with rare variations in terms of configuration and the type of reactors used. The treatment and purification of the synthesis gas for the production of ammonia is very uniform, with few variations being proposed in the evaluated works. This uniformity in the use of consecrated technologies is quite common in engineering projects of high capital demand for implementation.

Another relevant aspect that is evident in the analysis of the evaluated processes is that there is not a single process better than the others, in all the aspects. There are processes that respond well to a set of basic assumptions, specific to each scenario.

3. TECHNICAL-ECONOMIC ANALYSIS OF METHANOL PRODUCTION FROM NATURAL GAS IN BRAZIL

Abstract

This article presents a detailed study on the technical and economic feasibility of implementing a project to produce methanol from natural gas as a basic raw material, considering Brazilian specificities and needs in terms of the production of oxygenated chemical compounds derived from methanol. The study investigates the main technical and economic issues related to the implementation of an industrial methanol production plant, analyzing different values of nominal loads of the complex. The necessary investment and the potential revenue of each nominal capacity value are analyzed, generating results that allow the presentation of conclusions about the best economic conditions for the feasibility of the project. The total value of the investment in a methanol production plant is calculated as a function of the nominal capacity variation of the complex, considering in addition to the methanol conversion unit, also a synthesis gas plant to produce the necessary hydrogen for the methanol production. The methodology established by the authors is based on the calculation of the main equipment cost of the unit and the cost of implementation of the project, as well as the variable costs (raw material, operational cost and taxes) to determine its economic viability. The project's potential operating revenue is calculated based on average international methanol prices. The net present value analysis of the different nominal load values of the project allows determining the best range of nominal capacity of the project, considering the economical perspective. On the other hand, the use of international methanol prices and the natural gas price in the domestic market on the economic evaluation of the project ensures the correct measurement of the level of competitiveness that such a project would have in the international market, considering the possibility of exporting surplus methanol produced.

Keywords: natural gas, syngas, methanol, economic evaluation.

Introduction

Natural gas has been considered a very promising fuel due to its friendly chemical nature, high energy efficiency, great abundance and adequate cost for large-scale use. Natural gas is the fossil fuel that causes less aggression to the environment

(Gur, 2016) and has therefore been considered the "transition fuel" for low-carbon energy savings (Cole *et al.,* 2016; Kerr, 2010). According to this concept, Cochran *et al.* (2014) argues that natural gas and renewable sources can be sources of complementary energy supply for humanity.

As reported by BP Statistical Review of World Energy (BP, 2015), natural gas is the second most used energy source in the industry, behind only electricity. In some regions, plants generating electricity from natural gas have replaced nuclear power plants for safety reasons (Mazyan *et al.,* 2016). Natural gas is considered one of the most important energy sources and a strategic fuel (Bai and Li, 2016; Chong *et al.,* 2016) that will play an increasingly important role in the next decades (Mason and Wilmot, 2014).

On the other hand, notwithstanding the great importance of gas for power generation, the use of natural gas as raw material source in transformation processes for the production of important commodities in the chemical industry is currently been pointed out as the noblest use of it (Dong *et al.,* 2013). Unfortunately, this noble use is not yet a reality in Brazil, so there is a huge potential for expansion of the Brazilian natural gas market in the domestic production of chemicals currently imported in large quantities throughout the country, requiring the expenditure of millions of dollars in foreign exchange (ABIQUIM, 2017).

With the recent shutdown of the last active production plant in the state of Bahia, Brazil currently imports all the methanol it uses in the industrial processes of chemical transformation for the production of high value-added compounds (MDIC/Aliceweb, 2018), creating a condition of great strategic vulnerability and strong dependence of the Brazilian chemical industry on the supply of basic inputs by the international market (ABIQUIM, 2015). The domestic methanol production resumption may have a significant positive effect on the strengthening of the Brazilian economy.

In order to explore this possibility, this paper presents an extensive investigation on the methanol production from the syngas produced in a synthesis gas generation plant that uses natural gas as the basic raw material. For this purpose, synthesis gas and methanol production units were simulated in the PETRO-SIM®

software, according to common engineering practices, in order to determine the potential production of the units from different values of natural gas load.

The simulation assembly was carried out based on the technology of catalytic reforming in two reactors in series for the generation of synthesis gas. The first reactor uses steam reforming methane and the second reactor uses the autothermal reform with oxygen injection. For the simulation of the methanol plant, a thermodynamic equilibrium reactor was used to simulate the conversion of syngas to methanol.

The economic performance of the project for each nominal load value was determined through a methodology based on the design and calculation of the main equipment cost of the complex and the implementation costs of the project (CAPEX), as well as the variable costs (OPEX), taxes and revenue. The data obtained allow determining the capacity of the industrial complex of methanol production that presents the best economic performance, according to the feasibility study conducted, besides measuring the level of competitiveness of the complex against the methanol prices practiced by the international market.

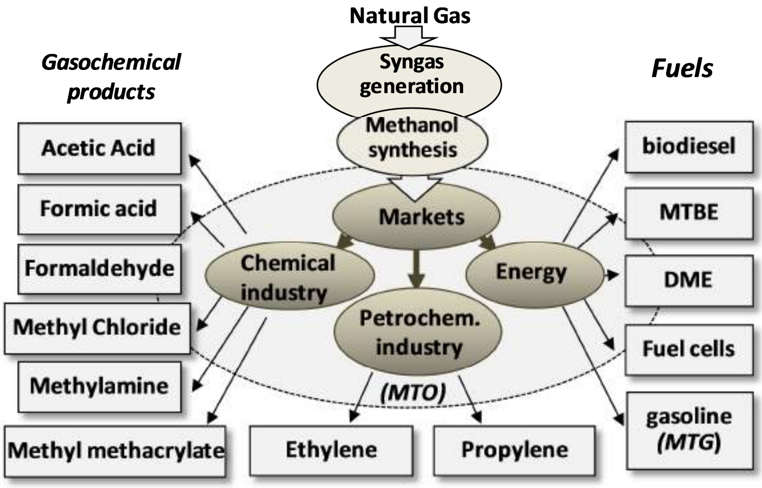
3.1 The strategic importance of methanol

Methanol is a chemical intermediate in a large number of synthesis routes of essential products to modern life. Methanol is the main feedstock for the production of several important organic chemical compounds, such as acetic acid, formic acid, formaldehyde, methyl methacrylate and its derivatives (Saade, 2011). On the other hand, we cannot forget the recent acquired function of methanol as a promising energy carrier (Peter *et al.,* 2012), nor the environmental benefits of processes still under study that use the reduction of CO_2 captured from other processes to methanol production (Riaz *et al*., 2013).

3.1.1 Applications of methanol

Methanol has direct use or as an intermediate compound in a large number of productive processes of chemical compounds. Figure 45 shows a schematic illustration of the multiple methanol applications to supply different markets, evidencing the high level of complexity of the production chain of this strategic feedstock of the world chemical industry.

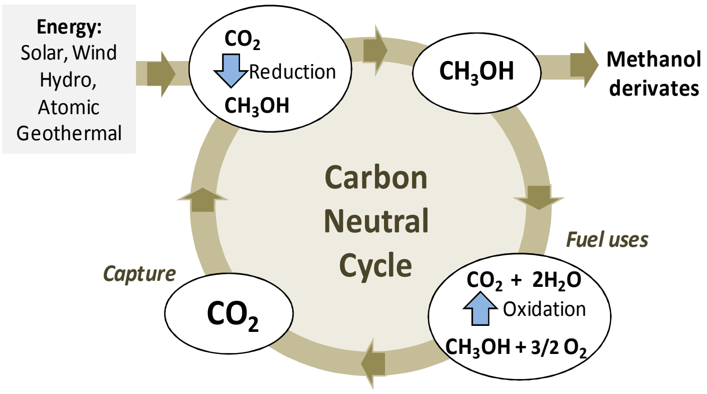
Figure 45 – Main applications of methanol.



Source: Adapted from Gerosa, 2007.

Recent developments have made the use of methanol as fuel for automotive engines a very interesting option for the transportation industry (Luyben, 2010). Methanol is easy to store and distribute, and can be mixed with gasoline and also used in methanol fuel cells (Masih *et al.*, 2010). The use of methanol as an energy source is what several authors call Carbon Neutral Cycle (Roh *et al.*, 2015, Olah *et al.*, 2009a), shown in Figure 46.

Figure 46 - Carbon Neutral Cycle.



Source: Adapted from Olah *et al.*, 2009a.

The methanol production, involving the choice of the production process and the quantity produced is obviously a function of the market to be supplied. Therefore, a brief description of the methanol market in Brazil and in the world becomes interesting, as a basis for the decisions developed in this article.

3.1.2 World market of methanol

The methanol market is at a transitional stage in which some products derived from methanol tend to have their output reduced, such as methyl terc-butyl ether (MTBE), while others are experiencing a sharp increase, such as biodiesel, gasoline, and light olefin production (Riaz *et al.,* 2013).

The potential demand for these new markets is highly dependent on the cost competitiveness of methanol over traditional alternatives such as naphtha and heavy gasoline fractions. Table 03 shows the 2011 world consumption profile of methanol and the forecast of demand occurred in 2012 for the year 2016, which came to fruition.

Table 03 – World consumption profile of methanol.

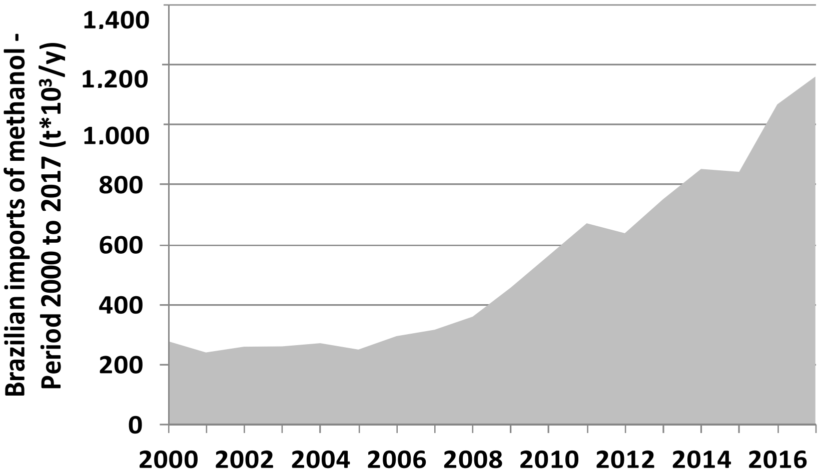
year produt	2011 (%)	2016 (%)
formaldehyde	32	25
Acetic acid	10	8
MTBE/TAME	10	7
Methyl methacrylate	2	1
gasoline	11	16
Dimethyl ether	11	8
Methylamines	4	3
Chloromethanes	1	1
MTO/MTP	6	22
Solvents	5	4
DMT/others	8	5
total:	100	100

Source: Adapted from Riaz *et al.,* 2013.

3.1.3 Brazilian methanol market

According to data from the Brazilian Ministry of Development, Industry and Foreign Trade - MDIC/Aliceweb system (2018), the Brazilian market for methanol has shown a steady evolution in recent years. Since the domestic production was interrupted, all methanol consumed in Brazil has imported origin. Only in 2017, more than 1.15 million tons of methanol were imported, generating an expenditure of foreign exchange in the order of US$ 364 million. Figure 47 shows the values of the Brazilian imports of methanol since the year 2000.

Figure 47 – Brazilian methanol imports.



Source: MDIC –Alice system, 2018.

The data presented demonstrate the strong dependence of the Brazilian market on the importation of the methanol, characterizing a relevant strategic fragility given that methanol is one of the main basic feedstock of the chemical industry.

With such great quantities been imported, the entire chain of the Brazilian chemical industry that uses methanol as a feedstock is held hostage by the natural oscillations of international prices of alcohol. This large dependence on imported methanol has deepened, as the country's main producer of the product (COPENOR) stopped producing methanol for economic reasons and decided to import all methanol used as feedstock into its production plants for methanol derivate.

3.2 Production of methanol

Industrially, methanol is typically produced by a basic three-step process: (i) syngas generation, (ii) catalytic methanol synthesis in the conversion reactor, and (iii) separation and purification of the product. Conceptually, syngas is a mixture of CO, CO_2 and H_2. The generation stage of syngas is the most complex and expensive step in the process of a methanol production plant, both in terms of investment and operating cost, requiring a great investment in technology. In a typical reformer reactor, natural gas is reacted with steam over a nickel catalyst to produce the syngas through the methane (endothermic reaction) vapor reforming reactions and the water-gas-shift reaction (exothermic reaction), which occurs in parallel with the main reaction (Ali Alizadeh and Jalali-Farahani, 2007).

Baliban *et al.* (2013) estimated that about 60% to 70% of the total cost of the methanol production complex is associated with syngas generation and 20% to 25% is associated with methanol production, with the remainder being applied in the product purification step. Syngas can be obtained by reforming natural gas and liquid hydrocarbons or gasification of coal and biomass; however, the steam reforming route for natural gas is currently responsible for the production of 75% of the world's produced methanol (Riaz, 2013; Cifre and Badr, 2007).

Since the beginning of use of the large-scale manufacturing process of methanol, there have been constant efforts to upgrade the technology and incorporate incremental improvements to the manufacturing process, in order to increase conversion efficiency and reduce process energy expenditure (Lange, 2001).

The first process, developed by BASF in 1923, to produce methanol had used high pressure and high temperature in the conversion reactor (Tijm *et al.,* 2001; Mota *et al.,* 2013). The production plants had operated with a pressure range of 24.5 MPa to 34.5 MPa (250 kgf/cm^2 to 350 kgf/cm^2) and 320°C to 450°C of temperature range. This technology had employed a ZnO/Cr2O3 catalyst, which was quite resistant to sulfur and chlorine contamination. The high temperature was required due to the low catalyst activity. This original process required a large investment in equipment due to high operating pressures, and high operating costs due to the great consumption of compression energy (Riaz, 2013).

In the 1960s, an evolution of this process was developed by ICI (Imperial Chemical Industries), which introduced a catalyst based on a mixture of copper and zinc oxides, which proved to be much more active than the catalyst previously used. This catalyst is more prone to deactivation at high temperatures, so the process required a better temperature control of the conversion reactor (Huertas-Flores, 2008).

Currently, ICI produces methanol at lower pressure (<10MPa) and lower temperature (220°C to 270°C) using a Cu/ZnO/Al2O3 based catalyst. Companies like Lurgi, Haldor Topsoe and Basf also use low pressure methanol synthesis using a mixture of Cu/ZnO/Al2O3/Cr2O3 as the catalyst. The process operates in the pressure range between 4.9 MPa and 9.8 MPa (50 kgf/cm^2 and 100 kgf/cm^2) (Ozturk and Shah, 1985). To ensure the activity of the catalyst and the efficient use of the heat of the reaction, the methanol converters are operated in the range of 200°C to 300°C.

Depending on the employed technology, the syngas can be washed, compressed and heated before entering the methanol synthesis section. This fresh charge is mixed with unreacted recycled gases and sent to the methanol converter, where alcohol formation reactions occur (Raudaskoski *et al.,* 2009):

$CO + 2H2 \leftrightarrow CH3OH$ [ΔH = -90.77 kj/mol] (Reaction 04)

$CO + 3H2 \leftrightarrow CH3OH + H2O$ [ΔH = -49.58 kj/mol] (Reaction 05)

$CO2 + H2 \leftrightarrow CO + H2O$ [ΔH = +41.19 kj/mol] (Reaction 01)

The selectivity of the catalyst relative to methanol formation is quite high; however, the conversion rate is low, necessitating recycling of the unreacted gases. To achieve a reasonable conversion rate, the use of specific and high pressure catalysts is required in order to compensate for the low conversion determined by the thermodynamic equilibrium during the synthesis (Manenti *et al.,* 2011).

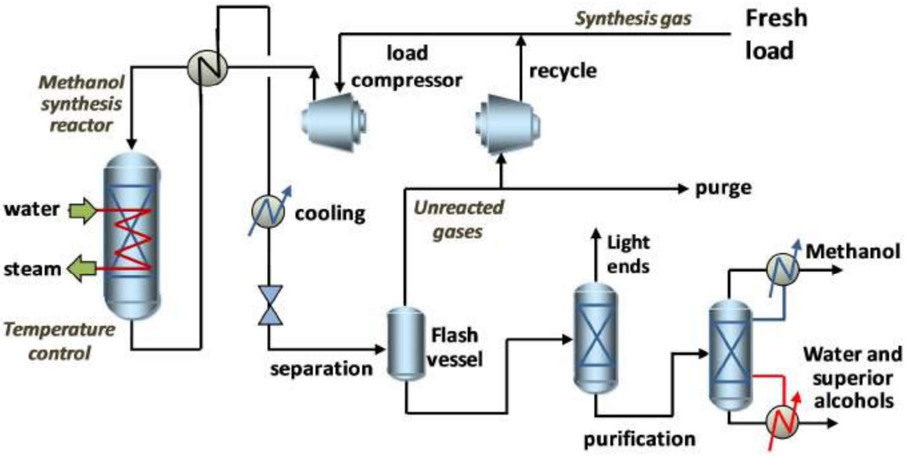
According to MHTL (Methanol Holding Trinidad Limited, 2005), the average methanol conversion rate is 5% to 10% at each pass through the reactor. This conversion is a result of the thermodynamic equilibrium reached in the reactor operating conditions. For this reason, a loop system is used which absorbs the unreacted compounds, heating them and sending them back to the synthesis reactor. By using unreacted gas recirculation, the methanol conversion process can achieve overall conversion in the order of 99% (Gerosa, 2007).

The produced methanol contains water, dissolved gases and small amount of hydrogen, so a purification step of the product, usually a distillation unit, is required (Riaz, 2013). The gases dissolved in the product are pre-separated in a flash vessel and returned to the methanol production reactor. Under normal operating conditions, only a small amount of by-products remains in the output stream (Gerosa, 2007).

The impurities are separated by distillation in one or two stages, depending on the required purity of the product. When two separation stages are used, in the first stage all components more volatile than methanol are removed in a light-ends or topping column (Riaz, 2013). The remaining solution is distilled into one or more distillation columns, generating the pure methanol, according to the necessary specification for its subsequent use. For use in the manufacture of gasochemicals the methanol must have a degree of 99% purity, being classified as refined methanol of class AA (Gerosa, 2007).

The methanol purification columns operate at different pressure levels and the heat from the vapor condensation of the column operating at higher pressure can be used as thermal energy for the column operating at a lower pressure level. Figure 48 shows a schematic illustration of the more usual methanol production process. It can be observed that in this process, the temperature control of the conversion reactor is carried out through the production of steam.

Figure 48 – Simplified diagram of methanol production.



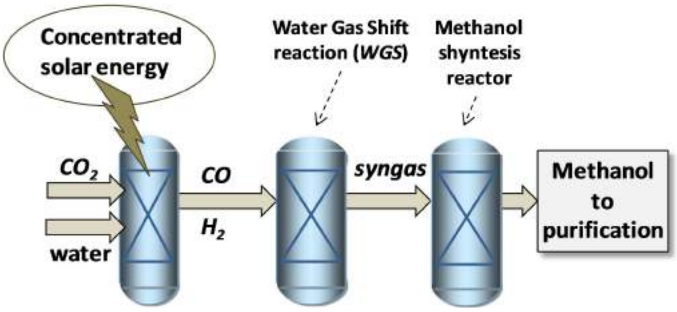
Source: Adapted from Riaz, 2013.

3.2.1 Alternative methanol production processes

A number of alternative processes that use methanol as feedstock have been gaining attention over the past few years. According to Johnson (2012), light olefins production technologies such as Methanol-To-Olefins (MTO) and Methanol-To-Propylene (MTP) also have prediction of strong growth, generating an extra increase in global demand for methanol. So many other processes are being proposed in the literature for the synthesis and new use of methanol. For example, it has been reported in the literature the direct conversion of methane to methanol, including conventional catalytic processes, photocatalysis and plasma technologies (Zakaria and Kamarudin, 2016; Dallos *et al.*, 2007).

Kim *et al.* (2011) presented a process for the methanol production from carbon dioxide and water. As differentiation, the process uses concentrated solar energy in a thermochemical reactor to reduce CO_2 to CO and then uses the water-gas-shift reaction (WGS) to produce synthesis gas, which ultimately feeds a methanol synthesis reactor. The process is quite similar to the one proposed by Agrafiotis *et al.* (2014), distinguishing itself from this, however, by the use of syngas for the production of methanol, rather than the production of other liquid fuels. Figure 49 shows a simplified schematic of the proposed process.

Figure 49 – Production of methanol from solar energy.



Source: Adapted from Kim *et al.*, 2011.

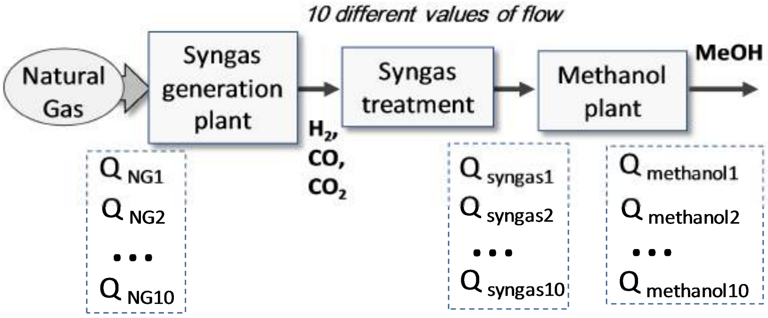
It should be emphasized that these alternative technologies have great potential for use, depending on their development stage. However, for large-scale production on a competitive basis in the international market, these alternative technologies currently do not yet have the appropriate efficiency and cost of production to compete with more traditional hydrocarbon reforming technologies and the conversion of synthesis gas to methanol in large production units. Nowadays, these new alternative technologies are a process for the future. Due to this reason, this work is focused on the use of more traditional technologies, such as catalytic hydrocarbon reform, which is able to meet the requirements of quantity and cost of production in a more adequate way.

3.3 Methodology

The methodology used to carry out the process simulation of the synthesis gas and methanol production industrial plants, operating in an integrated manner was based on the choice of the consecrated technologies and pointed by the specialized literature as the best design solutions for the unit operations of the chemical engineering required for the production of synthesis gas and methanol. The process simulations were carried out with the PETRO-SIM® commercial simulator. The proposed industrial complex consists of a synthetic gas generation unit, which supplies raw material to a methanol production unit, in an integrated system. Ten different nominal charge values of natural gas were simulated for the synthesis gas generation unit, each generating a nominal flow rate of distinct synthesis gas, which is used as the methanol production unit charge.

The ten nominal load values were chosen to cover an extensive range around the average amount of methanol consumed in the country. Considering consumption around 1.20 million tons per year, nominal load values were investigated for the complex varying from 40% to 300% of the value consumed by the country. Figure 50 shows a schematic of the applied system.

Figure 50 – Schematic of the methodology applied for the simulation of the methanol production unit.



Source: The Author, 2017.

From the results of the ten simulations, material and energy balances were generated to the proposed units (at the conceptual design level) and the basic design of the main process equipments were determined, as well as their costs were estimated. Table 04 shows the simulated natural gas load values of the complex.

Table 04 – Simulated natural gas load values.

Natural Gas load (t/h) - (Ten points)									
Q_{NG1}	Q_{NG2}	Q_{NG3}	Q_{NG4}	Q_{NG5}	Q_{NG6}	Q_{NG7}	Q_{NG8}	Q_{NG9}	Q_{NG10}
30.70	38.38	47.80	59.99	75.00	94.10	117.50	146.70	183.30	228.80

Source: The Author, 2017.

The preliminary design of the main equipments was obtained through the use of simulation data, with estimates of design parameters according to tables of global coefficients of heat transfer, specific weight tables of metal sheets according to ASME Code, Section VIII, Division I, to calculate the weight of static equipments (ASME, 2015).

The cost of the main equipments and the estimation of the CAPEX were realized according to parameters and equations presented elsewhere (Towler and Sinnott, 2013), plus some complementary factors used in manuals of project of the PETROBRAS. The estimated revenue with the sale of methanol was obtained based on the cost of importing this product, according to data from the Aliceweb System of the Ministry of Development, Industry and Foreign Trade (MDIC).

3.3.1. Simulation strategy

Units of synthesis gas generation from natural gas and methanol production were simulated in the PETRO-SIM® process simulator, version 5.5 (which is fully compatible with the commercial simulator HYSYS), in accordance with usual process engineering practices, in order to determine the production potential of the units, according to the different nominal natural gas loads tested.

In addition to the nominal natural gas flow of each investigated point, the main variables specified were the temperatures and operating pressures of the reaction units (methane reforming, CO conversion, methanation, methanol conversion), flow rate of steam and oxygen to reforming reactors, as well as the minimum quality of methanol produced and the temperature of cooling water.

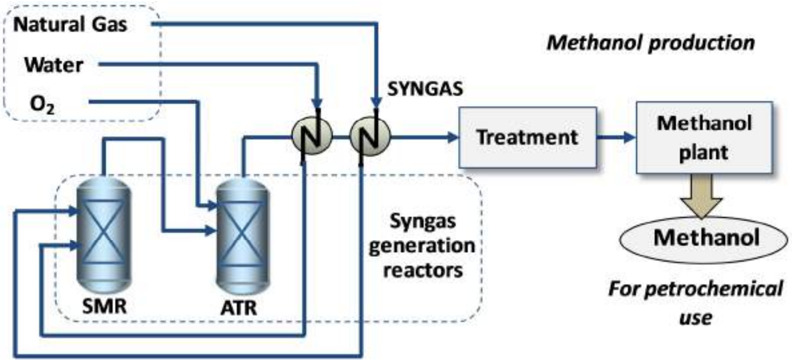
The demanded power of compressors and pumps, the conversion rate of reactors, and recycle flows were calculated by the simulator. The size of the static equipments was calculated based on simulator generated data.

3.3.2 Simulation of the synthesis gas generation unit

For this project, the configuration of two conversion reactors operating in series, was chosen, the first being an SMR reactor, operating at temperature of 800 °C and pressure of 4.41 MPa (45 kgf/cm^2) and the second a ATR reactor (Autothermal Reactor), operating at temperature of 1,200 °C and pressure of 4.21 MPa (43 kgf/cm^2), as proposed by Mujeebu (2016). The first reactor operates with a steam/methane ratio of 3:1. The reforming reaction in the first reactor is carried out in an atmosphere with excess steam, to allow the control of the tendency for coke deposition on the surface of the catalyst, causing its deactivation as related by Chiesa (2010).

The effluent gases from the first reactor enter the second reactor and are mixed with oxygen. The oxygen flow rate is the minimum required to burn all the unreacted residual methane in the first reactor. An excess of oxygen should be avoided, as the consequence is the increase of the hydrogen consumption and the increase of the CO_2 production in the ATR reactor. Figure 51 presents the block diagram of syngas production unit for loading methanol production unit.

Figure 51 – Block diagram of syngas generation for methanol production.



Source: The Author, 2017.

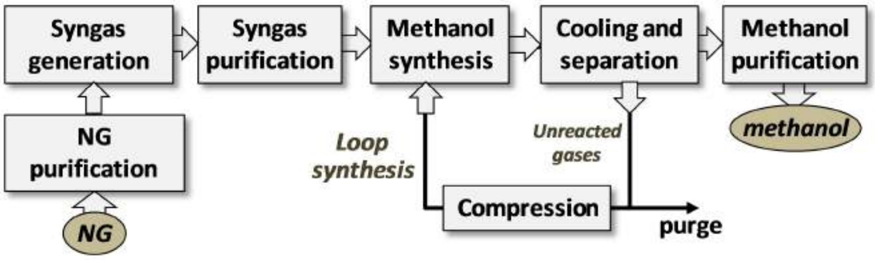
The excess steam favors the water gas shift - WGS reaction, which is fundamental in the control of coke deposition as described by YU *et al.* (2012). The process is conducted at moderate pressures, around 3.92 MPa (40 kgf/cm^2), thus reducing the need for additional compression of the synthesis gas effluent of the reforming reactors, as already reported by Chiesa (2010). It is also worth mentioning that the higher the pressure at which the reform occurs, the higher the temperature required establishing the desired thermodynamic equilibrium.

Figure E1 reproduced in large size in Appendix E shows the process flow diagram (PFD) of the simulation of the synthesis gas generation plant as implemented in the simulation software.

3.3.3 Simulation of the methanol production unit

The simulation of the methanol production unit follow the modeling strategy of ten different simulations, one for each nominal natural gas charge investigated in this article. The process chosen was the most widely presented in the literature, using a methanol conversion reactor, product separation, compression and recycle of unreacted gases and purification of final product. Figure 52 presents a schematic representation of the simulation strategy used.

Figure 52 - Block diagram of methanol production unit.



Source: The Author, 2017.

Figure E2 reproduced in large size in Appendix E shows the process flow diagram (PFD) of the methanol production plant, as implemented in the process simulator.

3. 3.4 Estimated cost of equipments

The preliminary cost estimation of individual equipment C was performed according the following equation (Towler and Sinnott, 2013):

$$\boldsymbol{C_i = a_i + b_i \cdot {Q_i}^{n_i} \quad \forall\ (i \in SE)} \qquad (1)$$

Where a, b, n are parameters associated to each equipment, Q is some measure of capacity, SE is the set of equipment and the index i is associated to each equipment in this set. For some equipment, Q is directly read from the simulation results (for example, flow rate for centrifugal pumps), while others demand additional calculations. For heat exchangers, Q is the area of the equipment, which demands the knowledge of global heat transfer coefficients, obtained from tables and compared carefully with similar systems of the industry. Table 05 presents the parameters of Equation 01.

Table 5 - Parameters of Equation 01.

Equipament	**Type**	**Dimensioning variable (Q)**	**unid.**	**Validity limits** $(Q)_{min}$	$(Q)_{max}$	**parameters** a	b	n
compressor	centrifugal	power	kW	75	30,000	580,000	20,000	0.60
Press. vessel	vertical	weight	kg	160	250,000	11,600	34	0.85
Press. vessel	vertical	weight	kg	160	50,000	10,200	31	0.85
Oven	box	thermal load	MW	30	120	43,000	111,000	0.80
Exchanger	shell and tube	area	m^2	10	1,000	28,000	54	1.20
Exchanger	floating S &T	area	m^2	10	1,000	32,000	70	1.20
Reactor	cylindrical	volume	m^3	0.5	100	61,500	32,500	0.80
Tray	valv tray	diameter	m	0.5	5	210	400	1.90
Pump	centrífugal	flow	l/s	0.2	126	8,000	240	0.90
Electric motor	exp. proof	power	kW	1	2,500	-1,100	2,100	0.60
reboiler	thermosiphon	area	m^2	10	500	30,400	122	1.10

Source: Towler and Sinnott, 2013.

For pressure vessels (like separators vessels, reactors and distillation columns), Q is the mass of such vessels, which must be calculated according to the nominal operating pressure (and, when appropriate, temperature); therefore, it was necessary to calculate the thickness of the shell of these equipments. The thickness of the shell of the pressure vessels, reactors and distillation towers are estimated based on the ASME code, section VIII, division 1. Equation 02 presents the proposed formula for calculating the thickness of the equipment (ASME, 2015).

$$\boldsymbol{e = \frac{\left(Pi.\frac{D}{2}\right)}{(S.E-0,6.Pi)} + C} \qquad (2)$$

Were *e* is thickness of the side (mm), *Pi* is internal pressure of the equipment (kgf/cm^2), *D* is nominal diameter of the equipment (m), *S* is the permissive tension (kgf/cm^2), *E* is welding efficiency and *C* is over thickness for external corrosion (mm). Details of such methodology can be found elsewhere (Towler and Sinnott, 2013). The costs with importation of chemicals were used to establish their prices, which are obtained elsewhere (MDIC/Aliceweb, 2015).

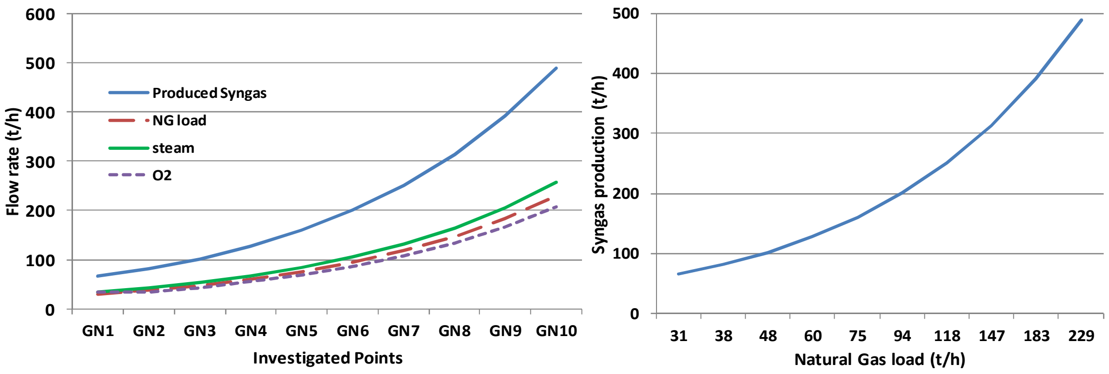
3.4 Results

Appendix C shows the auxiliary tables used for the elaboration of the graphs present below.

3.4.1 Costs of synthesis gas generation unit

Figure 53 shows (a) the value of NG load and syngas flow produced by the synthesis gas generation unit in the investigated points in this work and shows (b) the syngas flow produced as a function of the variation of the nominal natural gas load of the complex.

Figure 53 – (a) Value of NG load and syngas flow produced in the investigated points and (b) Syngas flow produced as a function of the nominal NG load of the unit.

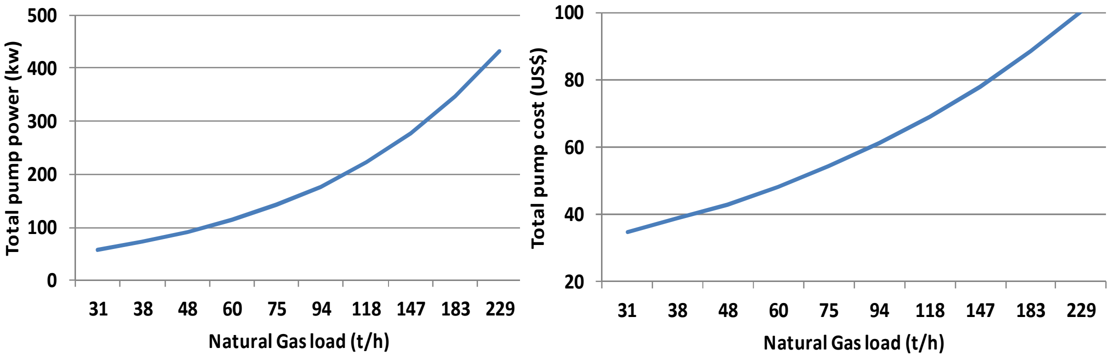


(a) (b)

Source: The Author, 2017.

Figure 54 shows (a) the graph of the pumps power against nominal natural gas load and (b) the graph of the pumps cost of the synthesis gas generation unit against nominal natural gas load of the complex.

Figure 54 – (a) Pump power and (b) pump cost of the syngas generation unit against nominal natural gas load.

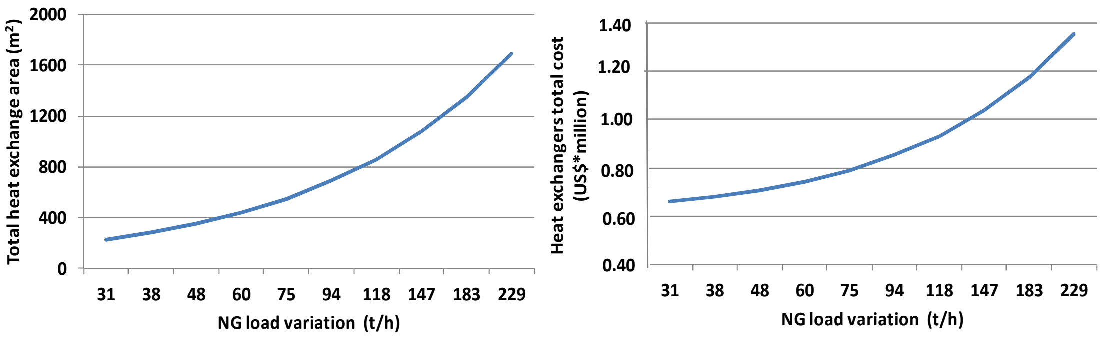


(a) (b)

Source: The Author, 2017.

Figure 55 shows (a) the graph of the heat exchangers area and (b) the graph of the heat exchangers cost of the synthesis gas generation unit against nominal natural load of the complex.

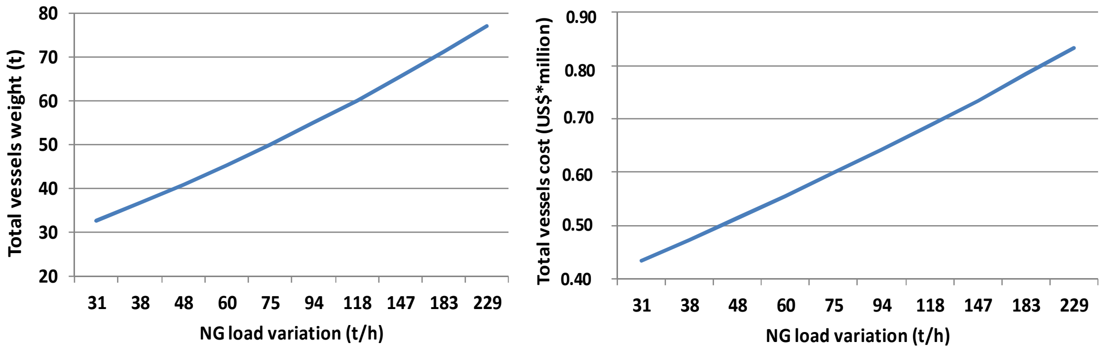
Figure 55 – (a) Heat exchangers area and (b) heat exchangers cost of the synthesis gas generation unit against nominal natural gas load of the complex.


(a) (b)

Source: The Author, 2017.

Figure 56 shows (a) the graph of the pressure vessels weight and (b) the graph of the pressure vessels cost of the synthesis gas generation unit against nominal natural gas load of the complex.

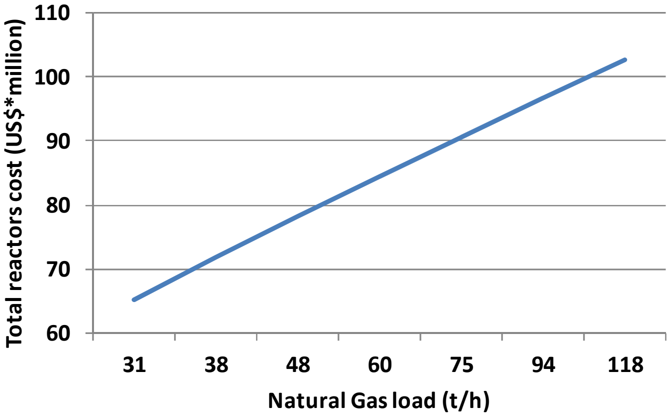
Figure 56 - (a) Pressure vessel weight and (b) pressure vessels cost of the synthesis gas generation unit against nominal natural gas load of the complex.


(a) (b)

Source: The Author, 2017.

Figure 57 shows the graph of the reactors cost against nominal natural gas load of the synthesis gas generation unit.

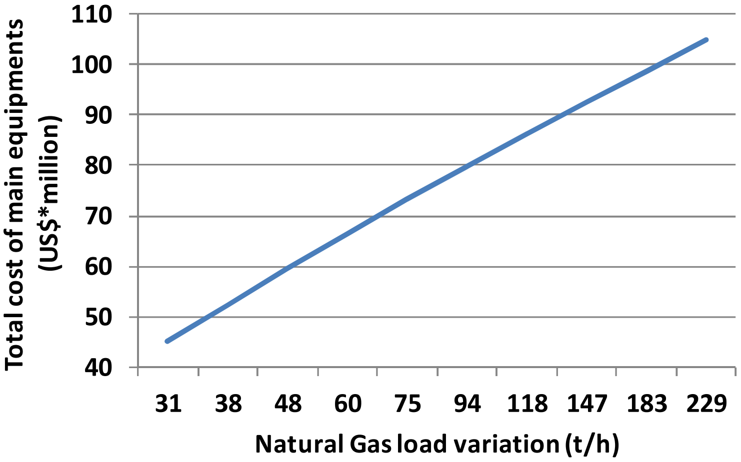
Figure 57 – Reactors cost against nominal natural gas load of the synthesis gas generation unit.



Source: The Author, 2017.

The graphical results presented in Figures 54 to 57 show the behavior of the cost of the main equipments of the synthesis gas generation unit as a function of the capacity of the unit. Making linear the abscissa of the graphs, it is possible to verify that there is a practically stable relation between the cost of the equipments and the nominal capacity of the unit. Figure 58 shows the graph of the main equipment cost against nominal natural gas load of the synthesis gas generation unit.

Figure 58 - Main equipment cost against nominal natural gas load of the synthesis gas generation unit.



Source: The Author, 2017.

The results presented in Figure 58 allow estimating the cost of the acquisition of the equipments of the synthesis gas generation unit as a function of the nominal natural gas load. As expected, there is a relationship between the cost of the equipments and the nominal capacity of the unit, within the limits of the investigated capacity.

Using the data generated on the estimated cost of the main equipments of the syngas generation unit, as well as the methodology presented in Section 3.3, it is possible to estimate the consolidated construction and assembly cost (CAPEX) of the unit. Appendix A present a detailed discussion about the indices and factors used in this estimation. Making this context more objective, Table 06 shows the consolidation of the construction & assembly cost of the synthesis gas generation unit (CAPEX of the unit) to methanol production for the investigated flows. Appendix A presents details about the factors used in this Table.

Table 06 - Consolidation of the construction & assembly cost of the synthesis gas generation unit to methanol production for the investigated flows.

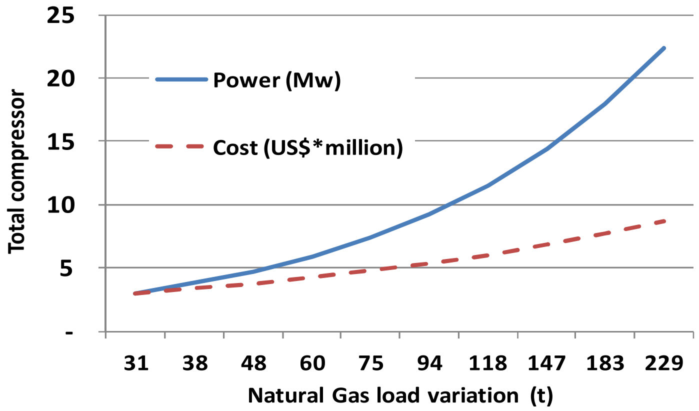
Nominal load of Natural Gas (t/h)		30.7	38.4	47.8	60.0	75.0	94.1	117.5	146.7	183.3	228.8
Total cost of main equipment of syngas unit (US$*million)		45.07	52.46	59.57	66.46	73.17	79.73	86.17	92.51	98.78	104.99
Implantation steps of the methanol production unit	factor	(US$*million)									
Detail design and engineering documents	0.20	9.01	10.49	11.91	13.29	14.63	15.94	17.23	18.50	19.75	20.99
BUILDINGS											
Land, wall/fence, gatehouse, sentry-house	0.15	6.76	7.86	8.93	9.96	10.97	11.95	12.92	13.87	14.81	15.74
Land leveling and containment basin	0.20	9.01	10.49	11.91	13.29	14.63	15.94	17.23	18.50	19.75	20.99
Inter.roads, sidewalks, adm.building, parking, urbaniz, lab.	0.15	6.76	7.86	8.93	9.96	10.97	11.95	12.92	13.87	14.81	15.74
Rainwater, gutters, dikes, passage and elevation boxes	0.10	4.50	5.24	5.95	6.64	7.31	7.97	8.61	9.25	9.87	10.49
Process civil install. (equip. bases, control rooms, pipe ways)	0.15	6.76	7.86	8.93	9.96	10.97	11.95	12.92	13.87	14.81	15.74
ASSEMBLY OF PIPING AND EQUIPMENT											
Equipment assembly	0.30	13.52	15.73	17.87	19.93	21.95	23.91	25.85	27.75	29.63	31.49
Acquisition of piping	0.35	15.77	18.36	20.85	23.26	25.60	27.90	30.16	32.38	34.57	36.74
Piping accessories	0.15	6.76	7.86	8.93	9.96	10.97	11.95	12.92	13.87	14.81	15.74
Piping assembly	0.30	13.52	15.73	17.87	19.93	21.95	23.91	25.85	27.75	29.63	31.49
ELECTRICAL INSTALLATIONS											
Elect.Inst.(cables, panels, controlroom, emerg. generatator)	0.20	9.01	10.49	11.91	13.29	14.63	15.94	17.23	18.50	19.75	20.99
Substation and high voltage switches and circuit breakers	0.15	6.76	7.86	8.93	9.96	10.97	11.95	12.92	13.87	14.81	15.74
Control instr. (sensors, transmitters, valves, panels, cables)	0.35	15.77	18.36	20.85	23.26	25.60	27.90	30.16	32.38	34.57	36.74
PLCs, IHM, control software, int.networks, no-breaks, panels	0.20	9.01	10.49	11.91	13.29	14.63	15.94	17.23	18.50	19.75	20.99
OTHER EQUIPMENT AND CONSUMABLE MATERIALS											
Secondary equipment and accessories	0.10	4.50	5.24	5.95	6.64	7.31	7.97	8.61	9.25	9.87	10.49
Safety equip. (tank, nets, pumps, hydrants, water cannons)	0.15	6.76	7.86	8.93	9.96	10.97	11.95	12.92	13.87	14.81	15.74
Catalysers, molecular sieves, membranes	0.20	9.01	10.49	11.91	13.29	14.63	15.94	17.23	18.50	19.75	20.99
Product storage tanks	0.15	6.76	7.86	8.93	9.96	10.97	11.95	12.92	13.87	14.81	15.74
Lubricants, filters, cartridges, consumables, chemical prod.	0.05	2.25	2.62	2.97	3.32	3.65	3.98	4.31	4.62	4.93	5.24
INSPECTION, TESTS, CONNECTIONS, COMMISSIONING											
Control loops tests and communication with internal networl	0.10	4.5	5.24	5.95	6.64	7.31	7.97	8.61	9.25	9.87	10.49
Inspection and painting	0.20	9.01	10.49	11.91	13.29	14.63	15.94	17.23	18.50	19.75	20.99
Offsites (external connections)	0.20	9.01	10.49	11.91	13.29	14.63	15.94	17.23	18.50	19.75	20.99
Commissioning and pre-operation	0.15	6.76	7.86	8.93	9.96	10.97	11.95	12.92	13.87	14.81	15.74
CONTINGENCY, LICENSES AND INDUSTRIAL FACILITIES											
Contingency and Health, Safety and Environment - HSE	0.10	4.50	5.24	5.95	6.64	7.31	7.97	8.61	9.25	9.87	10.49
Restrictions and environmental licenses	0.10	4.50	5.24	5.95	6.64	7.31	7.97	8.61	9.25	9.87	10.49
Industrial facilities (considering apportionments)	0.30	13.52	15.73	17.87	19.93	21.95	23.91	25.85	27.75	29.63	31.49
TRAINING											
Training of operational, maintenance, inspection teams	0.07	3.15	3.67	4.17	4.65	5.12	5.58	6.03	6.47	6.91	7.34
Total fixed cost of the complex – CAPEX (US$*million)		217	253	287	320	353	384	415	446	476	506

Source: The Author, 2017.

3.4.2 Costs of methanol production unit

Subsequently, the cost of the methanol production unit is estimated using the same methodology used to estimate the cost of the synthesis gas generation unit. Figure 59 shows the graph of the demanded compression power and compression cost of methanol production unit against natural gas load of the complex.

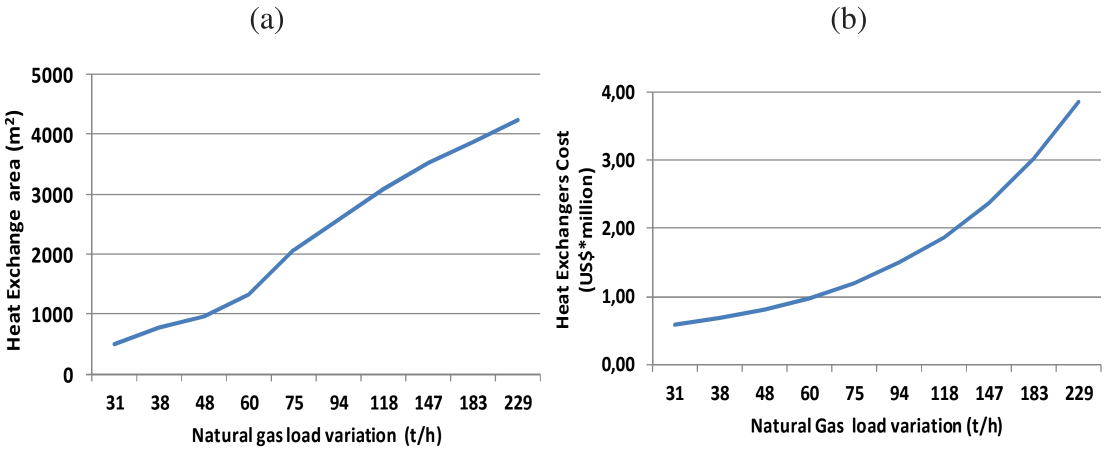
Figure 59 – Demanded compression power and compression cost of methanol production unit against natural gas load of the complex.



Source: The Author, 2017.

Figure 60 shows (a) the graph of the total thermal exchange area and (b) the total heat exchange cost of the methanol production unit against natural gas load of the complex.

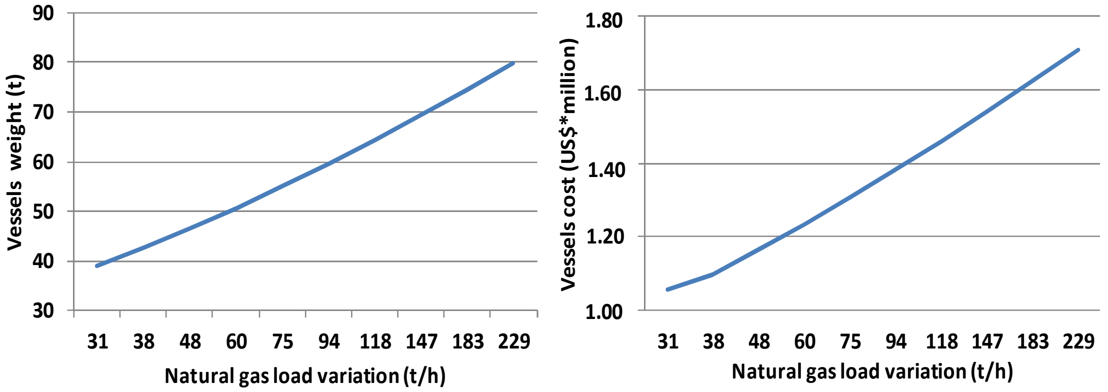
Figure 60 – (a) Total heat exchange area and (b) total heat exchange cost of the methanol production unit against natural gas load of the complex.



Source: The Author, 2017.

Figure 61 shows (a) the graph of the pressure vessels weight and (b) the graph of the pressure vessels cost of the methanol production unit against natural gas load of this complex.

Figure 61 - (a) Pressure vessels weight and (b) pressure vessels cost of the methanol production unit against natural gas load of this complex.

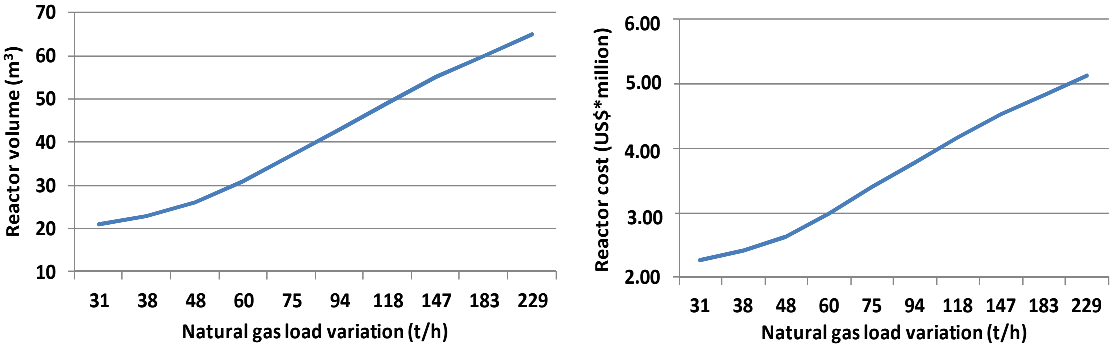

(a)

(b)

Source: The Author, 2017.

Figure 62 shows (a) the graph of reactor volume and (b) the graph of reactor cost of the methanol production unit against natural gas load of the complex.

Figure 62 – (a) Reactor volume and (b) reactor cost of the methanol production unit against natural gas load of the complex.

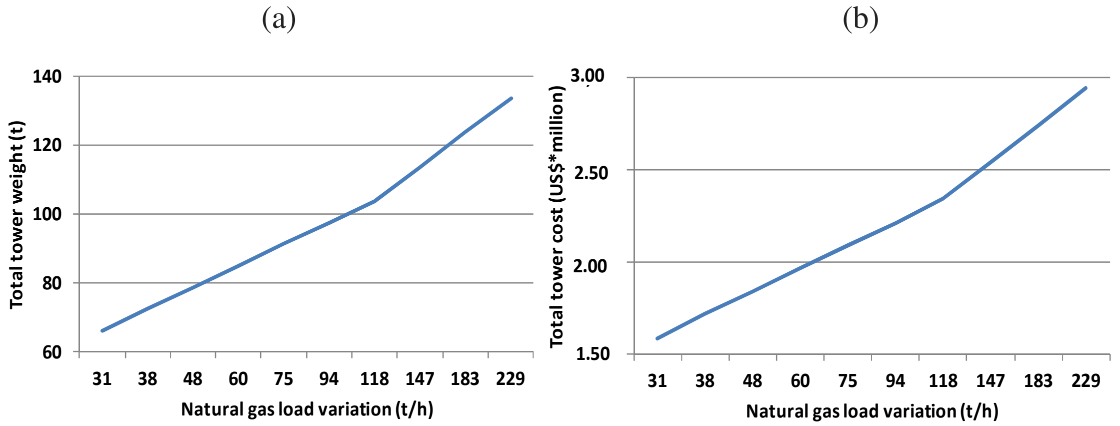

(a)

(b)

Source: The Author, 2017.

Figure 63 shows (a) the graph of tower weight and (b) the graph of the tower cost of the methanol production unit against natural gas load of the complex.

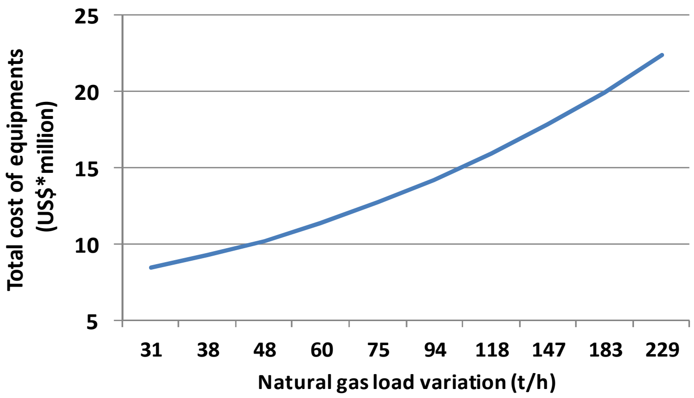
Figure 63 – (a) Tower weight and (b) tower cost of the methanol production unit against natural gas load of the complex.



Source: The Author, 2017.

The results presented in Figures 59 to 63 show the behavior of the cost of the main equipments of the methanol production unit as a function of the capacity of the unit. Making linear the abscissa of the graphs, it is possible to verify that there is a virtually stable relation between the cost of the equipments and the nominal capacity of the unit. Figure 64 shows the graph of the main equipment cost of the methanol production unit against natural gas load of this complex.

Figure 64 - Main equipment cost of the methanol production unit against natural gas load of the complex.



Source: The Author, 2017.

The result presented in Figure 64 allows estimating the acquisition cost of the equipments of the methanol production unit as a function of the nominal natural gas load. As expected, there is a relationship between the cost of the equipments and the nominal capacity of the unit, within the limits of the investigated capacity.

Using the data generated on the estimated cost for the main equipments of the methanol production unit and the methodology presented on Section 3.3, it is possible to estimate the consolidated construction and assembly cost (CAPEX) of the unit. Table 07 presents the consolidation of the total cost of construction & assembly of the methanol production unit (CAPEX of the unit) for the investigated flow rate points.

Table 07 - Consolidation of the total cost of construction & assembly (CAPEX) of the methanol production unit for the investigated flow rate points.

Nominal load of Natural Gas (t/h)		30.7	38.4	47.8	60.0	75.0	94.1	117.5	146.7	183.3	228.8
Total cost of main equipment of methanol unit (US$*million)		8.52	9.29	10.21	11.39	12.75	14.23	15.89	17.82	19.93	22.35
Implantation steps of the methanol production unit	factor	(US$*million)									
Detail design and engineering documents	0.20	1.70	1.85	2.04	2.27	2.55	2.84	3.17	3.56	3.98	4.47
BUILDINGS											
Land, wall/fence, gatehouse, sentry-house	0.15	1.27	1.39	1.53	1.70	1.91	2.13	2.38	2.67	2.99	3.35
Land leveling and containment basin	0.20	1.70	1.85	2.04	2.27	2.55	2.84	3.17	3.56	3.98	4.47
Inter.roads, sidewalks, adm.building, parking, urbaniz, lab.	0.15	1.27	1.39	1.53	1.70	1.91	2.13	2.38	2.67	2.99	3.35
Rainwater, gutters, dikes, passage and elevation boxes	0.10	0.85	0.92	1.02	1.13	1.27	1.42	1.58	1.78	1.99	2.23
Process civil install. (equip. bases, control rooms, pipe ways)	0.15	1.27	1.39	1.53	1.70	1.91	2.13	2.38	2.67	2.99	3.35
ASSEMBLY OF PIPING AND EQUIPMENT											
Equipment assembly	0.30	2.55	2.78	3.06	3.4	3.82	4.27	4.76	5.34	5.98	6.70
Acquisition of piping	0.35	2.98	3.25	3.57	3.98	4.46	4.98	5.56	6.23	6.97	7.82
Piping accessories	0.15	1.27	1.39	1.53	1.70	1.91	2.13	2.38	2.67	2.99	3.35
Piping assembly	0.30	2.55	2.78	3.06	3.4	3.82	4.27	4.76	5.34	5.98	6.70
ELECTRICAL INSTALLATIONS											
Elect.Inst.(cables, panels, controlroom, emerg. generatator)	0.20	1.70	1.85	2.04	2.27	2.55	2.84	3.17	3.56	3.98	4.47
Substation and high voltage switches and circuit breakers	0.15	1.27	1.39	1.53	1.70	1.91	2.13	2.38	2.67	2.99	3.35
Control instrum. (sensors, transmitters, valves, panels, cables)	0.35	2.98	3.25	3.57	3.98	4.46	4.98	5.56	6.23	6.97	7.82
PLCs, IHM, control software, int.networks, no-breaks, panels	0.20	1.70	1.85	2.04	2.27	2.55	2.84	3.17	3.56	3.98	4.47
OTHER EQUIPMENT AND CONSUMABLE MATERIALS											
Secondary equipment and accessories	0.10	0.85	0.92	1.02	1.13	1.27	1.42	1.58	1.78	1.99	2.23
Safety equip. (tank, nets, pumps, hydrants, water cannons)	0.15	1.27	1.39	1.53	1.70	1.91	2.13	2.38	2.67	2.99	3.35
Catalysers, molecular sieves, membranes	0.20	1.70	1.85	2.04	2.27	2.55	2.84	3.17	3.56	3.98	4.47
Product storage tanks	0.15	1.27	1.39	1.53	1.70	1.91	2.13	2.38	2.67	2.99	3.35
Lubricants, filters, cartridges, consumables, chemical prod.	0.05	0.42	0.46	0.51	0.56	0.63	0.71	0.79	0.89	0.99	1.11
INSPECTION, TESTS, CONNECTIONS, COMMISSIONING											
Control loops tests and communication with internal network	0.10	0.85	0.92	1.02	1.13	1.27	1.42	1.58	1.78	1.99	2.23
Inspection and painting	0.20	1.70	1.85	2.04	2.27	2.55	2.84	3.17	3.56	3.98	4.47
Offsites (external connections)	0.20	1.70	1.85	2.04	2.27	2.55	2.84	3.17	3.56	3.98	4.47
Commissioning and pre-operation	0.15	1.27	1.39	1.53	1.70	1.91	2.13	2.38	2.67	2.99	3.35
CONTINGENCY, LICENSES AND INDUSTRIAL FACILITIES											
Contingency and Health, Safety and Environment - HSE	0.10	0.85	0.92	1.02	1.13	1.27	1.42	1.58	1.78	1.99	2.23
Restrictions and environmental licenses	0.10	0.85	0.92	1.02	1.13	1.27	1.42	1.58	1.78	1.99	2.23
Industrial facilities (considering apportionments)	0.30	2.55	2.78	3.06	3.4	3.82	4.27	4.76	5.34	5.98	6.70
TRAINING											
Training of operational, maintenance, inspection teams	0.07	0.59	0.65	0.71	0.79	0.89	0.996	1.11	1.24	1.39	1.56
Total fixed cost of the complex – CAPEX (US$*million)		41	45	49	55	61	69	77	86	96	108

Source: The Author, 2017.

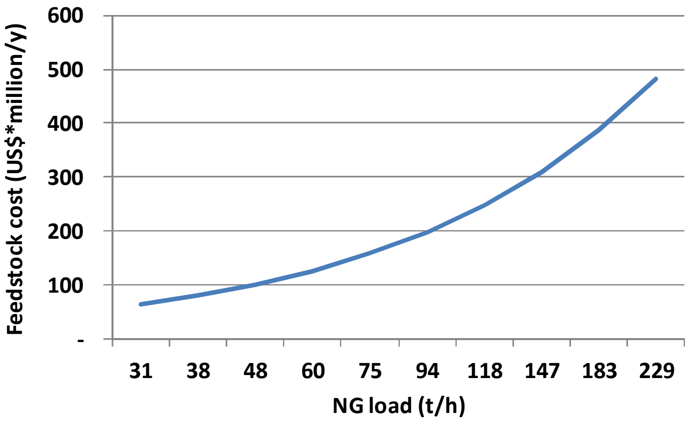
The methodology chosen to estimate the cost of equipments, based on the indicated reference (Towler and Sinnott, 2013), imposes some restrictions on the size of equipments. Thus, for higher values of nominal capacity of the units, it is necessary to increase the number of equipments (operating in parallel), to remain in the flow range allowed by the method. This constraint may cause some deviation in the expected linearity between the cost of the equipments and the nominal capacity of the production unit. Appendix A present a detailed discussion about the indices and factors used in Table 07.

3.4.3 Calculation of feedstock cost of the complex

The average reference price for the commercialization of natural gas in Brazil was defined based on the average prices practiced in the domestic market in the last five years, valued at US$ 247.30 per thousand cubic meters of natural gas (ANP, 2015). This average price was used to calculate the cost of the raw material for the proposed complex.

According to the investigated values of nominal natural gas load of the synthesis gas generation unit, Figure 65 shows the graph of the expected of the raw material cost for the complex as a function of the natural gas load variation, considering 24 hours per day and 330 days per year of operating.

Figure 65 – Estimation of the raw material cost for the complex for the nominal load values investigated.

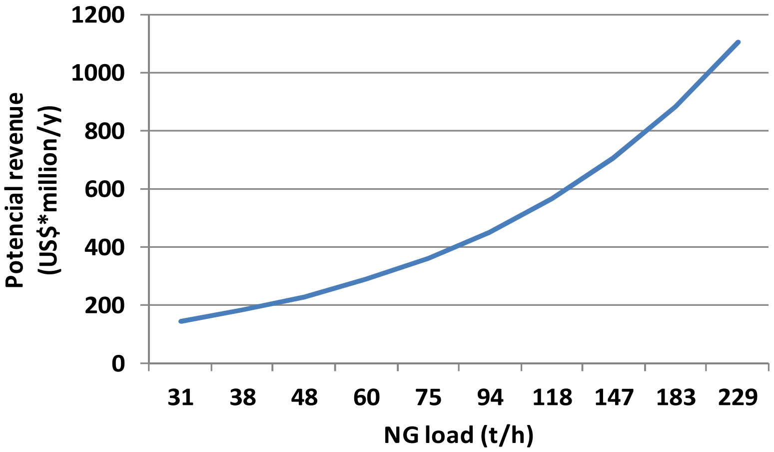


Source: The Author, 2017.

3.4.4 Calculation of the potential revenues from the complex

The average value of imports of methanol from 2011 to 2015 by Brazil (US$ 399.92/t on imported methanol) was used for the calculation of the potential revenue of the complex, as registered in the MDIC/Aliceweb system (MDIC, 2016). Figure 66 shows the graph of the potential gains of the complex as a function of the natural gas load variation, based on the amount of currency disbursement with methanol imports, according to data recorded in the MDIC/Aliceweb system (MDIC, 2016). The amount of methanol produced for each natural gas load value is given by the simulations of the syngas and the methanol plant.

Figure 66 – Graph of the potential project revenue for the nominal load values investigated.

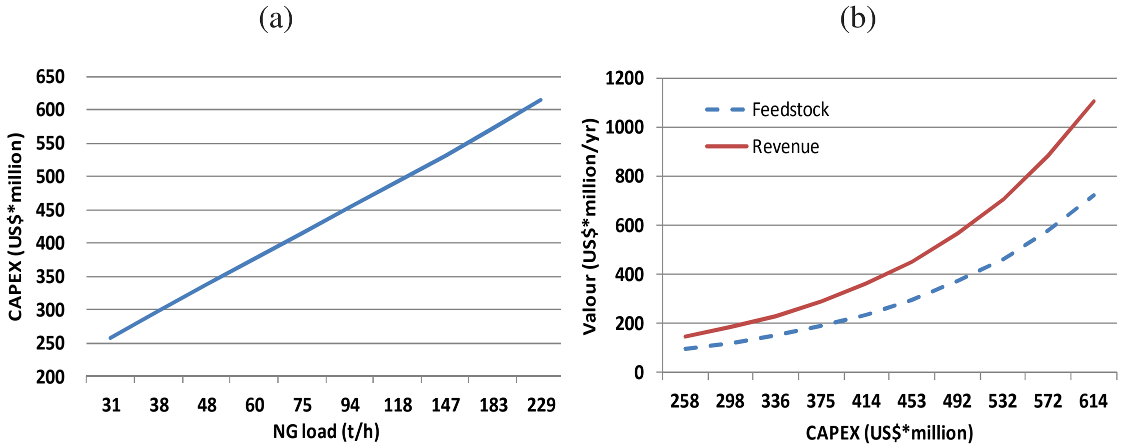


Source: The Author, 2017.

3.4.5 Complex implementation costs (CAPEX)

Figure 67 shows (a) the graph of the total consolidated cost (CAPEX) against Natural gas load of the complex and (b) the values of the Feedstock and Revenue of implementation of the complex (CAPEX), considering the construction of the synthesis gas generation unit and also the methanol production unit for each point investigated of natural gas load of the complex.

Figure 67 - (a) Consolidated cost (CAPEX) against natural gas load of the complex and (b) Values of the feedstock and revenue of the methanol production complex (CAPEX) for each investigated natural gas load or the complex.


(a) (b)

Source: The Author, 2017.

3.4.6 Implementation of the preliminary project Net Present Value (NPV)

Table 08 presents the assumptions used to calculate the Net Present Value (NPV) for each natural gas load value investigated. These premises are defined by the Technical-Economic Feasibility Study (TEFS) of the project.

Table 08 – Economic assumptions used in the calculation of the NPV.

INVESTIMENTS	TOTAL	ANNUAL DISTRIBUTION		
Capital Expenditure - CAPEX (US$*billion/y)		1st year	2nd year	3rd year
Annual disbursement		10%	20%	70%
DISBURSEMENTS		TAXES		
Raw materials cost (US$*billion/y)		PIS/COFINS/ISS/CSSL		23.25%
Operational Expenditure - OPEX (% CAPEX/y)	3%	Income tax		25%
ECONOMIC ASSUNPTIONS		INVESTIMENT REVENUE		
Minimum Attractiveness Rate - MTR (% a.a)	10%	Total (US$*billion/y)		
Economic Life of the project (years)	25	Start-up from the 4th year		
Depreciation: Linear in the horizon of studyNPV: Net Present Value				
NOTE: Tax benefits for tax recovery were not considered				

Source: The Author, 2017.

Table 09 shows the consolidated result of the technical-economic feasibility study (TEFS) performed for the methanol production complex, considering a Minimum Attractiveness Rate (MAR) of 10%, with a sensitivity analysis of 20% higher (MAR = 12%) and 20% lower (MAR = 8 %).

Table 09 - Consolidated results of TEFS of methanol production complex.

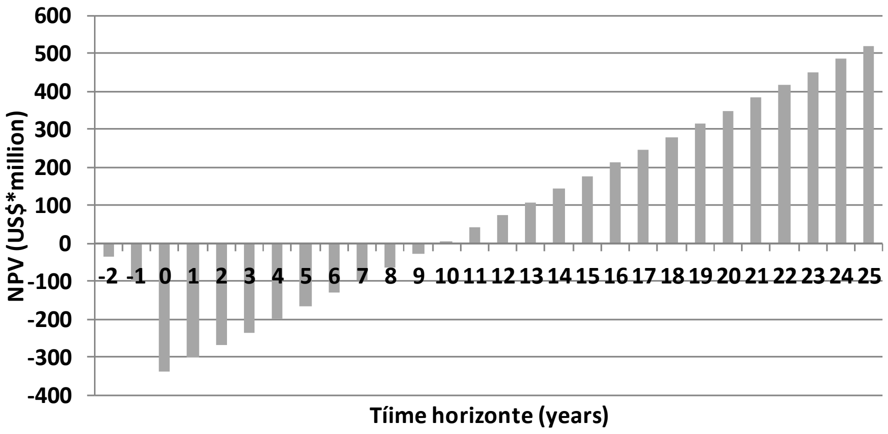
NG	Result of technical-economical feasibility study					
load	CAPEX of units (US$*million)			feedstock	OPEX	Revenue
(t/h)	syngas	methanol	total	(US$*million/y)		
30.7	217.26	41.08	258.34	138.42	7.75	147.78
38.4	252.88	44.81	297.70	173.05	8.93	184.78
47.8	287.14	49.25	336.40	215.49	10.09	230.55
60.0	320.34	54.91	375.25	270.43	11.25	289.21
75.0	352.68	61.46	414.14	338.24	12.42	361.71
94.1	384.31	68.61	452.93	424.23	13.58	451.03
117.5	415.35	76.58	491.93	529.87	14.75	565.37
146.7	445.92	85.92	531.85	661.49	15.95	705.68
183.3	476.13	96.11	572.24	826.50	17.16	884.96
228.8	506.06	107.77	613.83	1031.65	18.41	1104.77

Source: The Author, 2017.

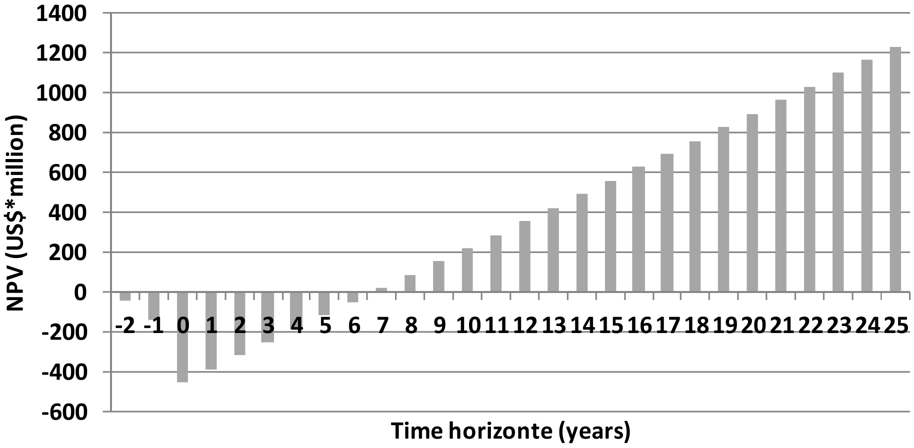
Figure 68 presents the consolidated result of NPV carried out, considering the economic life of the project in twenty five years and no discount on the price of raw material or taxes.

Figure 68 - Result of NPV carried out considering, a nominal load (a) equal to 200 ton/h of NG, (b) equal to 488 ton/h of NG.

(a)



(b)



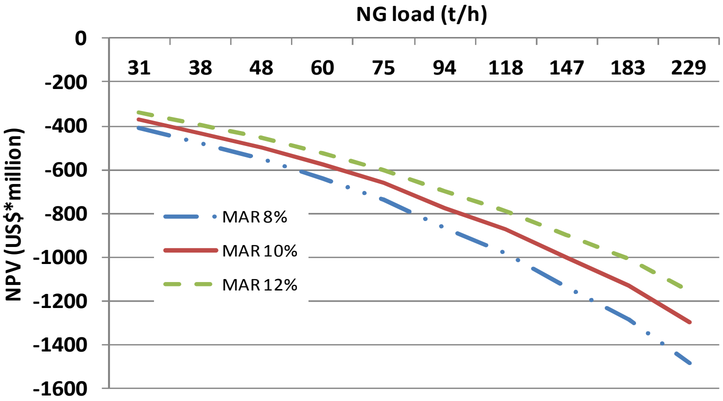
Source: The Author, 2017.

The behavior of the graphs presented in the Figures 68 is explained by the data presented in Table 09, where it is evident that the difference between the sum of the cost of the raw material and the cost of the OPEX and the value of the revenue of the complex is insufficient to pay the service of the CAPEX debt invested in the two cases considered.

3.4.7 Net Present Value (NPV) calculated

The results of the calculation of the Net Present Value (NPV) presented in both Figure 68 show that the proposed methanol production complex is not economically feasible for any investigated capacity value, considering the cost of the raw material (natural gas) in Brazil and the total percentage of taxes, according to Brazilian legislation. Figure 69 shows the evolution of the NPV of the project as a function of the nominal natural gas load values investigated, considering a Minimum Attractiveness Rate (MAR) of 10%, with a sensitivity analysis of 20% higher (MAR = 12%) and 20% lower (MAR = 8%). The graphic showed in the Figure 69 consolidates the result that none of the capacity values investigated in this article allows the feasibility of the project without some kind of external incentive.

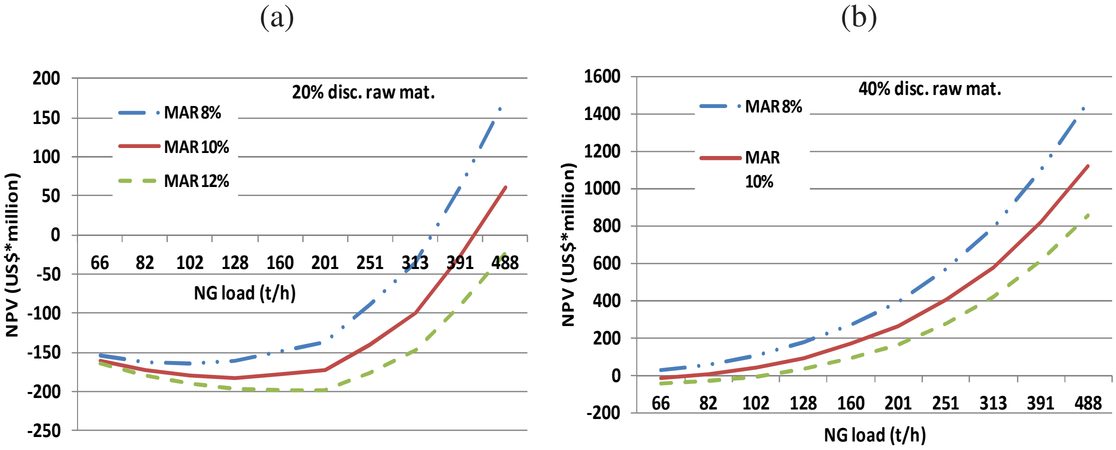
Figure 69 - Evolution of the NPV calculated of the project by nominal natural gas load variation, considering zero discounts in the cost of raw material and taxation.



It should be emphasized that this result is in accordance with the higher value of natural gas in the Brazilian domestic market, compared to the price of gas in the US market and in large exporters of the product. Due to this negative result, the technical-economic study investigated which conditions of discounts in the raw material value would make possible the complex, generating a positive NPV.

Figure 70 presents the NPV results, considering respectively, (a) 20% and (b) 40% of the discount in raw material cost of the complex (NG load cost).

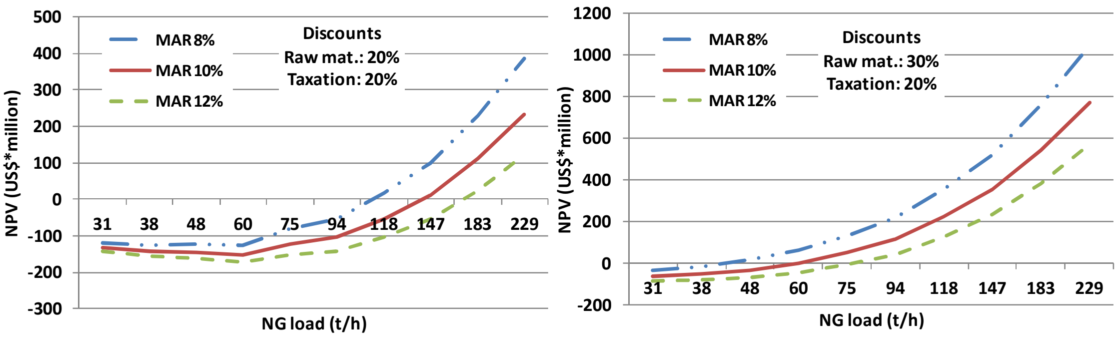
Figure 70 - Evolution of the NPV calculated of the project by nominal natural gas load variation, considering (a) 20% and (b) 40% of the discount in the cost of raw material of the complex.


(a) (b)

Source: The Author, 2017.

Results demonstrate that the complex of about 200 ton/h of natural gas flow is only economically feasible for discounts higher to 30% on the cost of the raw material. For lower flows of natural gas load, the project is only feasible from a 40% of discount on the cost of the raw material. Considering that 40% is a very high discount to become reality, an option to try to make the project feasible is to combine discount on raw material cost with discount on taxes due to the complex. Figure 71 presents the NPV results, considering (a) 20% and (b) 30% of the discount in raw material cost and 20% of discount on the taxation of the complex.

Figure 71 - Evolution of the NPV calculated of the project against nominal natural gas load variation, considering (a) 20% and (b) 30% of the discount in raw material cost and 20% of discount on the taxation of the complex.


(a)

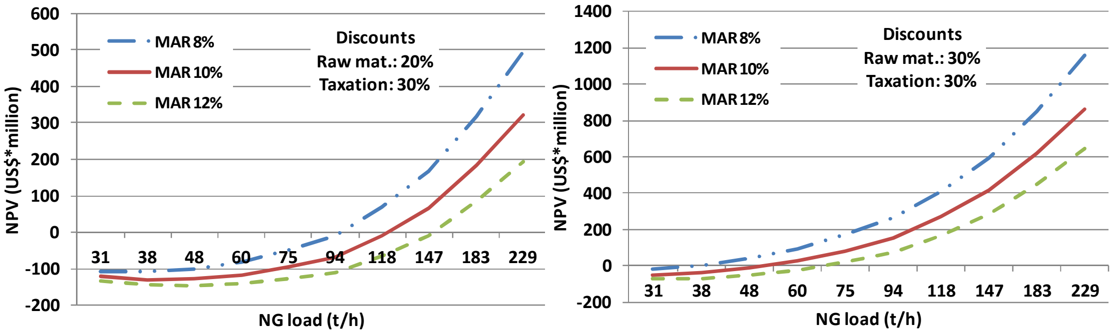
(b)

Source: The Author, 2017.

The results presented in Figure 71 shows that the complex can be economically feasible with some financial incentive, in the form of the price reduction of the raw material, combined with a discount in the taxation of the project. Basically, discounts of the order of 20% on the raw material and 20% on the taxation make the project economically feasible from the nominal capacity of 260 ton/h of natural gas. On the other hand, discounts of the order of 30% on raw material and 20% on taxation make the project economically feasible from the nominal capacity of 110 ton/h of natural gas.

Figure 72 presents the NPV results, considering (a) 20% and (b) 30% of the discount in raw material cost and 30% of discount on the taxation of the complex.

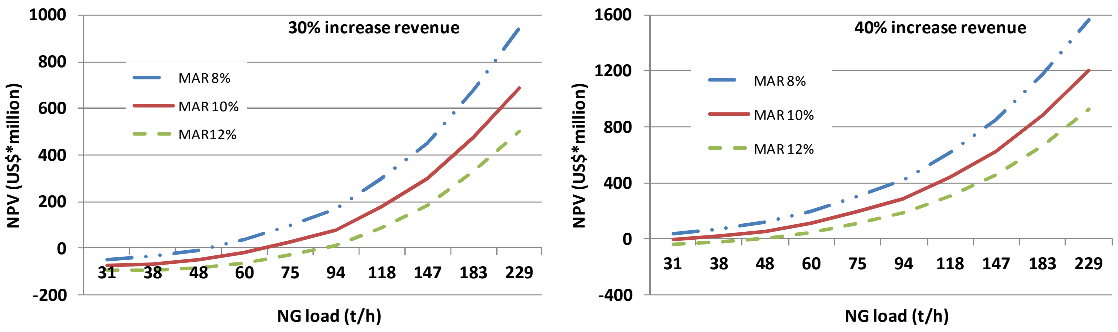
Figure 72 - Evolution of the NPV calculated of the project against nominal natural gas load variation, considering 30% of the discount on the taxation; (a) 20% and (b) 30% of the discount in the cost of raw material.


(a) (b)

Source: The Author, 2017.

The results presented in Figures 72 confirm that the complex can be economically feasible considering a reduction in the price of the raw material and in the taxation of the project. It is possible to verify that a discount of the order of 20% on the raw material and 30% on the taxation make the project economically feasible from the nominal capacity of 180 ton/h of natural gas. Otherwise, discounts of the order of 30% on raw material and 30% on taxation make the project economically feasible from the nominal capacity of 100 ton/h of natural gas. On the other hand, Figure 73 indicates that an increase in the price of methanol can make the alcohol production unit feasible without any discount on the raw material or taxation, evidencing that the presented economic result is not absolute and that variations in the cost of acquisition of methanol can modify the result of NPV.

Figure 73 - Evolution of the NPV calculated of the project against nominal natural gas load variation, considering (a) 20% and (b) 40%) of the increase of the revenue of the complex.


(a) (b)

Source: The Author, 2017.

The results show that revenue increases of the order of 30% already allow the feasibility of units with larger nominal capacity. From a 40% increase in revenue, practically all the points investigated allow economic viability.

3.5 Conclusions

The proposed complex for methanol production from natural gas converted into synthesis gas is still not feasible for any of the nominal capacities studied, due to the high price of natural gas in the Brazilian domestic market, as compared with the American market, for example. This main reason does not allow the simple viability of the investment, although this project is of extreme strategic importance for the country.

Nevertheless, a simple simulation and economic analysis with the application of discounts in the raw material of the project allows to verify that the complex is could be feasible, being enough for that a set of efforts by the part of the involved ones (government, investors, producers of gas natural, engineering companies).

It is not difficult to make the complex economical feasible by reducing the price of the raw material (NG), although a reduction in the taxation of the projects can facilitate the economic viability of the project, making the investment more attractive, together with a reduction in the cost of the raw material.

Analyzing the data generated and considering the prices of natural gas in the domestic market and the methanol price in the international market, it can be said that a complex of methanol production from natural gas, as proposed in this study, has a positive economic viability to the nominal capacity of the order of 100 ton/h of natural gas, or greater. These nominal load values translate into large production plants, in order to achieve an enough scale gain for project viability. For the economic analysis, it can be considered that this project has a perfect adherence to the governmental strategy of expansion and strengthening of the Brazilian chemical industry, eliminating the Brazilian dependence on imports of a so important basic product for the industry.

The study shows that a increase in the value of the alcohol molecule can bring economic data different from the one presented, indicating the economic feasibility of the methanol production complex, even maintaining current price of the raw material and the percentages of taxation.

4. TECHNICAL-ECONOMIC ANALYSIS OF THE PRODUCTION OF AMMONIA FROM NATURAL GAS IN BRAZIL

Abstract

This article presents a detailed study on the technical and economic feasibility of implementing a project to produce ammonia from natural gas as a basic raw material, considering Brazilian specificities and needs. The study investigates the main technical and economic issues related to the implementation of an industrial ammonia production plant, analyzing different values of nominal loads of the complex. The necessary investment and the potential revenue of each nominal capacity value are analyzed, generating results that allow the presentation of conclusions about the best economic conditions for the feasibility of the project. The total value of the investment in an ammonia production plant is calculated as a function of the nominal capacity variation of the complex, considering in addition to the methanol conversion unit, also a synthesis gas plant to produce the necessary hydrogen for the ammonia production. The methodology established by the authors is based on the calculation of the main equipment cost of the unit and the cost of implementation of the project, as well as the variable costs (raw material, operational cost and taxes) to determine its economic feasibility. The project's potential operating revenue is calculated based on average international ammonia prices. The net present value analysis of the different nominal load values of the project allows determining the best range of nominal capacity of the project, considering the economical perspective. On the other hand, the use of international ammonia prices and the natural gas price in the domestic market on the economic evaluation of the project ensures the correct measurement of the level of competitiveness that such a project would have in the international market.

Keywords: natural gas, syngas, ammonia, technical-economic evaluation.

Introduction

The use of natural gas as a source of raw material in chemical transformation processes for the production of important commodities in the chemical industry is currently referred to as the noblest use of gas (Dong *et al.,* 2013). Several authors have ratified this approach in their technical works (Galadima and Muraza, 2015; Xiang *et al.,* 2015).

Although this is not yet the Brazilian reality, there is an enormous potential for expansion of the Brazilian natural gas market in the domestic production of chemicals, currently imported in large quantities, requiring the expenditure of millions of dollars in foreign exchange (ABIQUIM, 2015).

Brazil currently imports about 25% of the ammonia it consumes (MDIC/ Aliceweb, 2015). As this is the main input for the production of urea, and considering the dependence of the Brazilian economy on the performance of agribusiness (Hernandez and Torero, 2011), the expansion of the national ammonia production could have a great economic and strategic impact in the strengthening of the Brazilian economy. In order to exploit this potential, the authors present in this work wide study on the production of ammonia from the hydrogen, arising from a unit of synthesis gas generation that uses the natural gas as basic raw material.

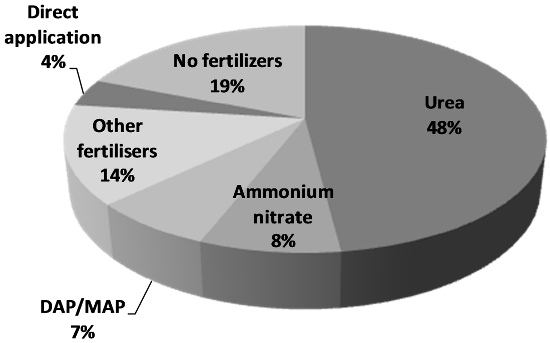
Synthesis and ammonia gas production units were simulated in PETRO-SIM® and HYSYS® softwares, according to common engineering practices, in order to determine the production potential of the units from different natural gas loads. The economic performance of the project for each nominal load value was determined through a methodology based on the design, calculation of the unit equipment cost and the implementation costs of the project (CAPEX), the variable costs (OPEX) and operating income. The data obtained allow determining the size of the industrial complex that presents the best economic performance, besides measuring the level of competitiveness of the complex against the international market prices of the product produced.

4.1 The ammonia market and its applications

The United States is currently the largest importer of ammonia, accounting for around 40% of world trade, while Europe accounts for approximately 25% of this trade, even at a higher cost of production (Bicer *et al.* 2016). In the near future, further growth in Asian imports is expected, mainly because of industrial development and the increased use of fertilizer products (Potashcorp, 2016).

According to Kyriakou *et al.* (2016) and Giddey *et al.* (2013), the current world production of ammonia is more than 200 million tons per year. Klinsrisuk *et al.* (2015) indicate that more than 80% of this quantity is used for the production of fertilizers. In addition to its main use as a source of nitrogen for agriculture, mainly in the form of urea, ammonia is also used as refrigerant in industrial refrigeration cycles, plastics, pharmaceuticals and the explosives industry (Edrisi et al, 2014). Figure 74 shows the main uses of ammonia in the period from 2010 to 2013.

Figure 74 – Principal uses of ammonia in the period from 2010 to 2013.



Source: Bicer, *et al.,* 2016.

The necessity of the increase food production has led many populous countries to seek industrial fertilizer production in the domestic market as a way of ensuring the food security of their populations (Aragaw and Disney, 1977). The use of ammonia and urea is strongly linked to the agricultural strategies of countries such as Brazil, which have shown a rapid and continuous growth in the use of industrially produced fertilizers, mainly nitrogen-based fertilizers.

Ammonia has been proposed to serve as a means of energy storage, constituting an alternative form of clean energy (Lan *et al.,* 2012; Giddey *et al.,* 2013). Generally, ammonia as a sustainable fuel can be used in all types of combustion engines, gas turbines, burners with only minor modifications and directly in fuel cells[1], which is an important advantage compared to other types of fuels (Lan and Tao, 2014). In combustion engines, a study reported that the cost of ammonia as fuel could reach US$ 2.00 per 100 km, considering the performance of an average car (Zamfirescu and Dincer, 2008).

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[1] *Fuel cells are devices that transform electrical energy through an electrochemical cycle, rather than a thermal cycle. The electrochemical cycle is not subjected to the thermodynamic limitations of a conventional Carnot cycle, thus offering higher energy conversion efficiency (Metkemeijer and Achard, 1994).*

In fuel cells, a number of studies have been presented, from the conversion of ammonia to hydrogen, to the use of ammonia directly in cells. AFIF *et al.* (2006), in their comparative study on energy generation methods from ammonia-fueled fuel cells, concluded that the use of ammonia as a source of hydrogen is capable of providing high energy density in transport systems. The use of ammonia as a source of hydrogen would bypass the logistical problems associated with the transport and storage of hydrogen (Koike *et al.,* 2012; Klinsrisuk *et al.,* 2015, Nozari and Karabeyoglu, 2015). According to Wojcik *et al.* (2003), ammonia presents an inexpensive and convenient form of hydrogen source and storage, and is particularly suitable for the transport segment or small-scale industrial production systems. Metkemeijer and Achard (1994) also concluded in their comparative study that ammonia is a more interesting choice than methanol for use as an indirect fuel in a hydrogen/air fuel cell, as a function of the greater overall conversion efficiency of ammonia. Lan *et al.* (2012) stated that significant progress has been made in fuel-cell projects using ammonia to generate electricity for applications in the transportation segment.

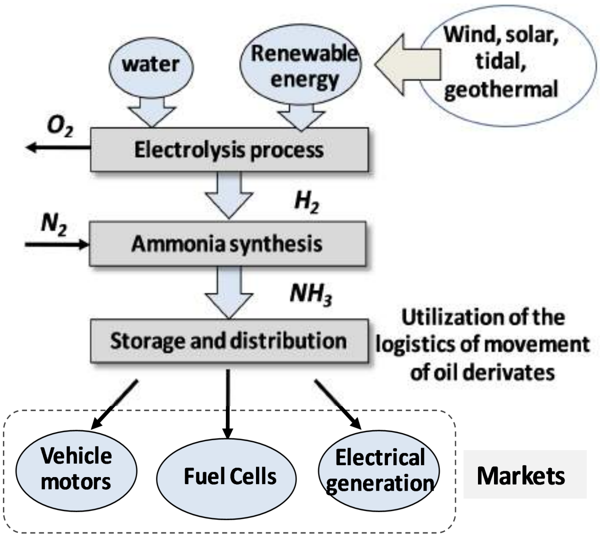
Such markets, which have not yet been developed on a large scale, have the potential to increase greatly the level of world consumption of the product, making industrial ammonia production complexes, such as the one proposed in this paper, more easily justified, because just like hydrogen, ammonia can be considered carbon free by end-users of fuels, in addition to having a high octane number (Zamfirescu and Dincer, 2008).

In relation to environmental preservation, Jilvero *et al.* (2015) proposed a system of CO_2 capture of gases exhausted from combustion processes using ammonia as an absorbent fluid, taking advantage of the high volatility and chemical stability of the ammonia and the consequent lower thermal demand for the regeneration of the solvent. A number of other authors have proposed carbon capture by absorption with ammonia (Mathias *et al*., 2009; Valenti *et al.,* 2012; Zhuang *et al.,* 2011). Han *et al.* (2012) presented a consolidated study on the challenges and opportunities of these technologies. In the same direction, Voldsund *et al.* (2015) explored and advocated the use of hydrogen produced from ammonia as a transition fuel. Miura and Tezuca (2014) presented a detailed study on the potential use of ammonia as a competitive mode of energy transport in terms of conversion efficiency, cost and CO_2 emissions.

Recent studies also indicate a worldwide trend towards sustainable projects for ammonia production plants from hydrogen, generated by renewable sources such as the use of water electrolysis by wind power (Allman and Daoutidis, 2016).

Solar energy generation systems may also be feasible through the use of ammonia. Patil *et al.* (2014) proposed the use of liquid ammonia as a "renewable energy buffer" in solar energy systems, where ammonia would serve as an accumulator, storing energy for later use. Figure 75 summarizes the concept of using ammonia as a sustainable fuel produced from renewable and carbon-free sources for application in diverse markets.

Figure 75 – Application of ammonia as a carbon-free fuel.



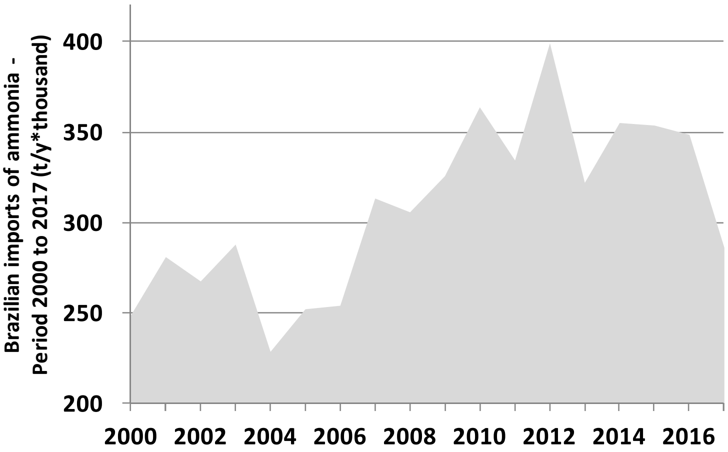
Source: The Author, 2017.

4.2 Brazilian ammonia market

Brazilian ammonia production has not accompanied the increase in consumption, generating the need to import large volumes to meet domestic demand (Florez-Orrego and Oliveira Júnior, 2016), which makes the country vulnerable to international market price variations and logistical problems of Brazilian ports (Hernandez and Torero, 2011).

According to data from the Brazilian Ministry of Development, Industry and Foreign Trade - MDIC/Aliceweb (2018), In the year 2017 alone, more than 285,000 tons of ammonia was imported, generating an expenditure of foreign exchange to the order of US$ 68.50 million. Figure 76 shows a graph with the Brazilian ammonia import values from the year 2000.

Figure 76 - Brazilian ammonia imports.



Souce: MDIC – Aliceweb System, 2018.

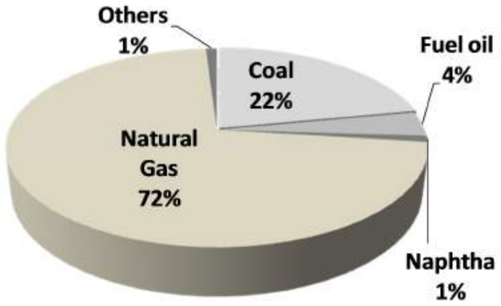
4.3 Development of the productive process of ammonia

The synthesis of ammonia from the interaction of hydrogen and nitrogen on a catalytic bed uses iron oxide doped with small amounts of aluminum and potassium oxides (Liyanage and Armentrout, 2004). The foundations of this catalytic synthesis were developed by Fritz Haber and Carl Bosch almost a century ago (Hellman *et al.,* 2013).

Even today the Haber-Bosch process is the main route of industrial production of ammonia (Nishibayash and Tanabe, 2013, Kyriakou *et al.,* 2016). This process combines hydrogen and nitrogen in the 3: 1 ratio to produce ammonia (Bartels, 2008). The exothermic conversion reaction is facilitated by a catalyst based on metal oxides, and occurs in the temperature range between 500°C and 600°C (Boyano *et al.,* 2011; Cetinkaya *et al.,* 2012).

The raw material used as a source of hydrogen for ammonia production may have different origins. There are in literature many technical and economic studies for ammonia production from coal gasification (Habgood *et al.,* 2015) and biomass gasification (Andersson and Lundgren, 2014), among others. However, natural gas is still the world's most widely used source for large-scale ammonia production, mainly because of the greater efficiency achieved by the use of gas. Ammonia production plants have moved from more developed countries to countries with large natural gas reserves, such as the Middle East and North Africa, taking advantage of the low price of the raw material and considerably reducing the costs of production. Figure 77 shows a graph with the main raw materials used worldwide for the production of ammonia.

Figure 77 - Brazilian ammonia imports.



Source: Institute for Industrial Productivity - IIP, 2016.

In spite of great advances already achieved in energy terms, conventional ammonia production is considered one of the least efficient processes of chemical transformation, from the perspective of the exergy concept, as published by the United States Department of Energy (DOE, 2006). In a recent study on the energy efficiency of ammonia production processes, Ghannadzadeh and Sadeqzadeh (2016) suggest that the internal and external losses of process exergy can reach values of 3,152 kJ and 6,364 kJ per kg of ammonia produced, respectively. Hellman *et al.* (2013) state that currently more than 1% of all energy produced globally is consumed by the ammonia production activity. Liu (2014) indicates that this percentage of energy consumption can reach 2%, and that the world production of ammonia accounts for more than 400 million tons of CO_2 released into the atmosphere, which represents about 1.6% of overall CO_2 emissions.

Kyrova-Yordanova (2004) argues that the exergy consumption of an ammonia plant depends heavily on the synthesis loop, because the low conversion level is limited by the thermodynamic equilibrium of the ammonia formation reaction. Therefore, the ammonia plants operate with recycling of the unreacted gases, generating high energy consumption for compression. More efficient and sustainable processes of ammonia production have been extensively studied, in order to reduce the energy consumption and, consequently, production cost of the product.

According to Khan and Kabir (1995), an ammonia production plant can be divided into several blocks of industrial processes, each involving a highly complex chemical engineering unit operation, and with controls and protection devices designed to prevent operational failures and errors of the operators. Synthesis gas generation is the main step of an ammonia production plant, producing the hydrogen needed to blend with the nitrogen separated from the atmospheric air. Thus, the choice of the synthesis gas generation process is fundamental for the economic viability of ammonia production.

4.3.1 Steps of the ammonia production process

The basic raw materials used for the production of ammonia are water for steam generation, atmospheric air for recovery of nitrogen and a stream of hydrocarbons, mainly natural gas, which is the raw material used as the main source of hydrogen in the process . Whatever the process used to generate the synthesis gas, the mixture generated in the reactors of hydrogen monoxide and carbon dioxide gases, mixed with steam and unreacted methane passes through conversion for the removal of the carbon monoxide and by treatment for removal of CO_2.

The percentage by volume of each component at the exit of the reactors depends on the reform process used (GEROSA, 2007). The main stages of ammonia production are described below, starting from the initial stages of generation and purification of the synthesis gas:

(i) Natural gas purification system: purification or filtration of natural gas is carried out through the liquid separator (scrubber), which has a mist eliminator as an internal aid for the filtration of the gas.

(ii) Unit load compression: natural gas is compressed to about 3.43 MPa (35 kgf/cm^2), depending on the operating pressure of the reforming reactors.

(iii) Natural gas desulfurization: in order to prevent sulfur poisoning of the catalysts used in the reform, natural gas is treated in a vessel with a fixed bed of metal oxides (Hellman *et al.,* 2013), whereby the content of sulfur present in the gas is reduced to less than 1 ppm. The most commonly used treatment is the passage of the gas through a reactor with a fixed bed formed by a mixture of metallic oxides. This patented technology can use several metals, but the most commonly used is zinc oxide.

(iv) Catalytic reform of natural gas: treated natural gas is mixed with superheated steam and enters the reforming reactor (primary reformer), where the reforming reactions occur in the presence of the catalyst to produce hydrogen, carbon monoxide and carbon dioxide. The reform reactions, presented in the synthesis gas production section, are strongly endothermic and require high energy application (Hellman *et al.,* 2013).The primary reformer outlet gas mixture is mixed with preheated oxygen and goes to the secondary reformer, where the oxygen extinguishes the unreacted methane in the first reformer. Reactions with steam also occur in the second reformer, producing even more hydrogen and carbon monoxide.

(v) Conversion of carbon monoxide by shift conversion: oxygenated compounds should not be inserted into the ammonia conversion reactor, so that the quenching or separation of these compounds is necessary before the ammonia conversion step. In large-scale ammonia production plants, two shift reactors are typically used, the first one being operated at high temperature and the second at a lower temperature.

(vi) Carbon dioxide removal process: carbon dioxide is removed from the syngas through the absorption step using a solution of monoethanolamine (MEA). When co-production of urea occurs at the same site, the separated CO_2 is used as the raw material of the synthesis, together with the ammonia. The purified syngas is sent to the methanation process. In older ammonia production plants using an aqueous solution of copper salts for the removal of carbon monoxide, the amount of residual CO_2 present in the syngas could reach values in the range of 0.2% to 0.5% by volume (Bakemeier *et al.,* 2002).

(vii) Methanation process: when the target of the syngas is ammonia production, the final purification process is the complete extinction of the oxygenated compounds, through the hydrogenation reaction of these compounds in the methanation reactor.

(viii) Load compression: nitrogen required for ammonia synthesis is supplied in the stoichiometric amount of the reaction (1:3) and the mixture is then compressed to the reactor operating pressure (19.6 MPa or 200 kgf/cm^2). Due to the high pressure of the reactor and also the high recycle rate of unreacted gases, this stage consumes a lot of energy.

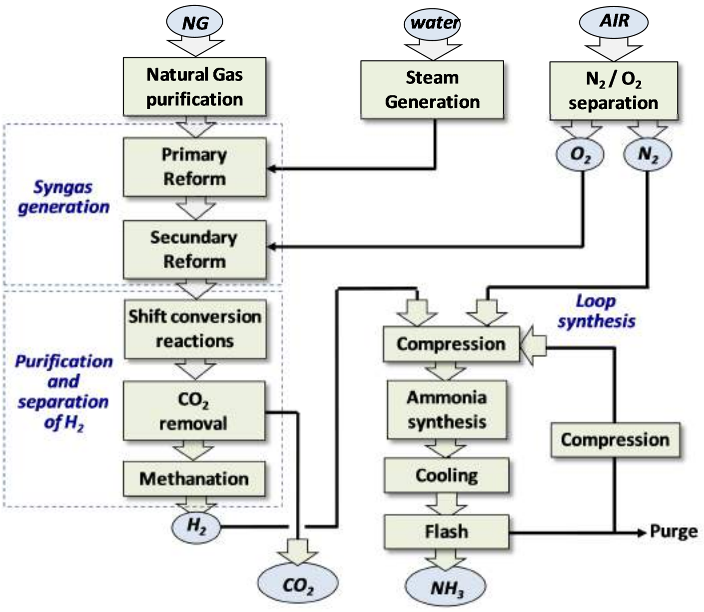
(ix) synthesis of ammonia: ammonia synthesis reaction occurs in the synthesis reactor, in the presence of a catalyst based on alumina-doped iron oxide and calcium and potassium oxides (Liu *et al.,* 2014). An optimum temperature should be maintained to maximize the conversion of the ammonia to the equilibrium condition of the reactor. Ammonia synthesis reaction is presented below.

$N2 + 3H2 \leftrightarrow 2NH3$ [$\Delta H = -92.0$ kj/mol] (Reaction 09)

(x) Separation of the ammonia: reactor output gases are cooled with the aid of a cooling cycle (using ammonia) and then proceed to the production separation vessel (flash vessel), where ammonia in the liquid phase is separated from the unreacted gases and intended for storage tanks. The unreacted gases are reheated, compressed and mixed with the fresh charge, for a further conversion cycle in the reactor.

Figure 78 shows a simplified schematic diagram with the main steps of the most widespread process of ammonia production. Haber-Bosch process sequence is followed, with a few modifications in the syngas purification systems and improvements implemented in the iron catalyst bed of the main ammonia conversion reactor.

Figure 78 – Principal steps of ammonia production.



Source: Adapted from Khan and Kabir, 1995.

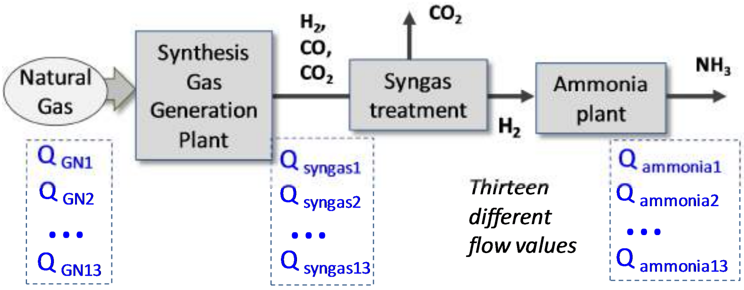
The main objective of the research on the ammonia conversion catalyst is to formulate a catalyst that is capable of providing high conversion rates of ammonia at low temperatures. A catalyst based on iron oxide added to other oxides, such as potassium and aluminum oxide, which help increase the conversion efficiency at relatively lower temperatures of around 450ºC (Gerosa, 2007), is currently used.

4.4 Methodology

4.4.1 Basic design assumptions

The methodology used by the authors is based on the engineering simulation of syngas and ammonia industrial plants of various nominal capacities, operating in an integrated manner. The process simulations were generated using the PETRO-SIM® commercial simulator. Thirteen distinct nominal load values of natural gas were simulated for the synthesis gas generation unit, each generating a distinct syngas flow rate, which is used with load from the ammonia production unit, after the separation of the oxygenated compounds. Figure 79 shows a schematic diagram of the applied system and Table 10 shows the simulated natural gas charge values of the complex.

Figure 79 – Schematic of methodology for simulation of ammonia production.



Source: The Author, 2017.

Table 10 – Simulated natural gas load values.

Natural gas load (t/h) - [13 points]												
Q_{GN1}	Q_{GN2}	Q_{GN3}	Q_{GN4}	Q_{GN5}	Q_{GN6}	Q_{GN7}	Q_{GN8}	Q_{GN9}	Q_{GN10}	Q_{GN11}	Q_{GN12}	Q_{GN13}
44.49	66.69	88.98	133.40	178.00	222.40	266.90	311.40	355.90	400.40	444.90	489.40	534.00

Source: The Author, 2017.

From the result of the thirteen simulations, material and energy balances were generated from the proposed units (at the conceptual design level) and the basic design of the main process equipment was determined, as well as the estimated cost of the same. The preliminary design of the main equipment was obtained through the use of simulation data, with estimates of design parameters according to tables of global coefficients of heat transfer, specific weight tables of sheet metal according to ASME Code, Section VIII, Division I (ASME, 2015), to calculate the weight of static equipment.

The cost of the main equipments and the estimation of the CAPEX were realized according to parameters and equations presented elsewhere (Towler and Sinnott, 2013), plus some complementary factors used in manuals of project of the PETROBRAS. The estimated revenue with ammonia sale was obtained based on the cost of importing this product, according to data from the Aliceweb System of the Ministry of Development, Industry and Foreign Trade (MDIC).

4.4.2 Simulation strategy

Units of synthesis gas generation from natural gas and ammonia production from hydrogen separated from syngas and atmospheric nitrogen were simulated in the PETRO-SIM® process simulator, version 5.5 (which is fully compatible with the commercial simulator HYSYS®), in accordance with usual process engineering practices, in order to determine the production potential of the units, according to the different nominal natural gas loads tested.

4.4.3 Simulation of the synthesis gas generation unit

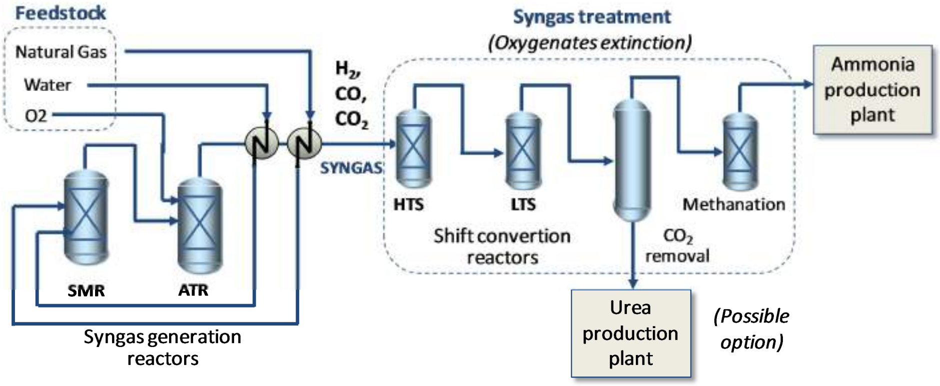
The most commonly used process for the generation of syngas is the methane vapor reform (SMR), which requires the external combustion of the fuel to the reactor to supply the thermal energy necessary to maintain the endothermic methane reforming reactions (Martínez *et al.,* 2014). In installations designed to use natural gas as feedstock, methane itself is used as fuel (Wu *et al.,* 2014).

For this project, the configuration of two series conversion reactors was chosen, the first being an SMR reactor, operating at 700°C and 4.51 MPa (46 kgf/cm^2), and the second, a ATR reactor (Autothermal Reforming reactor), operating at 1,200 °C and 4.21 MPa (43 kgf/cm^2) (Mujeebu, 2016). The first reactor admits steam and methane (3:1 ratio), with the reacted gases feeding the second reactor, together with the admission of oxygen. The temperature of the reagents at the inlet of the catalytic bed ranges from 450°C to 650°C and the products run at 800°C to 950°C (Rostrup-Nielsen, 2015). For this project a temperature profile of the conversion reactors was chosen a little higher, in order to improve the conversion efficiency.

The reforming reaction is carried out in an atmosphere with excess steam, to allow the control of the tendency for coke deposition on the surface of the catalyst, causing its deactivation (Chiesa, 2010). Otherwise, the excess steam favors the water gas shift - WGS reaction, which is fundamental in the control of coke deposition (Yu *et al.*, 2012).

The process is conducted at moderate pressures, ranging from 1.96 MPa to 3.92 MPa (20 kgf/cm^2 to 40 kgf/cm^2)), reducing the need for additional compression of the synthesis gas at the exit of the reactors (Chiesa, 2010). However, the higher the pressure at which the reform occurs, the higher the temperature required to establish the desired thermodynamic equilibrium. In this work, the simulation of the ammonia production unit followed the strategy presented in Figure 80. Thirteen different simulations were run, one for each rated natural gas charge value.

Figure 80 – Block diagram of syngas generation for ammonia production.



Source: The Author, 2017.

Figure E1 reproduced in large size in Appendix E shows the process flow diagram (PFD) of the simulation of the synthesis gas generation plant as implemented in the simulation software.

4.4.4 Simulation of the ammonia production unit

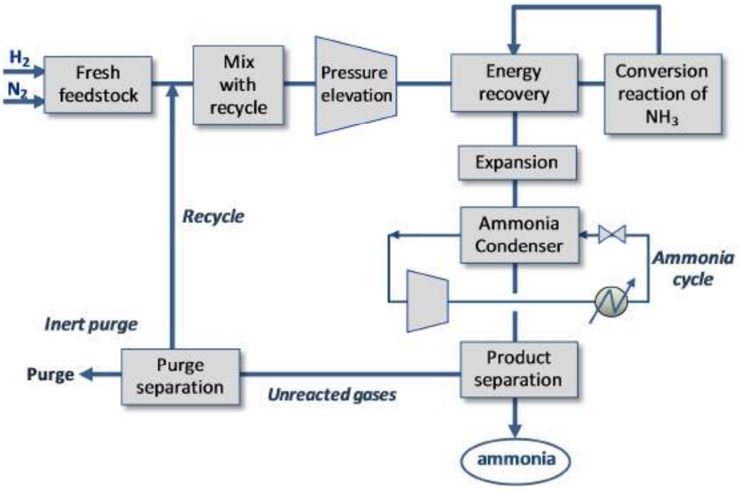
Kyrova-Yordanova (2004) argues that the energy consumption of an ammonia plant depends on the synthesis loop. This is due to the low conversion level, limited by the thermodynamic equilibrium of the ammonia formation reaction, and ammonia plants operate with high flows of unreacted gases, generating high energy consumption for compression. A temperature to the order of 400 °C to 500 °C should be maintained in the reactor to maximize the conversion of the ammonia to the reactor equilibrium condition (Boyano *et al.,* 2011; Cetinkaya *et al.,* 2012).

The exhausted gases from the reactor are cooled to about -21 °C with the aid of a refrigeration cycle, which uses ammonia as a refrigerant, and then go to the production separation vessel where the ammonia is condensed and separated from the unreacted gases, being destined to the storage tanks. The unreacted gases are reheated, compressed and mixed with the fresh charge for a new conversion cycle in the reactor (Gerosa, 2007).

According to Khan and Kabir (1995) the simulation of an ammonia production unit is formed by a set of unitary operations divided into process blocks, with extensive use of dynamic mechanical equipment such as compressors, and high flows of recycled unreacted gases, with process control systems and complex protection devices. For the ammonia conversion, a thermodynamic equilibrium reactor was simulated, with the conversion rate defined by the thermodynamic equilibrium as a function of the temperature and pressure conditions of the reactor. An ammonia refrigeration cycle was simulated to ensure adequate cooling of the reactor outlet gases and to allow condensation and separation of the ammonia produced.

The unreacted gases feed the reactor after mixing with fresh charge. The purge rate (discard) of unreacted gases was determined according to the assumption of 100% inertness from the looping of the reactor, in order to avoid its accumulation in the unit. In practice, the removal of aggregates by the purge gas equals the inlet value with the fresh charge. The thermodynamic conditions of the conversion reactor used were those found in literature. In general, the simulation defined served all the nominal flows tested. However, some adjustments in each simulation were necessary to achieve the conversion, such as cooling cycle flow, reactor thermal load, temperature of reaction and energy recovery. Figure 81 shows the strategy of the simulation of the ammonia unit.

Figure 81 – Block diagram of ammonia production.



Source: The Author, 2017.

Figure E3 reproduced in large size in Appendix E shows the process flow diagram (PFD) of the simulation of the ammonia production plant as implemented in the simulation software.

4.4.5 Estimated cost of equipment

The preliminary cost estimation of individual equipment C was performed according the Equation 01, which is showed in the Chapter 3. Parameters of Equation 01 were already presented in Table 05 of Chapter 3 (Towler and Sinnott, 2013).

Pressure vessels weight was calculated according to the nominal operating pressure (and, when appropriate, temperature). The thickness of the shell of the pressure vessels, reactors and distillation towers were estimated based on the ASME code, section VIII, division 1. Equation 02 showed in Chapter 3 was used for calculating the thickness of the equipment (ASME, 2015).

Details of such methodology can be found elsewhere (Towler and Sinnott, 2013). The costs with importation of chemicals were used to establish their prices, obtained elsewhere (MDIC/Aliceweb, 2015).

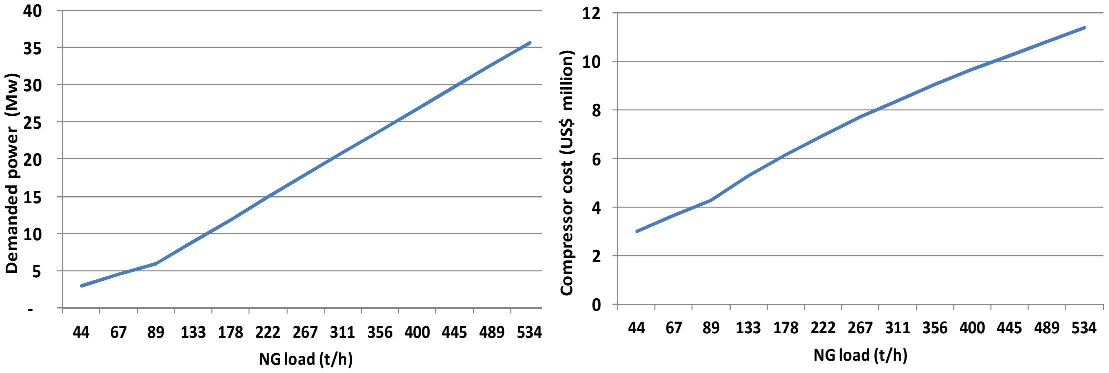
4.5 Results

Appendix D presents the auxiliary tables used for the elaboration of the graphs below.

4.5.1 Cost of synthesis gas generation unit

Figure 82 shows the graph of the (a) compression power demanded and (b) compression cost of the syngas generation plant against nominal natural gas load of the complex.

Figure 82 – (a) Compression power demanded and (b) compression cost against nominal natural gas load of the complex.



(a)

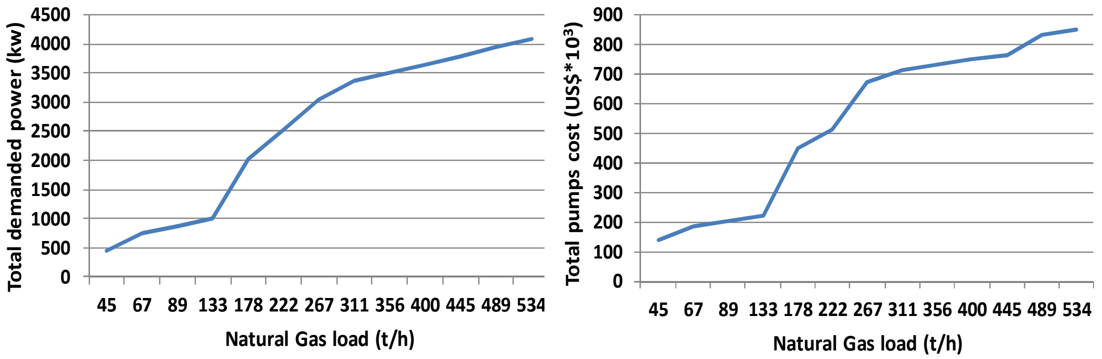
(b)

Source: The Author, 2017.

Figure 83 shows the graph of the (a) pumps power and (b) pumps cost of the syngas generation plant against nominal natural gas load of the complex.

Figure 83 – (a) Pumps power and (b) pumps cost of the syngas generation plant against nominal natural gas load of the complex.

(a) (b)

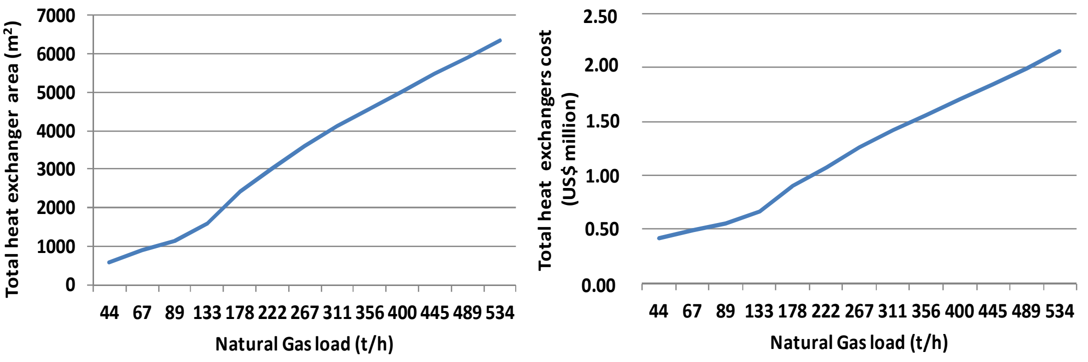


Source: The Author, 2017.

Figure 84 shows the graph of the (a) heat exchanger area and (b) heat exchangers cost of the syngas generation plant against nominal natural gas load of the complex.

Figure 84 – (a) Heat exchangers area and (b) heat exchangers cost of the syngas generation plant against nominal natural gas load of the complex.

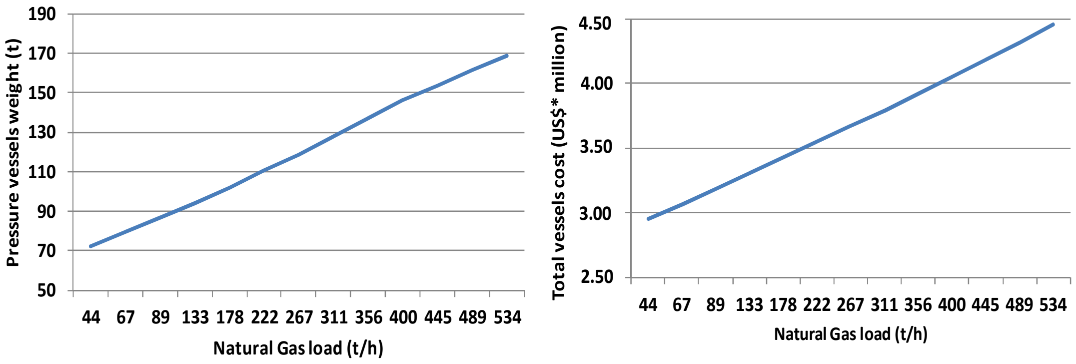
(a) (b)



Source: The Author, 2017.

Figure 85 shows the graph of the (a) pressure vessels weight and (b) pressure vessels cost of the syngas generation plant against nominal natural gas load of the complex.

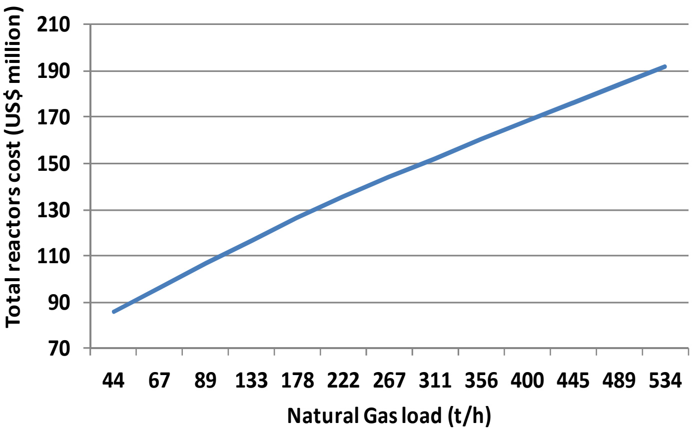
Figure 85 – (a) Pressure vessel weight and (b) pressure vessels cost of the syngas generation plant against nominal natural gas load of the complex.


(a) (b)

Source: The Author, 2017.

Figure 86 shows the graph of reactors cost of the syngas generation plant against nominal natural gas load of the complex.

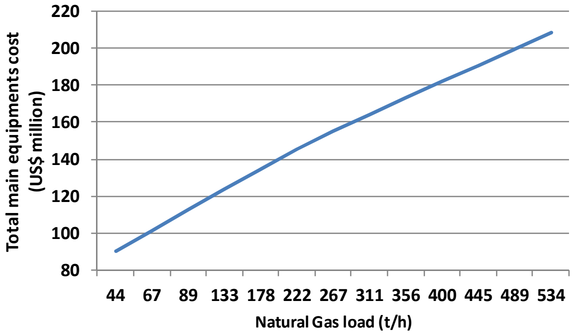
Figure 86 – Reactors cost of the syngas generation plant against nominal natural gas load of the complex.



Source: The Author, 2017.

The results presented in Figures 82 to 86 show the behavior of the cost of the main equipments of the synthesis gas generation unit as a function of the capacity of the unit. Making linear the abscissa of the graphs, it is possible to verify that there is a practically stable relation between the cost of the equipments and the nominal capacity of the unit. Figure 87 shows the graph of the main equipment cost of the syngas generation plant against nominal natural gas load of the complex.

Figure 87 - Main equipment cost of the syngas generation plant against nominal natural gas load of the complex.



Source: The Author, 2017.

The result presented in Figure 87 allows estimating the cost of the acquisition of the equipments of the synthesis gas generation unit as a function of the nominal natural gas load. As expected, there is a relationship between the cost of the equipments and the nominal capacity of the unit, within the limits of the investigated capacity.

Using the data generated on the estimated cost of the main equipments of the syngas generation unit and the methodology presented on Section 4.4, it is possible to estimate the consolidated construction and assembly cost (CAPEX) of the unit. Appendix A presents details of the indices and factors used in this estimation. Making this context more objective, Table 11 shows the consolidation of the construction & assembly cost of the synthesis gas generation unit (CAPEX of the unit) to ammonia production for the investigated flows. Appendix A presents details about the factors used in this Table.

Table 11 - Consolidation of the construction & assembly cost of the synthesis gas generation unit to ammonia production for the investigated flows.

Cost of Construction and Assembly of shyntesis gas generation unit to ammonia production

Nominal load of Natural Gas (t/h)		44.5	66.7	89.0	133.4	178.0	222.4	266.9	311.4	355.9	400.4	444.9	489.4	534.0
Total cost of main equipment (US$*million)		90.4	101.6	112.6	123.9	134.8	145.3	154.8	164.0	173.0	181.9	190.7	199.4	208.1
Implantation steps of the methanol production unit	factor	(US$*million)												
Detail design and engineering documents	0.20	18.08	20.32	22.53	24.78	26.97	29.06	30.97	32.81	34.61	36.39	38.14	39.88	41.63
BUILDINGS														
Land, wall/fence, gatehouse, sentry-house	0.15	13.56	15.24	16.90	18.58	20.23	21.80	23.30	24.61	25.96	27.29	28.60	29.91	31.22
Land leveling and containment basin	0.20	18.08	20.32	22.53	24.78	26.97	29.06	30.97	32.81	34.61	36.39	38.14	39.88	41.63
Inter.roads, sidewalks, adm.building, parking, urbaniz, lab.	0.15	13.56	15.24	16.90	18.58	20.23	21.80	23.30	24.61	25.96	27.29	28.60	29.91	31.22
Rainwater, gutters, dikes, passage and elevation boxes	0.10	9.04	10.16	11.26	12.39	13.48	14.53	15.48	16.40	17.30	18.19	19.07	19.94	20.81
Process civil install. (equip. bases, control rooms, pipe ways)	0.15	13.56	15.24	16.90	18.58	20.23	21.80	23.30	24.61	25.96	27.29	28.60	29.91	31.22
ASSEMBLY OF PIPING AND EQUIPMENT														
Equipment assembly	0.30	27.12	30.48	33.80	37.17	40.46	43.60	46.46	49.22	51.92	54.59	57.21	59.82	62.45
Acquisition of piping	0.35	31.64	35.56	39.43	43.37	47.20	50.86	54.20	57.42	60.58	63.69	66.75	69.79	72.86
Piping accessories	0.15	13.56	15.24	16.90	18.58	20.23	21.80	23.30	24.61	25.96	27.29	28.60	29.91	31.22
Piping assembly	0.30	27.12	30.48	33.80	37.17	40.46	43.60	46.46	49.22	51.92	54.59	57.21	59.82	62.45
ELECTRICAL INSTALLATIONS														
Elect.Inst.(cables, panels, controlroom, emerg. generatator)	0.20	18.08	20.32	22.53	24.78	26.97	29.06	30.97	32.81	34.61	36.39	38.14	39.88	41.63
Substation and high voltage switches and circuit breakers	0.15	13.56	15.24	16.90	18.58	20.23	21.80	23.30	24.61	25.96	27.29	28.60	29.91	31.22
Control instrum. (sensors, transmitters, valves, panels, cables)	0.35	31.64	35.56	39.43	43.37	47.20	50.86	54.20	57.42	60.58	63.69	66.75	69.79	72.86
PLCs, IHM, control software, int.networks, no-breaks, panels	0.20	18.08	20.32	22.53	24.78	26.97	29.06	30.97	32.81	34.61	36.39	38.14	39.88	41.63
OTHER EQUIPMENT AND CONSUMABLE MATERIALS														
Secondary equipment and accessories	0.10	9.04	10.16	11.26	12.39	13.48	14.53	15.48	16.40	17.30	18.19	19.07	19.94	20.81
Safety equip. (tank, nets, pumps, hydrants, water cannons)	0.15	13.56	15.24	16.90	18.58	20.23	21.80	23.30	24.61	25.96	27.29	28.60	29.91	31.22
Catalysers, molecular sieves, membranes	0.20	18.08	20.32	22.53	24.78	26.97	29.06	30.97	32.81	34.61	36.39	38.14	39.88	41.63
Product storage tanks	0.15	13.56	15.24	16.90	18.58	20.23	21.80	23.30	24.61	25.96	27.29	28.60	29.91	31.22
Lubricants, filters, cartridges, consumables, chemical prod.	0.05	4.52	5.08	5.63	6.19	6.74	7.26	7.74	8.20	8.65	9.09	9.53	9.97	10.40
INSPECTION, TESTS, CONNECTIONS, COMMISSIONING														
Control loops tests and communication with internal network	0.10	9.04	10.16	11.26	12.39	13.48	14.53	15.48	16.40	17.30	18.19	19.07	19.94	20.81
Inspection and painting	0.20	18.08	20.32	22.53	24.78	26.97	29.06	30.97	32.81	34.61	36.39	38.14	39.88	41.63
Offsites (external connections)	0.20	18.08	20.32	22.53	24.78	26.97	29.06	30.97	32.81	34.61	36.39	38.14	39.88	41.63
Commissioning and pre-operation	0.15	13.56	15.24	16.90	18.58	20.23	21.80	23.30	24.61	25.96	27.29	28.60	29.91	31.22
CONTINGENCY, LICENSES AND INDUSTRIAL FACILITIES														
Contingency and Health, Safety and Environment - HSE	0.10	9.04	10.16	11.26	12.39	13.48	14.53	15.48	16.40	17.30	18.19	19.07	19.94	20.81
Restrictions and environmental licenses	0.10	9.04	10.16	11.26	12.39	13.48	14.53	15.48	16.40	17.30	18.19	19.07	19.94	20.81
Industrial facilities (considering apportionments)	0.30	27.12	30.48	33.80	37.17	40.46	43.60	46.46	49.22	51.92	54.59	57.21	59.82	62.45
TRAINING														
Training of operational, maintenance, inspection teams	0.07	6.32	7.11	7.88	8.67	9.44	10.17	10.84	11.48	12.11	12.73	13.35	13.95	14.57
Total fixed cost of the complex – CAPEX (US$*million)		436	490	543	597	650	701	746	791	834	877	919	961	1003

Source: The Author, 2017.

4.5.2 Cost of ammonia production unit

Subsequently, the cost of the ammonia production unit is estimated using the same methodology used to estimate the cost of the synthesis gas generation unit. Figure 88 shows the graph of the (a) demanded compression power and (b) total compression cost of the ammonia production unit against nominal natural gas load of the complex.

Figure 88 – (a) Demanded compression power and (b) total compression cost of the ammonia production unit against nominal natural gas load of the complex.

(a) (b)

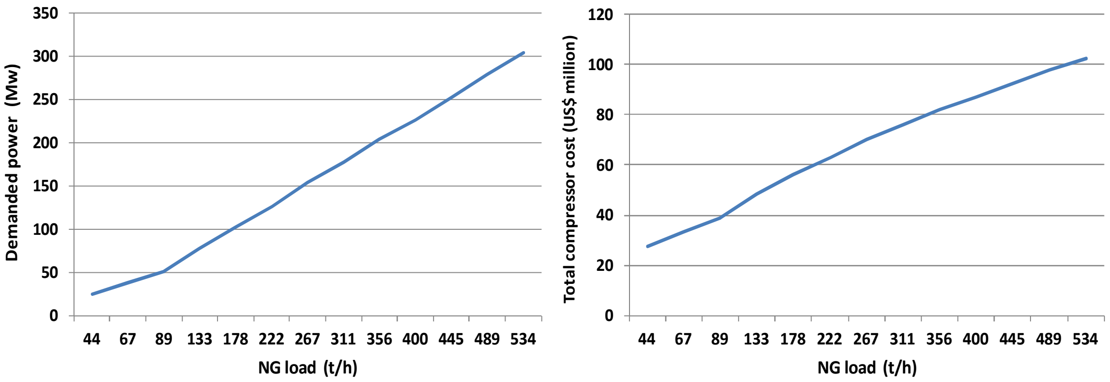
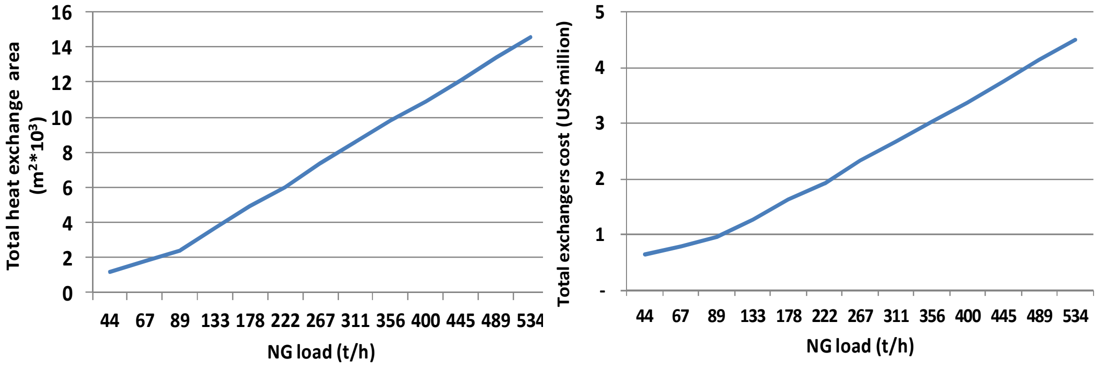


Figure 89 shows the graph of the (a) heat exchange area and (b) total exchangers cost of the ammonia production unit against nominal natural gas load of the complex.

Figure 89 – (a) Heat exchange area and (b) total exchangers cost of the ammonia production unit against nominal natural gas load of the complex.


(a) (b)

Source: The Author, 2017.

Figure 90 shows the graph of the (a) pressure vessels weight and (b) pressure vessels cost of the ammonia production unit against nominal natural gas load of the complex.

Figure 90 – (a) Pressure vessels weight and (b) pressure vessels cost of the ammonia production unit against nominal natural gas load of the complex.

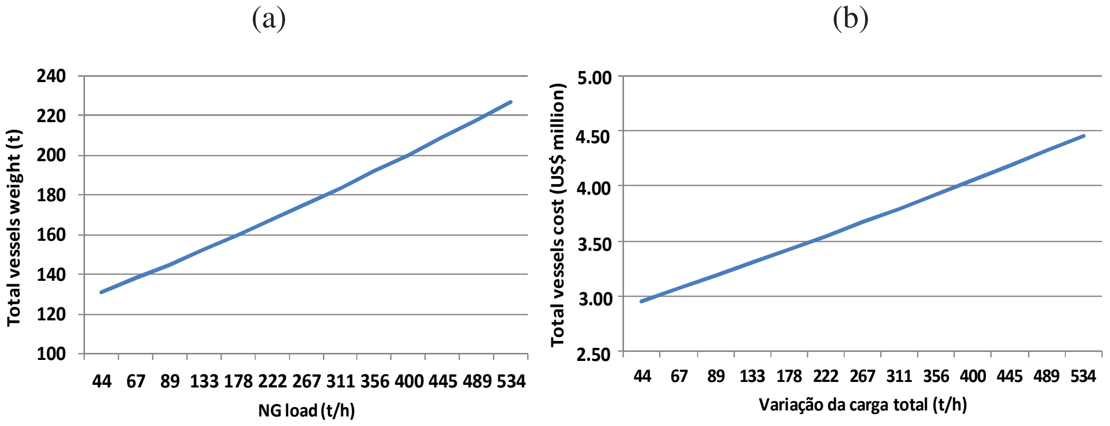
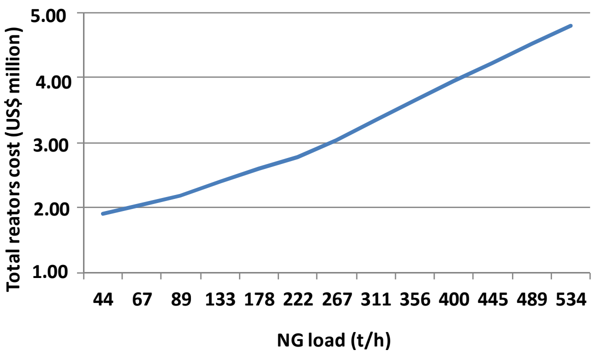


Figure 91 shows the graph of reactors cost of the ammonia production unit against nominal natural gas load of the complex.

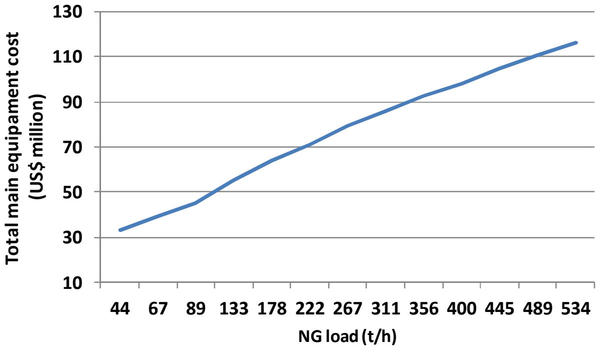
Figure 91 - Reactors cost of the ammonia production unit against nominal natural gas load of the complex.



Source: The Author, 2017.

Such as the synthesis gas unit, the results presented in Figures 88 to 91 show the behavior of the cost of the main equipments of the ammonia production unit as a function of the unit capacity. Making linear the abscissa of the graphs, it is possible to verify that there is a practically stable relation between the cost of the equipments and the nominal capacity of the unit. Figure 92 shows the graph of the main equipment cost against nominal natural gas load of the ammonia production unit.

Figure 92 - Main equipment cost of the ammonia production unit against nominal natural gas load of the complex.



Source: The Author, 2017.

The result presented in Figure 92 allows estimating the cost of the acquisition of the equipments of the ammonia production unit as a function of the nominal natural gas load. As expected, there is a relationship between the cost of the equipments and the nominal capacity of the unit, within the limits of the investigated capacity.

It should be noted that the methodology chosen to estimate the cost of equipments, based on the indicated reference (Towler and Sinnott, 2013), imposes some restrictions on the size of equipments. Thus, for higher values of nominal capacity of the units, it is necessary to increase the number of equipments (operating in parallel), to remain in the flow range allowed by the methodological. This constraint may cause some deviation in the expected linearity between the cost of the equipments and the nominal capacity of the production unit.

Using the data generated on the estimated cost of the main equipments of the ammonia production unit and the methodology presented on Section 4.4, it is possible to estimate the consolidated construction and assembly cost (CAPEX) of the unit. Appendix A presents details the indices and factors used in determining this estimate. Table 12 presents the consolidation of the total cost of construction & assembly of the ammonia production unit (CAPEX of the unit) for the investigated flow rate points. Appendix A presents details about the factors used in the Table 12.

Table 12 - Consolidation of the total cost of construction & assembly of the ammonia production unit for the investigated flows.

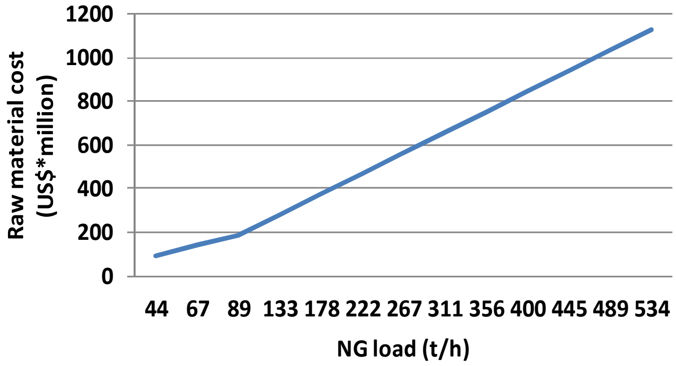
Cost of Construction and Assembly of the ammonia production unit														
Nominal load of Natural Gas (t/h)		57.3	86.0	114.7	172.0	229.4	286.7	344.1	401.5	458.8	516.2	573.7	630.8	688.4
Total cost of main equipment (US$*million)		32.9	39.3	45.1	55.24	63.9	71.2	79.1	85.8	92.6	98.3	104.5	110.7	116.2
Implantation steps of the methanol production unit	factor	(US$ milhões)												
Detail design and engineering documents	0.20	6.59	7.86	9.03	11.04	12.78	14.24	15.83	17.17	18.52	19.66	20.90	22.15	23.25
BUILDINGS														
Land, wall/fence, gatehouse, sentry-house	0.15	4.94	5.89	6.77	8.28	9.58	10.68	11.87	12.88	13.89	14.75	15.67	16.61	17.43
Land leveling and containment basin	0.20	6.59	7.86	9.03	11.04	12.78	14.24	15.83	17.17	18.52	19.66	20.90	22.15	23.25
Inter.roads, sidewalks, adm.building, parking, urbaniz, lab.	0.15	4.94	5.89	6.77	8.28	9.58	10.68	11.87	12.88	13.89	14.75	15.67	16.61	17.43
Rainwater, gutters, dikes, passage and elevation boxes	0.10	3.29	3.93	4.51	5.52	6.39	7.12	7.91	8.58	9.26	9.83	10.45	11.07	11.62
Process civil install. (equip. bases, control rooms, pipe ways)	0.15	4.94	5.89	6.77	8.28	9.58	10.68	11.87	12.88	13.89	14.75	15.67	16.61	17.43
ASSEMBLY OF PIPING AND EQUIPMENT														
Equipment assembly	0.30	9.88	11.79	13.55	16.57	19.17	21.36	23.75	25.76	27.79	29.50	31.35	33.23	34.87
Acquisition of piping	0.35	11.53	13.76	15.81	19.33	22.37	24.92	27.71	30.05	32.42	34.42	36.58	38.77	40.68
Piping accessories	0.15	4.94	5.89	6.77	8.28	9.58	10.68	11.87	12.88	13.89	14.75	15.67	16.61	17.43
Piping assembly	0.30	9.88	11.79	13.55	16.57	19.17	21.36	23.75	25.76	27.79	29.50	31.35	33.23	34.87
ELECTRICAL INSTALLATIONS														
Elect.Inst.(cables, panels, controlroom, emerg. generatator)	0.20	6.59	7.86	9.03	11.04	12.78	14.24	15.83	17.17	18.52	19.66	20.90	22.15	23.25
Substation and high voltage switches and circuit breakers	0.15	4.94	5.89	6.77	8.28	9.58	10.68	11.87	12.88	13.89	14.75	15.67	16.61	17.43
Control instrum. (sensors, transmitters, valves, panels, cables)	0.35	11.53	13.76	15.81	19.33	22.37	24.92	27.71	30.05	32.42	34.42	36.58	38.77	40.68
PLCs, IHM, control software, int.networks, no-breaks, panels	0.20	6.59	7.86	9.03	11.04	12.78	14.24	15.83	17.17	18.52	19.66	20.90	22.15	23.25
OTHER EQUIPMENT AND CONSUMABLE MATERIALS														
Secondary equipment and accessories	0.10	3.29	3.93	4.51	5.52	6.39	7.12	7.91	8.58	9.26	9.83	10.45	11.07	11.62
Safety equip. (tank, nets, pumps, hydrants, water cannons)	0.15	4.94	5.89	6.77	8.28	9.58	10.68	11.87	12.88	13.89	14.75	15.67	16.61	17.43
Catalysers, molecular sieves, membranes	0.20	6.59	7.86	9.03	11.04	12.78	14.24	15.83	17.17	18.52	19.66	20.90	22.15	23.25
Product storage tanks	0.15	4.94	5.89	6.77	8.28	9.58	10.68	11.87	12.88	13.89	14.75	15.67	16.61	17.43
Lubricants, filters, cartridges, consumables, chemical prod.	0.05	1.64	1.96	2.25	2.76	3.19	3.56	3.95	4.29	4.63	4.91	5.22	5.53	5.81
INSPECTION, TESTS, CONNECTIONS, COMMISSIONING														
Control loops tests and communication with internal network	0.10	3.29	3.93	4.51	5.52	6.39	7.12	7.91	8.58	9.26	9.83	10.45	11.07	11.62
Inspection and painting	0.20	6.59	7.86	9.03	11.04	12.78	14.24	15.83	17.17	18.52	19.66	20.90	22.15	23.25
Offsites (external connections)	0.20	6.59	7.86	9.03	11.04	12.78	14.24	15.83	17.17	18.52	19.66	20.90	22.15	23.25
Commissioning and pre-operation	0.15	4.94	5.89	6.77	8.28	9.58	10.68	11.87	12.88	13.89	14.75	15.67	16.61	17.43
CONTINGENCY, LICENSES AND INDUSTRIAL FACILITIES														
Contingency and Health, Safety and Environment - HSE	0.10	3.29	3.93	4.51	5.52	6.39	7.12	7.91	8.58	9.26	9.83	10.45	11.07	11.62
Restrictions and environmental licenses	0.10	3.29	3.93	4.51	5.52	6.39	7.12	7.91	8.58	9.26	9.83	10.45	11.07	11.62
Industrial facilities (considering apportionments)	0.30	9.88	11.79	13.55	16.57	19.17	21.36	23.75	25.76	27.79	29.50	31.35	33.23	34.87
TRAINING														
Training of operational, maintenance, inspection teams	0.07	2.30	2.75	3.16	3.86	4.47	4.98	5.54	6.01	6.48	6.88	7.31	7.75	8.13
Total fixed cost of the complex – CAPEX (US$*million)		159	190	218	266	308	343	382	414	447	474	504	534	560

Source: The Author, 2017.

4.5.3. Calculation of raw material cost of the complex

The average reference price for the commercialization of natural gas in Brazil was defined based on the average prices practiced in the domestic market in the last five years, valued at US$ 247.30/thousand cubic meters (ANP, 2015). This average price was used to calculate the cost of the raw material for the proposed complex. Considering the investigated values of nominal natural gas load of the synthesis gas generation unit, Figure 93 shows the graph of the expected of the raw material cost for the complex against natural gas load of the synthesis gas generation unit.

Figure 93 – Estimation of the raw material cost for the complex for the nominal load values investigated.

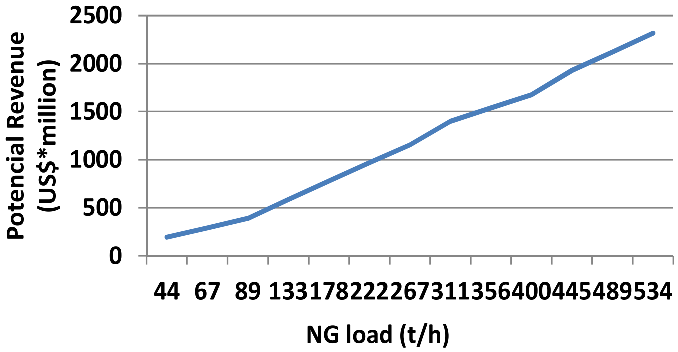


Source: The Author, 2017.

4.5.4 Calculation of the potential revenues from the complex

Figure 94 shows the graph of the potential gains of the complex as a function of the natural gas load variation, based on the amount of currency disbursement with ammonia imports, according to data recorded in the MDIC/Aliceweb system (MDIC, 2016). The amount of ammonia produced for each natural gas load value is given by the simulations of the syngas plant and the ammonia plant.

Figure 94 – Potential project revenue for the nominal load values investigated.

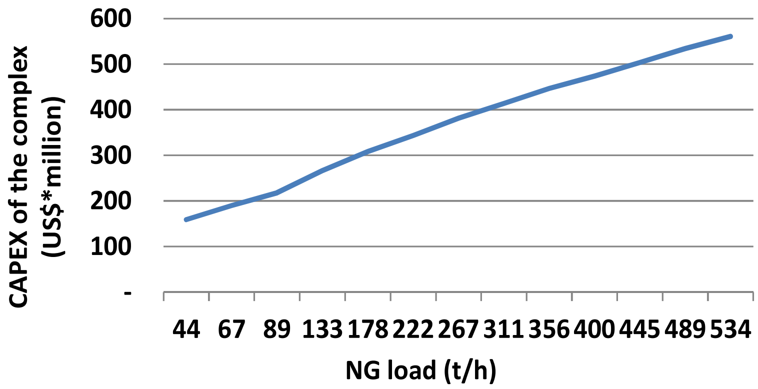


Source: The Author, 2017.

4.5.5 Complex implementation costs (CAPEX)

Figure 95 shows the graph of the total consolidated cost of implementation of the complex (CAPEX), considering the construction of the synthesis gas generation unit and the ammonia production unit for each investigated natural gas load value.

Figure 95 – Consolidated cost of the ammonia production complex for each investigated natural gas load value.



Source: The Author, 2017.

Table 13 presents the consolidated data of the economic analysis result of the project, considering the thirteen natural gas load points investigated.

Table 13 – Consolidated data of the economic analysis result of the project.

Investigated points	Q_{NG1}	Q_{NG2}	Q_{NG3}	Q_{NG4}	Q_{NG5}	Q_{NG6}	Q_{NG7}	Q_{NG8}	Q_{NG9}	Q_{NG10}	Q_{NG11}	Q_{NG12}	Q_{NG13}
Load (t/h)	44	67	89	133	178	222	267	311	356	400	445	489	534
Raw mat. Cost (US$*million/y)	94.00	140.90	187.99	281.90	375.94	469.94	564.17	657.89	752.07	845.79	939.97	1,033.69	1,127.87
CAPEX (US$*million)	158.86	189.50	217.75	266.28	308.14	343.23	381.72	413.94	446.53	474.03	503.84	533.99	560.35
OPEX (US$*million)	4.77	5.69	6.53	7.99	9.24	10.30	11.45	12.42	13.40	14.22	15.12	16.02	16.81
Pot. Revenue (US$*million)	194.06	291.04	389.74	585.42	778.06	970.28	1,154.57	1,399.75	1,538.18	1,674.95	1,931.80	2,121.93	2,317.07

Source: The Author, 2017.

4.5.6 Implementation of the preliminary project

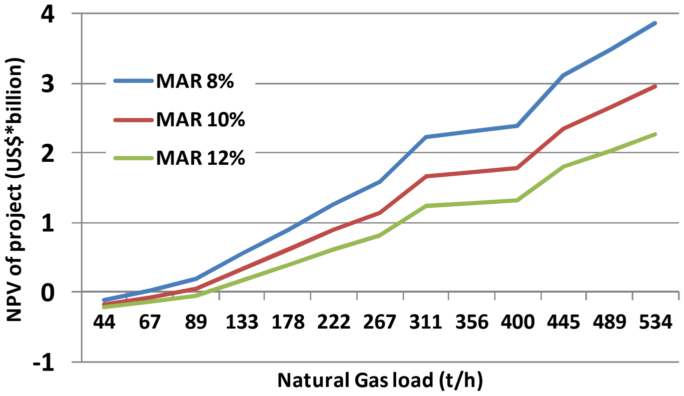
Table 08 showed in Chapter 3 presents the assumptions used to calculate the Net Present Value (NPV) for each natural gas load value investigated. These premises are defined by the Technical-Economic Feasibility Study (TEFS) for the project.

4.5.7 Net Present Value (NPV) calculated

Figure 96 shows the evolution of the NPV of the project as a function of the nominal natural gas load values investigated, considering a Minimum Attractiveness

Rate - MAR of 10%, with a sensitivity analysis of 20% higher (MAR = 12%) and 20% lower (MAR = 8 %).

Figure 96 - Evolution of the NPV calculated of the project by nominal natural gas load.



Source: The Author, 2017.

Table 14 shows the consolidated result of the technical-economic feasibility study – TEFS performed, of ammonia production complex, considering a Minimum Attractiveness Rate - MAR of 10%, with a sensitivity analysis of 20% higher (MAR = 12%) and 20% lower (MAR = 8 %).

Table 14 - Consolidated results of TEFS of ammonia production complex.

NG		CAPEX		Raw	OPEX	revenue		NPV (2017)	
Load	syngas	NH3	total	mat.			MAR8%	MAR10%	MAR12%
(t/h)		(US$*billion)			(US$*billion/y)			(US$*billion)	
44	0.43	0.15	0.59	0.09	0.02	0.19	-0.12	-0.18	-0.22
67	0.48	0.19	0.68	0.14	0.02	0.29	0.03	-0.07	-0.14
89	0.54	0.22	0.76	0.19	0.02	0.39	0.19	0.05	-0.05
133	0.60	0.27	0.86	0.28	0.03	0.58	0.55	0.33	0.17
178	0.65	0.31	0.96	0.38	0.03	0.78	0.90	0.61	0.39
222	0.70	0.34	1.04	0.47	0.03	0.97	1.26	0.89	0.62
267	0.74	0.38	1.13	0.56	0.03	1.15	1.58	1.15	0.82
311	0.79	0.42	1.20	0.66	0.04	1.40	2.24	1.67	1.25
356	0.83	0.44	1.28	0.75	0.04	1.54	2.32	1.73	1.28
400	0.87	0.47	1.35	0.85	0.04	1.67	2.39	1.78	1.32
445	0.92	0.50	1.42	0.94	0.04	1.93	3.12	2.36	1.80
489	0.96	0.53	1.50	1.03	0.04	2.12	3.48	2.65	2.03
534	1.00	0.56	1.56	1.13	0.05	2.32	3.87	2.96	2.28

Source: The Author, 2017.

4.6 Conclusions

The technical-economic feasibility study of the implementation of an ammonia production plant from natural gas indicates a great possibility of success for the project.

This type of production unit has a major strategic bias for countries such as Brazil, which has an economy heavily dependent on agribusiness, and is therefore a major consumer of nitrogen-based fertilizers.

The ammonia units and generation of syngas proposed have good production efficiency in relation to the values usually found in literature. The data generated show good proportionality between the nominal load variation and the cost variation of the main equipment of the unit within the studied range.

Nominal load values of natural gas above 100 ton/h make the project viable (they generate positive NPV), even considering high minimum attractiveness rates. This data reinforces the need to gain scale in the production of basic commodities such as ammonia and is in accordance with the nominal load values found in literature for large industrial complexes.

The technical study conducted shows that CO_2 segregated in the purification of syngas for ammonia production can be used for the production of ammonia and urea in the same site, adding value to the project and improving the rates of return on the investment as a whole.

5. WHAT TO DO WITH NATURAL GAS FROM BRAZILIAN PRE-SALT: HIGHER ADDED-VALUE PRODUCTS OR BURN IT AS A FUEL?

Abstract

The present paper deals with the best choice for the natural gas from Brazilian Pre-Salt: transforming it in higher benefit products or selling it as a fuel. It is presented a study about the economic feasibility of using NG for end up the demand of Brazilian importation of methanol, ammonia and urea. Units of such products from NG were simulated, allowing estimating their capital and operational costs. Investment analyses are then performed under different scenarios. The results indicate in which scenarios the choice of NG as feedstock becomes economically feasible. Potential energy integration between plants is also investigated.

Keywords: natural gas, syngas, ammonia, methanol, urea, economic analysis, pre-salt.

Introduction

Natural gas (NG) has attracted attention as much nobler applications in chemical transformation than used as fuel (Dong *et al.,* 2013). Currently, natural gas is one of the most important raw materials in the chemical industry. (Galadima and Muraza, 2015; Xiang *et al.,* 2015).

NG as a feedstock may lead to positive environmental impacts. First, it reduces the offer of non-renewable energy sources, favoring renewable ones. Second, it is cleaner than many other sources for feedstock, like coal or oil. For example, Dong *et al.* (2013) investigated technologies for methanol synthesis, concluding that NG is the most efficient technology, mainly in large scale; Xiang *et al.* (2015) showed that, compared to the process *Coal-To-Olefins* (CTO), NG use is much more efficient energetically and less polluting, although not economical for this case; Ren and Patel (2009) compared petrochemicals synthesis from naphtha, NG, coal and biomass, concluding that investigated energy consumption and CO_2 emissions was much better for NG and naphtha; Zhou *et al.* (2009) investigated DME synthesis from coal and NG simultaneously, where NG allowed to adjust carbon to hydrogen ratio, also allowing to reduce CO_2 formation.

However, NG as feedstock needs to be economically feasible. It is well known that NG is a much cheaper feedstock than coal or oil for ammonia synthesis (Aragaw and Disney, 1977); not surprising, 67% of all ammonia in word is produced from NG. Nonetheless, economical NG market presents local features, especially due to logistic necessity of storing and distribution. Thus, studies are necessary to evaluate the feasibility of using NG as feedstock in specific markets, investigating countries or regions of the world, as performed in this study for Brazilian scenario.

Brazilian market uses NG as fuel. Recently, economic problems interrupted the ongoing structuring projects, strategic for expansion of NG in Brazil (PETROBRAS, 2015). The greater example was COMPERJ, a project with nominal consumption of 21 million of Nm³/d of NG (PETROBRAS, 2011), from route 3 of Brazilian Pre Salt. For this route, an undersea pipeline is now almost ready for starting operation (PETROBRAS, 2015); then, it is necessary to analyze technical and economical projects for the use of NG. Thus, a natural question arises about what is the best destination for this NG, and the use as feedstock becomes a natural option.

Products such as ammonia, urea, methanol and carboxylic acids, when synthesized from NG, are denominated gasochemicals. Such products are imported in great amounts for Brazil, demanding millions of dollars in expenditures (ABIQUIM, 2015), besides environmental impact associated to such transport. In Brazil, the importation of such products is very significant: around 78% of urea for fertilizers and 100% of methanol used for Brazilian industry in chemical transformation (MDIC/ Aliceweb, 2018).

The present work presents a preliminary analysis of synthesis of methanol, ammonia and urea from NG, using the Brazilian scenario as an example, also investigating material and energetic synergies between these plants. In an environmental and economical appealing, the amount of such productions seeks to substitute the importation of such products in Brazil. Typical unit operations for such processes were considered in the development of the Process Flow Diagrams (PFDs), according to engineering common practices. Such processes were then simulated in PETRO-SIM®, and preliminary capital and operation costs were obtained. We considered possible scenarios, performing economic and environmental preliminary evaluations about the implementation of such processes. Although presented for Brazilian scenario, capital costs methodology can be easily extended to similar processes everywhere, and can be used for comparison with similar plants in future researches.

5.1 Gasochemicals from NG in Brazilian scenario

Nowadays, NG consumption in Brazil is around 100 million of m³/d (MME, 2016), almost all used as fuel, being responsible for 13% of Brazilian energy demand (MME, 2015). Is expected a continuous increase of NG production, as shown in Figure 08, which was showed in Chapter 1.

5.1.1 Methanol

Methanol is one of the most important chemicals, and its main production route is from NG due to availability and efficiency in conversion (Riaz *et al.*, 2013). The Brazilian market has increased significantly in last years, as shown in Figure 47 of the Chapter 3. Only in 2017, more than 1.15 million tons of methanol were imported, generating an expenditure of foreign exchange in the order of US$ 364 million.

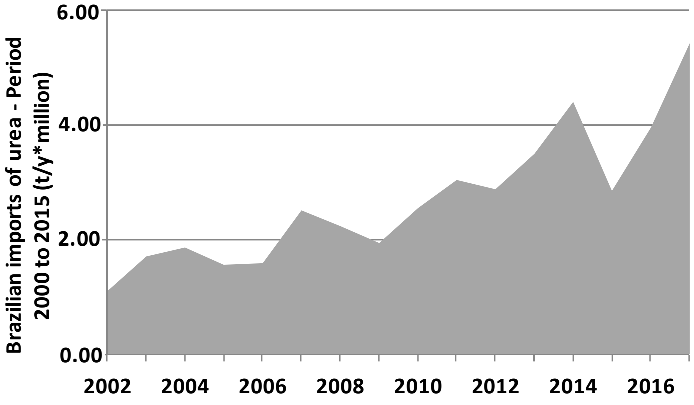
5.1.2 Ammonia

The worldwide ammonia production is up to 200 million tons per year (Kyriakou *et al.*, 2016; Giddey *et al.,* 2013), with 80% to fertilizers production (Klinsrisuk *et al.,* 2015). Another important use of ammonia includes industrial refrigeration cycles, besides uses in plastic, pharmaceutical and explosives industries (Edrisi *et al,* 2014). In Brazil, more than 60% of the ammonia consumption comes from importation (Florez-Orrego and Oliveira Júnior, 2016). The evolution of ammonia importation along years can be seen in Figure 76 presented in Chapter 4.

5.1.3 Urea

More than 90% of urea is destined to fertilizer production. Brazil is the fourth greater consumer of fertilizers of the word, responsible for 6% of worldwide fertilizer production. The Brazilian capacity of urea production is around 1.65 million tons per year, while the consumption is up to 5.0 million tons per year (ANDA, 2015). Figure 97 shows the Brazilian imports of urea.

Figure 97 – Brazilian urea imports.



Source: Aliceweb system - MDIC, 2018.

5.1.4 Potential income of the complex

Table 15 shows the potential gains of the complex, based on the value of currency disbursement with ammonia, methanol and urea imports.

Table 15 – Imported amounts of ammonia, methanol and urea.

	Ammonia			Methanol			Urea		
Year	import		price	import		price	import		price
	(t*10^3/Y)	(US$*$10^6$)	(US$/kg)	(t*10^3/Y)	(US$*$10^6$)	(US$/kg)	(t*10^6/Y)	(US$*$10^6$)	(US$/kg)
2013	322.07	174.55	0.54	750.33	332.08	0.44	3.49	1308.25	0.37
2014	355.03	181.97	0.51	851.47	389.77	0.46	4.40	1482.84	0.34
2015	353.67	155.96	0.44	841.82	288.45	0.34	2.84	882.14	0.31
2016	348.49	92.78	0.27	1,066.36	228.85	0.21	3.96	903.14	0.23
2017	286.19	68.49	0.24	1,157.99	364.95	0.32	5.43	1,244.56	0.23
average	333.09	134.75	0.40	933.60	320.82	0.35	3.33	1,256.40	0.30
	Total spending on imports:		**1.71**	(US$ billion/y)					

Source: MDIC –Aliceweb system, 2016.

5.2 Methodology

Simulation of the plants of syngas, ammonia, methanol and urea were implemented in the software PETRO-SIM®. From simulations, material and energy balances (in conceptual stage) were determined, allowing estimating the cost of such plants.

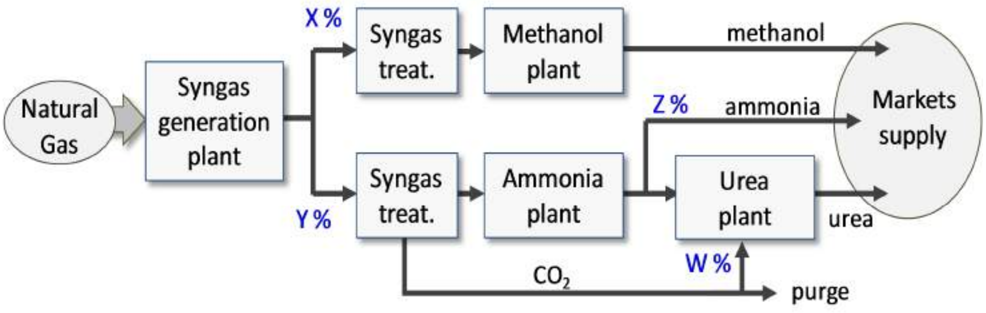
The preliminary cost estimation of individual equipment C was performed according the Equation 01, which is showed in the Chapter 3. Parameters of Equation 01 were already presented in Table 05 of Chapter 3 (Towler and Sinnott, 2013).

Pressure vessels weight was calculated according to the nominal operating pressure (and, when appropriate, temperature). The thickness of the shell of the pressure vessels, reactors and distillation towers were estimated based on the ASME code, section VIII, division 1. Equation 02 showed in Chapter 3 was used for calculating the thickness of the equipment (ASME, 2015).

Details of such methodology can be found elsewhere (Towler and Sinnott, 2013). The costs with importation of chemicals were used to establish their prices, obtained elsewhere (MDIC/Aliceweb, 2015). The costs with importation of chemicals were used to establish their prices, obtained elsewhere (MDIC/Aliceweb, 2015).

The configuration of systems consists in a plant of syngas production from NG, with posterior division of syngas for methanol and ammonia plants, where ammonia can be feed to a urea plant. Nonetheless, the project allows ammonia as final product too. The distribution of syngas between units was investigated; including the case where importation of such products could be substituted, as lower as possible spend of NG. Figure 98 illustrates the proposed configuration.

Figure 98 - Basic configuration of units of such process.



Source: The Author, 2017.

Since the available NG comes from Route-3 of Brazilian Pre-Salt, it is limited to a nominal flow of 21 million of cubic meters per day, with a maximum flow of 24 million cubic meters per day. (PETROBRAS, 2011). The composition of NG is shown in Table 16.

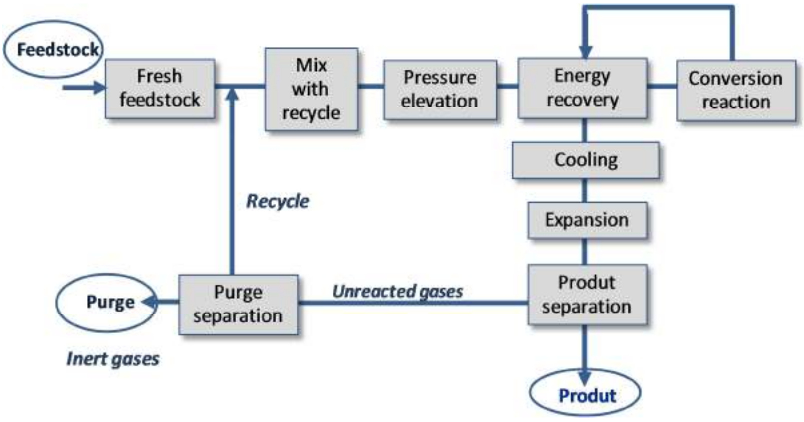
Table 16 - Gas composition and Maximum flow rate of the complex.

Comp.	N_2	CO_2	C1	C2	C3	iC4	nC4	iC5	nC5	C6	C7	C8
(kgmol/h)	266	1,168	31,108	4,461	2,889	370	794	224	170	79	33	8

Source: PETROBRAS, 2011.

The typical strategy for simulating chemical plants is presented in Figure 99. Almost all reactors were simulated as thermodynamic reactors (Gibbs or Equilibrium reactors), and in cases of ammonia and urea production, conversion reactors were employed, with conversion values from literature or known from industrial values. Residual reactants in effluent of reactors were separated and re-feed to the reactor. Purge was determined in order to avoid buildup of inert reactors, with typical industrial values.

Figure 99 - Strategy of the process simulations.



Source: The Author, 2017.

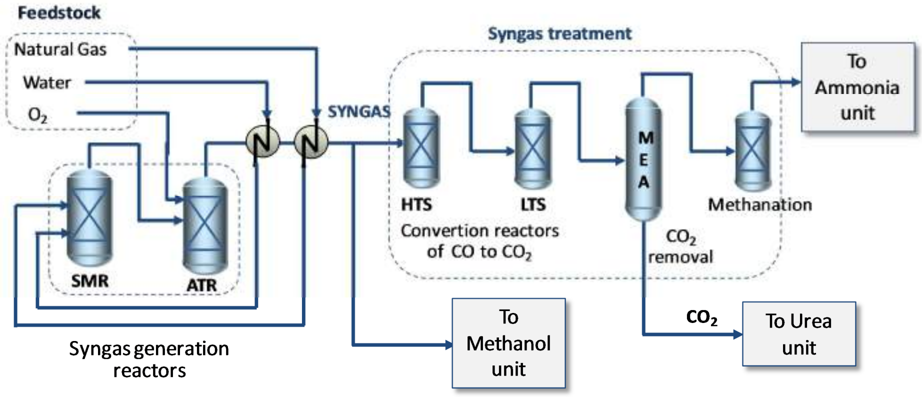
Below, is presented some details of simulation of units of syngas, methanol, ammonia and urea.

5.2.1 Syngas plant

Syngas plant is generally composed by two main reaction steps: methane reforming (and/or partial oxidation) and water-gas-shift (WGS). The WGS can be avoided for some uses if partial oxidation is employed. For the first step, the most usual choice is Steam Methane Reforming (SMR), an endothermic process demanding energy from a fuel (Martínez *et al.,* 2014); in plants that NG is the main reactant, it is also used as fuel to supply energy demand (Wu *et al.,* 2014). Partial Oxidation of Methane (POX) and Autothermal reforming (ATR), exothermic processes, can also be employed to produce syngas, reducing energy demand. SMR reactor is composed by tubes, filled with Ni or Co-based catalysts, generally containing alkaline metals in their composition (Richardson, 1994).

The effluent of the reactors contains H_2, CO, CO_2, besides not reacted CH_4 and H_2O. The processes are limited to chemical equilibrium, which justify the use of equilibrium reactors to simulate the reactors in these blocks. In SMR, excess of water is used to avoid coke formation over catalyst, which could lead to deactivation or damage the catalyst (Chiesa, 2010). Typical inlet temperature of SMR is around 450 °C - 650 °C and outlet temperature is around 800 °C - 900 °C (Rostrup-Nielsen, 2015), with pressures around 20 bar-50 bar (Chiesa, 2010; Mujeebu, 2016). POX and ATR reactors operate typically with higher temperatures (around 1,200 °C), and in the same range of pressure of SMR. In general, higher the pressure, higher will be the temperature for reaching desired equilibrium conversions. The reactor effluent contains H_2/CO (mol/mol) around 2:3. In this study, we considered the scheme illustrated in Figure 100.

Figure 100 - Bock diagram of syngas generation for methanol, ammonia and urea production.



Source: The Author, 2017.

In the first step, we admitted SMR and ATR in a series arrangement. The outlet of SMR is around 700°C to 800°C and 45 bar, and the outlet of ATR is around 1200°C and 43 bar, as reported by Mujeebu (2016). The molar H_2O/CH_4 ratio in the inlet of SMR is 3, where the effluent of such reactor is feed, together with O_2, to the reactor of ATR.

The syngas is then divided in two streams, one for ammonia synthesis, and the other to methanol synthesis (as shown in Figure 98). The syngas destined to ammonia and urea is firstly treated in two reactors to convert CO in CO_2, increasing the amount of H_2.

The first HTS reactor (high temperature shift) operates at 450 °C and 40 bar, and the second LTS (low temperature shift) operates at 230 °C and 37 bar, as related by LINDE (2006). After, syngas goes to a system of CO_2 removal consisting on an absorption tower with monoethanolamine.

Then, syngas goes to a methanation reactor, where residual CO and CO_2 are converted to methane, removing such compounds that would poison the catalyst of ammonia synthesis, as described by Sunny *et al.* (2016).

Figure E1 reproduced in large size in Appendix E shows the process flow diagram (PFD) of the simulation of the synthesis gas generation plant as implemented in the simulation software.

5.2.2 Ammonia plant

Haber-Bosh is the main route for industrial synthesis of ammonia (Nishibayash and Tanabe, 2013; Kyriakou *et al.,* 2016). Such process is an exothermic reaction from nitrogen and hydrogen in a molar proportion of $N_2/H_2 = 3$ over Fe-based catalyst, containing also a small amount of aluminum oxides, calcium and potassium (Bartels, 2008, Liyanage and Armentrout, 2004; Liu *et al.,* 2014). The bock diagram is illustrated in Figure 81 presented in Chapter 4.

The exergy consumption of an ammonia plant depends on the loop of the synthesis (Kirova-Yordanova, 2004), since the conversion is low for one single pass in the reactor, in a trade-off between kinetic rate and limitation of thermodynamic conversion. Thus, internal loop operates with high flow rate and an enormous consumption of energy in recompression steps. It is recommended that the temperature of reactor outlet be around 500 °C to maximize the yield of ammonia (Boyano *et al.,* 2011; Cetinkaya *et al.,* 2012).

The effluent of the reactor is cooled to -21 °C in a refrigeration cycle where ammonia is the refrigerant fluid. Then, the main stream goes to a drum of gas liquid separator, where ammonia in liquid phase is separated from non-reacted gases, which are compressed and recycled to the reactor (Gerosa, 2007).

Figure E3 reproduced in large size in Appendix E shows the process flow diagram (PFD) of the simulation of the ammonia production plant as implemented in the simulation software.

5.2.3 Methanol plant

The reduction of CO to methanol is an exothermic process limited by thermodynamic equilibrium, and thus favored thermodynamically by lower temperatures. The companies Lurgi, Haldor Topsoe and Basf operate at more low pressures (in relation to old process) with catalyst $Cu/ZnO/Al_2O_3/Cr_2O_3$ (Ozturk and Shah, 1985). The process operates in the pressure range between 4.9 MPa and 9.8 MPa (50 kgf/cm^2 and 100 kgf/cm^2), to ensure the activity of the catalyst and the efficient use of the heat of the reaction, the methanol converters are operated in the range of 200°C to 300°C of temperature (Malhotra, 2012). Nowadays, the synthesis of methanol from syngas is carried out in the range of 220°C to 270°C, in a $Cu/ZnO/Al_2O_3$ catalyst (Riaz, 2013). The block diagram of methanol synthesis is presented in Figure 52 of the Chapter 3.

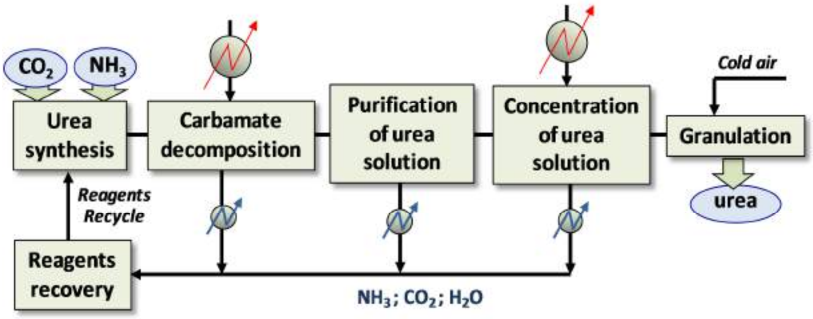
Catalysts are generally very selective; however, the conversion by pass is low, limited to thermodynamic equilibrium (Manenti *et al.,* 2011). This conversion is around 5-10% per pass (Methanol Holdings Trinidad Limited, 2005). Then, not reacted compounds must be separated by absorption/stripping processes and recycled to the reactor. Then, the global conversion can reach around 99% (Gerosa, 2007). The methanol produced contains small amounts of water and hydrogen, which are removed generally by flash and distillation (Riaz, 2013).

Figure E2 reproduced in large size in Appendix E shows the process flow diagram (PFD) of the simulation of the methanol production plant as implemented in the simulation software.

5.2.4 Urea plant

The main route for urea production is from reaction between NH_3 and CO_2 in gas phase (Vashishtha and Chakraborty, 2014) or in liquid phase, with lower temperatures and pressures around 200 bar to 240 bar (Sinngh *et al.,* 1989). Firstly, the reactants lead to ammonium carbamate, and exothermic reaction from which heat is recovered in a boiler for steam generation. In the second reaction, carbamate is dehydrated, producing urea and water (Isla *et al.,* 1993; Claudel *et al.,* 1986). These reactions are limited to equilibrium. The reactor molar feed ratio of NH_3/CO_2 is 2. According to Copplestone *et al.* (2008), the conversion is 60%, but can be optimized with recycles, reaching values of the global conversion of CO_2 around 78% (Vashishtha and Chakraborty, 2014). The block diagram of urea plant is presented in Figure 101.

Figure 101 - Bock diagram of urea production.



Source: The Author, 2017.

The main impurities in the output of the reactor are water and unconsumed reactants, besides non-decomposed carbamate. Unconsumed reagents are removed in three stages of separation, with different pressure levels, avoiding hydrolysis of urea and biuret formation. According to Singh *et al.* (1989), 40% of the ammonium carbamate generated in the reactor is recovered, being decomposed to CO_2 and NH_3 and recycled to the reactor.

For the simulation of urea plant, it was chosen the liquid phase reactor, due to its higher conversion values (PETROBRAS/UFN-IV, 2011). Once carbamate is not present in the most of commercial simulators, it was chosen the conversion reactor for simulate the reactor. The reactor was admitted to operate at 200 bar and 180°C, and with conversion of CO_2 of 40% according typical data in the literature (Singh *et al.,* 1989).

Figure E4 reproduced in large size in Appendix E shows the process flow diagram (PFD) of the simulation of the urea production plant as implemented in the simulation software.

5.2.5 Energy performance

The methodology to evaluate the energy performance of units follows procedures described on Section 5.3.1.

5.3 Results

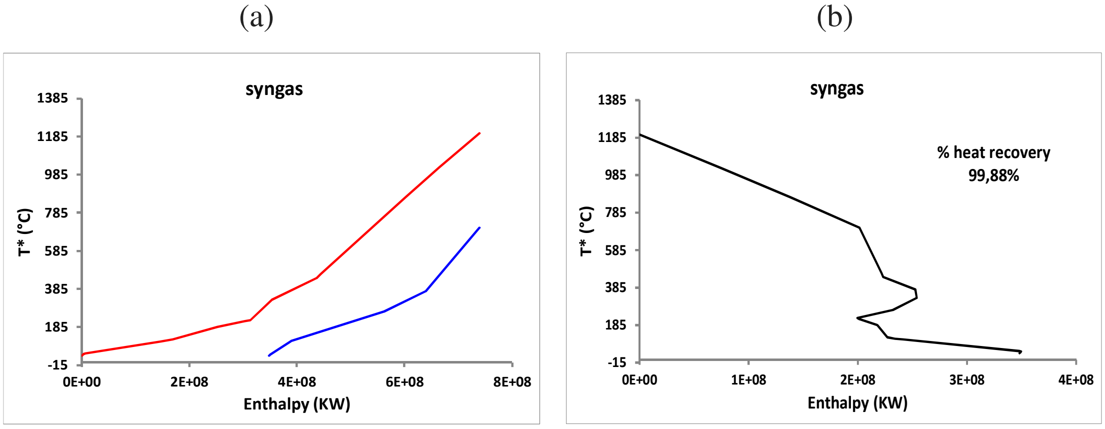
5.3.1 Energy analysis

The Energy Analysis calculator of the software HYSYS version 8.8 was used to obtain the energy consumption analysis of the proposed production units (synthesis gas, ammonia, methanol and urea). This calculator compares the value of the hot utilities and the cold utilities of the plants with the optimum value, considering the lowest consumption possible and the greater energy use resulting from thermal changes between hot and cold chains of the units. This optimization premise therefore defines the lowest operating cost. One can define *% of heat recovery* as:

$$\%\ of\ heat\ recovery = \frac{\begin{pmatrix} heat\ recovery\ in \\ proposed\ design \end{pmatrix}}{\begin{pmatrix} maximum\ heat\ recovery \\ according\ to\ pinch\ methodology \end{pmatrix}} \qquad (03)$$

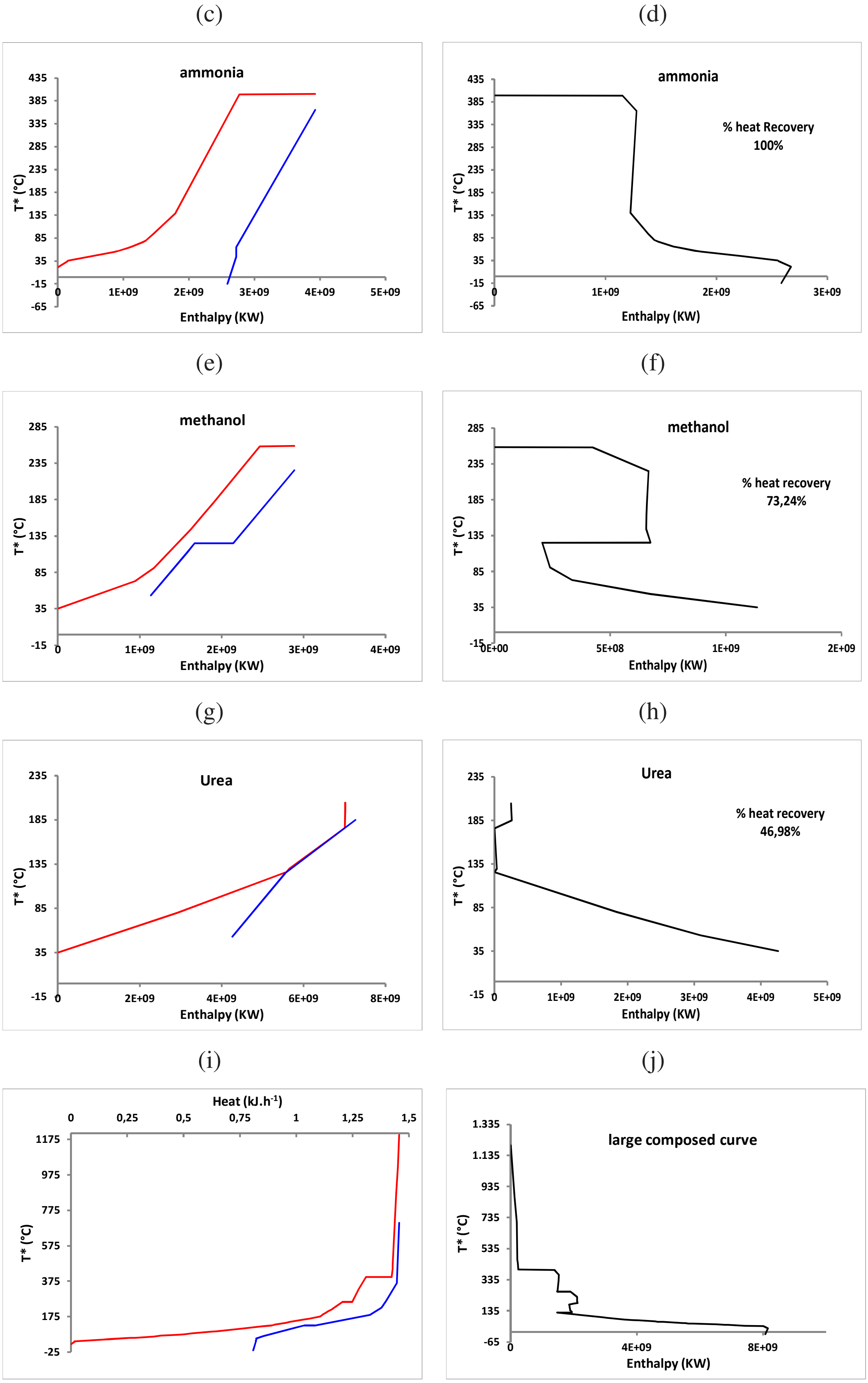
Figure 102 shows the results of composite curves and large composite curves of the units, for: (a, b) syngas, (c, d) ammonia, (e, f) methanol, (g, h) urea and (i, j) all units together with % heat recovery in the units.

Figure 102 – Composite curve and Great Composite Curve for: (a, b) syngas, (c, d) ammonia, (e, f) methanol, (g, h) urea and (i, j) all units together.



(a)

(b)



Source: The Author, 2017.

Table 17 presents the results of the simulated values of the hot and cold utilities of the separate units, as well as the values defined as targets of the energy optimization, considering the separate units. The first two columns of the table then show how much heat recovers in the current simulation with the separate units (comparison of columns 1 and 2). The last column (3) shows the target value of the energy optimization considering the assembled units.

Table 17 – Total hot and cold utility values comparation.

utility	Proposed design	Separated units according pinch analysis	All units according to pinch
hot utility (kw)	2.18×10^{9}	2.49×10^{8}	0.00
cold utility (kw)	1.03×10^{10}	8.33×10^{9}	8.08×10^{9}
recovered heat (kw)	4.31×10^{9}	6.25×10^{9}	6.50×10^{9}

Source: The Author, 2017.

Table 18 shows how much is recovered of the heat by comparing the targets of the separated units with them together and integrated. The current simulation is recovering approximately 70% of the maximum possible heat to be recovered, considering the separated units.

Table 18 – Proposed design compared to pinch for separate units[a].

% excess of hot utility	88.61%
% excess of cold utility	18.84%
% heat recovery	69.04%

Source: The Author, 2017.

[a] Hot and cold excess was calculated as $\left(1-\frac{\substack{Target\ according\ pinch \\ (separed\ units)}}{Proposed\ Desing}\right) \times 100\%$, while % heat recovery is calculated according Equation (03).

Table 19 presents the pinch targets for separate compared to pinch targets to integrated units.

Table 19 – Pinch targets for separate compared to pinch targets to integrated units.

Comparison of separated target units and joined target units	
% excess of hot utility[a]	100.00%
% excess of cold utility[a]	2.99%
% heat recovery	96.17%

Source: The Author, 2017.

[a] Hot and cold excess was calculated as $\left(1-\frac{\substack{Target\ according\ pinch\\(integrated\ units)}}{\substack{Target\ according\ pinch\\(separed\ units)}}\right)\times 100\%$, while % heat recovery as calculated as $\frac{\substack{Maximum\ heat\ recovery\\(integrated\ units)}}{\substack{Maximum\ heat\ recovery\\(separed\ units)}}$

The results show that the target values are almost the same, and that the heat target recovered in the separated units is 96% of the target of the joined units. That is, it is not worth integrating from the energy point of view. In theory, the joint energy analysis of all the streams in the units can provide more efficient solutions of thermal exchange and allow the reduction of the energy expenditure and, as a consequence, the reduction of the operational cost of the industrial complex.

However, this type of analysis must be done with much criterion and great care, because when a thermal exchange is proposed between streams of distinct production units, we add operational restrictions to the project, due to the possibility of an operational problem in a plant being propagated to other production plants. This occurrence has great potential to cause very expensive operational shutdown of the entire industrial complex.

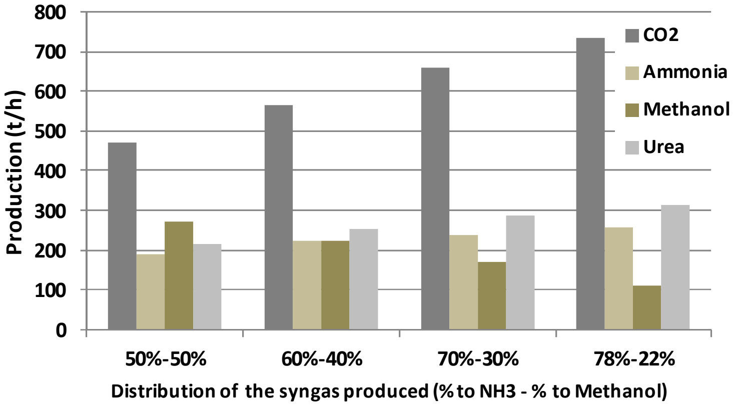
5.3.2 Nominal load for the complex necessary to substitute all importation of ammonia, methanol and urea

a) First case studied: nominal load of 50% of the maximum flow of Route-3, equivalent to 12.0 million cubic meters per day of natural gas. In this case, no simulated distribution of syngas between the ammonia plant and methanol meets the full import substitution of urea. Figure 103 (a) presents the result of CO_2, ammonia, methanol and urea production, considering the nominal load of 50% of the maximum flow of Route-3.

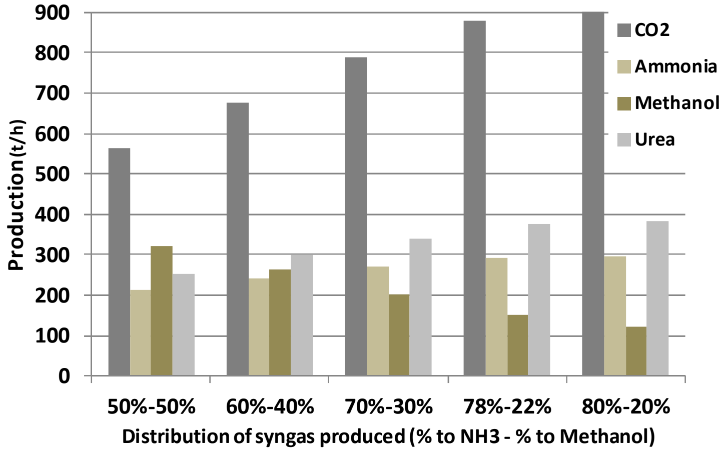
b) Second case studied: nominal load of 60% of the maximum flow of Route-3, equivalent to 14.4 million cubic meters per day of natural gas. In this case, both the distribution of the syngas produced from 78% ammonia and 22% methanol, and the alternative 80% ammonia and 20% methanol, account for the complete import substitution of the products studied. However, the 80%-20% distribution generates a surplus quantity of products (in relation to imported quantities) more balanced, allowing greater operational flexibility in the case of necessity for produced flow adjustments. It should be noted that other nominal load values were tested, but fell below or beyond the load required to meet the basic premise of replacing the imported flows of the products studied. Figure 103 (b) presents the result of CO_2, ammonia, methanol and urea production, considering the nominal load of 60% of the maximum flow of Route-3.

Figure 103 - Production obtained with (a) 50% of the nominal Route-3 flow and (b) 60% of the nominal Route-3 flow.

(a)



(b)



Source: The Author, 2017.

5.3.3 Complex implementation costs (CAPEX)

The cost of the main equipment of the units was estimated according to the methodology described in Chapter 3. The consolidated result of this calculation is presented in Table 20.

Table 20 – Cost of the main equipment of the units.

PRODUCTION UNIT (US$*million)	Consolidated cost of main equipment of process units						
	VESSEL	REACTOR	COMPRESSOR	EXCHANGER	PUMP/MOT.	TOWER	TOTAL:
Syngas unit	2.76	21.92	12.77	5.87	0.99	5.07	49.38
Ammonia unit	5.00	4.92	13.35	5.56	-	-	148.96
Methanol unit	1.22	3.02	13.18	1.63	-	2.50	21.54
Urea unit	10.44	6.77	94.96	14.49	6.17	-	132.83
cost per equip. type	19.42	3.67	254.39	27.54	7.16	7.56	352.71

Source: The Author, 2017.

Table 21 shows the total consolidated cost of complex implementation considering the load defined as 60% of the nominal flow of the pre-salt Route-3 and the distribution of the syngas produced in the ratio of 80% for the ammonia unit and 20% for the methanol unit.

The quantities of ammonia, methanol and urea produced are sufficient to fully avoid the imported quantities of these products, taking into account the base year of 2015.

Table 21 - Consolidated total cost of the complex.

Unit	Syngas	NH3	MeOH	Urea	Total
Total fixed cost of the complex - CAPEX (US$*million)	287	863	127	773	2,050

Source: The Author, 2017.

5.3.4 Complex raw material cost survey

Considering the premise of defining the nominal load of the complex equal to 60% of the maximum flow of Route 3, equivalent to 14.4 million cubic meters per day of natural gas and the average cost of natural gas of US$ 247.34 per thousand of normal cubic meters (ANP, 2015), there is a total cost of raw material for the complex of US$ 1.30 billion per year. Table 22 shows the estimated cost of the complex raw material.

Table 22 - Estimated cost of the complex raw material.

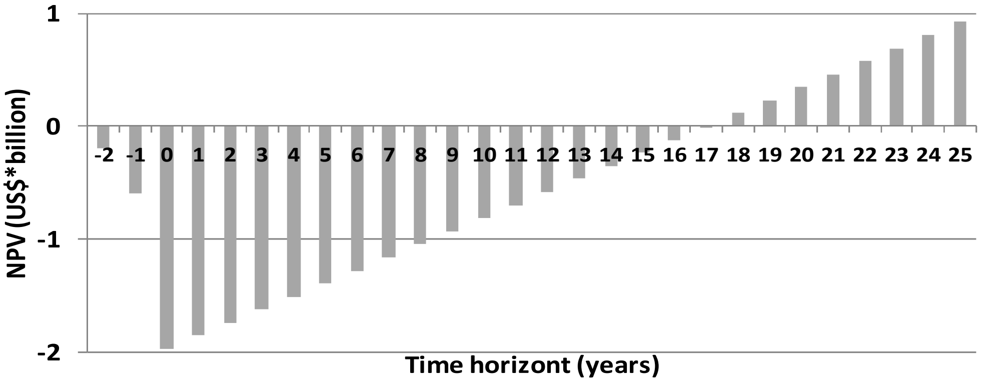
Flow of Route-3	60%
Load of the complex	$(14.4 * 10^6)$ m^3/d
Annual load	$(5.26 * 10^9)$ m^3/d
Gas price reference:	247.34 US$/thousand m^3 (ANP, 2015)
Total cost of the raw material of the complex: 1.30 US$ billion/y	

Source: The Author, 2017.

5.3.5 Preliminary Technical and Economic Feasibility Study

The project feasibility study shows that the project only begins to make a financial return in the 17th year after starting operations in the complex. This weak economic result is due to the high cost of raw materials in relation to the potential revenues from the project. In a market with natural gas available at lower prices, the project would be more viable. Table 08 showed in Chapter 3 presents the Economic assumptions of the project to calculate the Net Present Value (NPV), as well as defined by the Technical and Economic Feasibility Study of the project. Figure 104 presents the consolidated result of NPV carried out, considering the economic life of the project in years.

Figure 104 - Result of NPV carried out.



Source: The Author, 2017.

5.3.6 Evaluation of scenarios for Economic Viability of the project

The Net Present Value (NPV) was calculated considering a Minimum Attractiveness Rate of 10%, with a sensitivity analysis of 20% for more (MAR = 12%) and 20% for less (MAR = 8%). The three values present negative results, indicating an economic unfeasibility for the enterprise (considering the Minimum Attractiveness Rate used for evaluation of this project). The Internal Rate of Return (IRR) would be around 3%.

In the Economic Viability Study presented, it is verified that the profit margin is greatly impacted by the (high) cost of the raw material. The difference between the potential revenues and the cost of the raw material is small, considering the high value of the CAPEX of the project. It is evident that the project, as proposed, is not attractive from the economic point of view, presenting negative NPVs for the attractiveness rate values defined as the premises of the study.

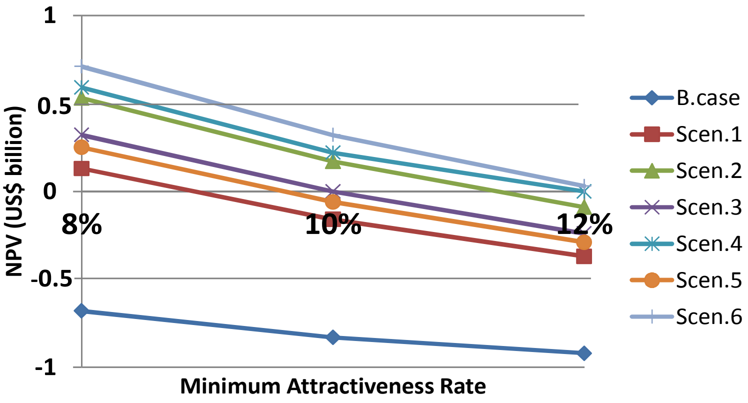
However, an alternative scenario assessment shows that a raw material cost reduction negotiation or even obtaining tax incentives could make the NPV of the project positive. A discount for the purchase of natural gas in large quantity could bring an economic result to the project. The Economic Viability analysis shows that a 12.3% discount in the price of the natural gas that serves as raw material for the complex is enough to nullify the NPV, considering a Minimal attractiveness rate of 10% (Scenario 1). This discount would bring the start of the project's financial return back to the ninth year of operations. Even considering a MAR of 12% (upper limit of the sensitivity analysis), a 16.9% discount on the gas price would be enough to make the project viable. This discount would bring the start of the project's financial return back to the eighth year of operations.

A negotiation at governmental level for the use of tax incentives in the project (considering its structuring project characteristics) can also allow the investment viability. The scenario shows that a tax reduction of around 60% in Brazilian taxes such as PIS, ISS, COFINS and CSSL, is enough to nullify the project's NPV, considering a 10% MAR. This reduction of tax burden would bring the beginning of the financial return to the ninth year of operations. A 75% reduction in taxes would be enough to make the project viable even considering a 12% MAR. This reduction would bring the beginning of the financial return to the eighth year of operations.

A third line of scenario study for economic feasibility of the project simulates the revenue increase of the complex. A 10.8% increase in the value of the sale of the products would be sufficient to make feasible the project, considering a MAR of 10 %. This increase would bring the beginning of the return of the investment to the ninth year after the startup of the complex. An increase of 14.9% would be enough to zero the NPV, even considering a MAR of 12%. This reduction would bring the beginning of the financial return of the project to the eighth year of operation of the complex.

Figure 105 presents the consolidated result of studied scenarios of the project. It should be noted that the analysis of the potential revenue of the project did not consider sales values of excess production of ammonia, methanol and urea in relation to the imported volumes (3.01% of ammonia, 14.45% of methanol and 6.30% of urea), basically because these values of excess production do not have internal demand and would have to compete in the international market, with prices defined by the international market.

Figure 105 - Consolidated results of the scenarios study.



Source: The Author, 2017.

Legend:

Base case: without discounts;
Scenario1: Raw material discount (natural gas) of 10%;
Scenario2: Raw material discount (natural gas) of 15%;
Scenario3: Taxation reduction (tributes) of 60%;
Scenario4: Taxation reduction (tributes) of 75%;
Scenario5: Increase in the selling price of the products by 10%;
Scenario6: Increase in the selling price of the products by 15%.

5.4 Conclusions

The present paper simulated the simultaneous and integrated production of methanol, ammonia and urea, and their capital and operational costs were estimated. Proposed designs achieved 70% of heat recovery taking pinch analysis as reference. Based on pinch analysis, the maximum recovery heat operating units separately and considering all units as one are basically the same; thus, there is no advantage in integrate all units for energy saving.

The economic viability study carried out shows that there is a positive financial solution for the proposed industrial complex, provided that some economic adjustments are sought, such as obtaining a discount in the value of the raw material (natural gas) or a reduction of the tax burden for the plant. A third possibility would be to try to increase the revenues; however, the quest for greater revenue collection is more difficult as the price of the commodities produced is determined by the international market. To consider that the internal market would be willing to pay a price higher than the amount stipulated by the international market is a very big risk.

For the viable financial solution, the possibility of substituting critical inputs for the national chemical industry, currently imported in large quantities, may make the country less vulnerable to the availability and pricing policy dictated by the international market. Although not analyzed in a specific scenario, a combined solution may facilitate negotiation with possible gas suppliers and government representatives, so that it is possible to afford the project in economic terms with lower gas discount and lower tax incentives.

6. A TECHNICAL PROPOSITION FOR THE BRAZILIAN CASE OF USAGE OF NATURAL GAS TO PRODUCE METHANOL, AMMONIA AND UREA CONSIDERING NON-DEFAULT OPTIONS

Abstracts

A proposal for the production of chemical products derived from natural gas through the generation of synthesis gas to supply the Brazilian market is presented below. The proposal presented here makes use of the technologies most appropriate to the needs of the country in terms of the profile of products generated and also the availability of raw material. This proposal is technically based on the study of the patents of the coproduction processes carried out and presented in Chapter 2, besides taking into account the current conditions and specific needs of the Brazilian market of chemical products produced from natural gas presented in Chapter 3, 4, and 5.

Introduction

In general, the reserves of a nation's strategic resources only become economic and social value for its inhabitants when these reserves are developed and exploited economically, becoming them financial resources for the collective social development. This scenario represents well the current scenario of the part of the natural gas reserves of the Brazilian Pre-salt, which will be moved by Route-3 of first stage of exploration of the Pre-salt. Originally, it was foreseen that the gas moved by this Route would be used as raw material by the phase 2 petrochemical plants of the COMPERJ project (PETROBRAS, 2011). It happens that, due to competitiveness of gas prices in the American market, the project was canceled and the gas of Route-3 lost specific destination. On the other hand, it is quite reckless Brazil's economic situation of relying almost entirely on imports of basic chemicals such as ammonia, methanol and urea to supply its chemical industry.

The issues presented in Chapter 1 allow us to discuss the use of natural gas that would be destined to the second phase of COMPERJ and that currently does not have guaranteed consumption. On the other hand, the study on patents and technologies used for the combined production of chemicals from natural gas presented in Chapter 2 allows to evaluate and propose mature and tested technological routes for the production of chemical products from natural gas that are more advantageous for the Brazilian scenario. The lessons learned from the various technological alternatives studied in Chapter 2 provide a lot of security for proposing a specific set of technologies adequate to the needs of chemical products in the Brazilian market.

The data collected in Chapters 3, 4 and 5 provide technical and economic support to the proposed configuration of a Brazilian complex for the production of basic chemicals for domestic market supply. The proposed complex should use only natural gas as raw material, taking advantage of the large availability of natural gas that the Brazilian pre-salt will provide to the country. Only Route-3 of the first phase of exploration of the pre-salt will provide about nominal 21 million cubic meters of natural gas (maximum capacity of 24 million cubic meters of natural gas) per day until 2020.

According to a study presented in the Chapter 5, the nominal natural gas flow that satisfies the basic premise of substitution of imports of ammonia, methanol and urea for Brazilian domestic market is 60% of the maximum flow of the pre-salt Route-3 project, which is equivalent to a nominal flow of 14.4 million cubic meters per day of natural gas for feeding the proposed complex.

Thus, this work aims to propose an industrial complex capable of producing these three chemical products from natural gas, using the technologies most appropriate to the product profile that the country needs and also to the specificities of the Brazilian market. The basic premise used to compose the proposal presented here is to produce the total amount of ammonia, methanol and urea currently consumed in the Brazilian domestic market, thereby completely eliminating the need to import such products. In the next paragraphs are presented the steps of the produce the target chemicals. In these sections, numbers between parentheses indicate equipment that is presented at the end of this chapter (Figure 106).

6.1 Catalytic reforming of natural gas

As the project only provides for the use of natural gas as raw material, the treatment for the removal of sulfur compounds can be dispensed with, which reduces the cost of the project. To allow a better energy recovery, the project provides for the alternative preheating of the natural gas charge of the complex from the recovery of part of the thermal energy of exhausted gases from the stage of catalytic reform. To this end, a heat exchanger (1) can alternatively be positioned upstream of the reforming reactors.

The project envisages the section of catalytic reform of natural gas as two stages in series. The first stage consists of a methane vapor reforming reactor (SMR) (2), operating under the conditions of 802°C and 4.41 MPa (45 kgf/cm^2). The reform reaction is conducted in an environment with excess steam. This steam excess has the function of controlling the tendency of deposition of elemental carbon (coke) on the surface of the catalyst used in the reactor, thus avoiding its deactivation. Thus, the feedstock of the SMR reactor must be supplied in the molar proportion of vapor\methane equal to 3:1.

The second reform stage consists of a self-thermal reactor (ATR) (3), operating under the conditions of 1,206 °C and 4.21 MPa (43 kgf/cm^2). This self-thermal reactor operates by providing combustion of the small amount of unreacted methane in the SMR steam reforming reactor. The large amount of heat generated by the combustion reactions in the self-thermal reactor (3) is used as the energy source of the SMR steam reforming reactor (2). The oxidant gas stream responsible for methane combustion in the ATR reactor is composed of oxygen, which is separated from atmospheric air. Oxygen is produced in an ASU (4) air separation unit capable of distilling atmospheric air into high purity oxygen and nitrogen streams.

The syngas generated in the catalytic reform stage leaves the self-thermal reactor with very high temperature. Part of this thermal energy is used to preheat the natural gas in the exchanger (1). This preheating step raises the temperature of the natural gas, which is the charge of the complex to about 700°C. In sequence, the still very hot syngas is cooled by exchanging heat in a set of exchangers (5). The thermal energy exchanging of the syngas in these heat exchangers allows generating all the steam needed for the steam reforming step that occurs in the SMR reactor. It should be noted that this thermal energy recovery makes the reform stage practically self-sufficient in energy terms.

After the energy recovery stage, which causes of the synthesis gas cooling, syngas is divided into two streams: one stream is used directly for production of methanol and the other stream is used for the production of ammonia. A great flexibility of the process here proposed is to be able to change the flow rates generated by this division and to feed the methanol synthesis and ammonia synthesis units with adequate syngas quantities to attenuate any momentary imbalance in the supply of the markets of these products. It is to be noted that this solution for dividing the synthesis gas is employed in the patents US 2001/6333014-B1, US 2007/0299144-A1 and US 2016/0083260-A1, presented in Chapter 2.

6.2 Methanol production system

The syngas stream used for the methanol production is cooled by water in a heat exchanger (6). The water which is condensed by cooling of the vapor present in the gas flow exiting the reforming step is separated in the separator vessel (7). After water separation, the non-condensed gases of this syngas stream are preheated by thermal exchange in the heat exchanger (9) and then are sent to the methanol synthesis reactor (8), where a part of the carbon oxides combines with hydrogen to form the alcohol. This reactor operates with only one passage through the catalytic bed (without recycle flow) and under the conditions of 263 °C and 4.9 MPa (50 kgf/cm^2).

The non-use of unreacted gas recycle allows the use of smaller, simpler and cheaper equipment. Obviously, this option also generates a smaller amount of product, but for the Brazilian market, this is not a problem, given that Brazilian consumption of ammonia is about eight times higher than methanol consumption, considering the ammonia required to produce all the urea consumed in the country, according to the study presented in Chapter 5.

It is to be noted that the most conventional solution to this alternative is to feed the ammonia and methanol reactors separately in parallel and using the recycle of the unreacted gases into both conversion reactors. This solution was adopted in its entirety only by patent US 2001/6333014-B1 and adopted to a greater or lesser extent by patents US 1993/5180570-A, US 2014/8692034-B2 and US 2012/0148472-A1.

The output gases from the methanol synthesis reactor pre-heat the reactor inlet gases in the heat exchanger (9) and then are sent to a cooling section with water in the heat exchanger (10). After the final cooling, the produced methanol is separated from the unreacted gases in a separator vessel (11). The unreacted gas stream is composed largely of hydrogen and water, as well as oxides of carbon and traces of methane and methanol. After treatment, this gas is also used for the production of ammonia.

The crude methanol in the liquid phase which is separated in vessel (11) follows to the purification section composed of two distillation columns (12). In the first purification column the contaminants lighter than the methanol are eliminated by the top and in the second column the heavier contaminants such as waste water and higher alcohols are removed from the bottom. The purified methanol is recovered by the top of this second column.

6.3 Synthesis gas treatment system

Returning to the fraction of the syngas that is directly destined for ammonia production, this stream is sent to the treatment section for purification of the syngas, by separating the oxygenated compounds from the hydrogen stream. This step is necessary because the oxygenated compounds are considered poisons for the catalysts used in the ammonia conversion reactor, causing them to be deactivated.

In a first step, the conversion of CO into CO_2 occurs through the water-gas-shift reaction (WGS) or simply shift reaction. This reaction is widely used for the removal of carbon monoxide from the syngas and for the maximization of the hydrogen produced. The process is moderately exothermic and the conversion is limited by the chemical reaction equilibrium, which is a function of the reaction temperature.

Because it is an exothermic reaction in the equilibrium condition, the shift reaction is favored at low temperature, although the reaction kinetics is quite impacted, with a great decrease in the conversion rate of the monoxide. Thus, the step of converting CO to CO_2 into two different reactors is proposed. The first water-gas-shift HTS reactor (13) operates at high temperature under the conditions of 448 °C and 3.92 MPa (40 kgf/cm^2). The syngas for the production of ammonia enters the HTS reactor (12), where the shift reactions occur, with conversion of CO to CO_2. In this reaction, carbon monoxide reacts with water vapor and is converted to CO_2 and hydrogen. It should be noted that this two-stage carbon monoxide conversion solution is currently used by all of the designers of this type of unit.

The output syngas of the HTS reactor is mixed with the unreacted gases from the methanol synthesis reactor. The mixture is cooled in the heat exchanger (14) and is then sent to the second CO conversion reactor. This second LTS water-gas-shift reactor (15) operates at lower temperature under the conditions of 228 °C and 3.72 MPa (38 kgf/cm^2). Also in this reactor the shift reactions occur, with conversion of CO into CO_2 and formation of more hydrogen.

In a second treatment step, CO_2 is separated from the syngas stream. Removal of CO_2 occurs by washing with an amine solution. The CO_2-rich syngas passes through a packed absorber tower (16), where it finds in counter-current a solution of monoethanolamine (MEA). In the equilibrium stages of the tower occurs the absorption of carbon dioxide by the MEA solution, with the formation of complex salts. The saturated MEA solution leaves the column and proceeds to the regeneration stage, where, by heat action (120 °C to 125 °C), the chemical bonds of the complex salts are broken and the process reverses itself, with regeneration of the original reagents. The absorbent column operates under the conditions of 40 °C at the top, 120 °C at the bottom and 0.29 MPa (3.0 kgf/cm^2). The CO_2 separated by the top of the column is destined for the production of urea.

After treatment in the shift reactors and the CO_2 separation, the synthesis gas used for ammonia conversion still needs to undergo a complementary treatment step to ensure the complete extinction of traces of oxygenated compounds from the gaseous stream. A methanator reactor (17) is used for this step. In this reactor, hydrogen reacts with residual carbon oxides to form methane and water. The methanator reactor operates under the conditions of 222 °C and 3.63 MPa (37 kgf/cm^2). These operating conditions guarantee a CO and CO_2 concentration at the process output of less than 5 ppm.

Since the hydrogenation reactions are highly exothermic, the heat generated in this reactor can be recovered for heating water or for generating low pressure steam. The main advantages of the methanation process are the simplicity of facilities, low energy consumption, low initial investment and low maintenance costs. The main disadvantage of the process is the consumption of a small amount of the hydrogen present in the syngas.

6.4 Ammonia production system

The syngas treated in the previous step receives the addition of nitrogen, maintaining a ratio of 1 mole of nitrogen to every 3 moles of hydrogen and then is compressed to the level of 19.6 MPa (200 kgf/cm^2) in the compressor (19). The required nitrogen is produced in the atmospheric air separation unit (4). The compressed syngas is dehydrated in a molecular sieve unit (20) to allow the gas drying to a level of just a few parts per million of residual water.

After drying, the gaseous feed stream for the ammonia conversion reactor (22), made up of nitrogen and hydrogen, exchanges heat in the heat exchanger (21) with the exhaust gases from that reactor. After this preheating, this stream feeds the ammonia reactor (22).

The output gases from the ammonia reactor then exchange heat with the inlet gases for the reactor and then, pass through an expansion stage (23) to pressure values not much higher than atmospheric pressure. Thereafter, the ammonia produced is condensed in a heat exchanger (24) which operates with an ammonia refrigeration cycle (25). Cooling at about -21 ° C allows condensation of the produced ammonia, which is separated from the hydrogen rich gas, into a separator vessel (26).

The incondensable gases exiting the separator vessel (26) are returned to the ammonia compressor (19) in the form of a recycle stream and mixed with the fresh charge feeding the ammonia reactor.

A small gas flow is purged (27) from the system (about 8% to 12%) in order to maintain the inert content of the reaction stream under operational control. It should be noted that the purge gas flow is rich in hydrogen, so that this gas can be used for combustion in some auxiliary equipment of the complex.

A smaller part of the ammonia produced is withdrawn from the separator vessel (26) as the final product and is sent to storage and later supply to the domestic ammonia market. Most of the ammonia produced follows for feed to the urea synthesis unit.

6.5 Urea production system

After compressing in the compressor (28) up to 19.6 MPa (200 kgf/cm^2), most of the ammonia produced feeds the urea synthesis reactor (30), which operates under the conditions of 178 °C and 19.6 MPa. The same is true for the CO_2 stream, which is separated in the absorption column (16). This stream is compressed in the compressor (29) to 19.6 MPa and is also sent to the urea synthesis reactor.

Feeding of the urea synthesis reactor follows the molar ratio of 2 moles of NH_3 for 1 mol of CO_2. The conversion rate of carbon dioxide into urea reaches 78%. In the reactor, ammonia and CO_2 react to form ammonia carbamate (the first reaction stage of urea formation). Reagents not consumed in the urea reactor are removed in three distinct stages of pressure. The purpose of three-stage purification is to reduce the occurrence of undesirable reactions of urea hydrolysis and biuret formation, which occur simultaneously with the formation of urea. This configuration is in accordance with the traditional patents which describe the urea production.

The urea reactor output stream is heated in the heat exchanger (31) and then goes to the decomposition stage of ammonium carbamate (32) into urea and water (second reaction stage of the urea formation).

The urea purification section consists of three stages of pressure reduction and heating. The process starts by reducing the pressure of the urea solution from 19.6 MPa to 1.67 MPa (200 kgf/cm^2 to 17 kgf/cm^2) in the pressure reducing valve (33) and heating the solution in a heat exchanger (34). Thereafter, the purification process continues in the secondary purification reactor (35) with two further steps of pressure reduction and heating, in order to allow residual ammonium carbamate, still present in the reaction medium decomposes into ammonia and carbon dioxide. Two phases are then separated at this stage of purification, being a liquid phase and another vapor phase, consisting of ammonia and CO_2.

The liquid phase receives further heating in the purification section and its pressure is reduced to 0.20 MPa (2.0 kgf/cm^2) to facilitate the release of the NH_3 and CO_2 gases. Finally, the last stage of depressurizing of the purification step occurs, with the pressure of the urea solution stream being reduced to 0.064 MPa (0.65 kgf/cm^2), with more ammonia and carbon dioxide being released from the urea solution. After purification, the concentration step of the urea solution is started.

The urea solution is again heated in the heat exchanger (36) and sent to the vacuum concentrating vessel (37) through the use of the vacuum pump system (38), causing part of the water in the solution to evaporate, and increasing the concentration of the urea solution from 68% by weight to 80%. At this stage, some urea crystals form. The solution is then heated from 80 °C to 110 °C to dissolve these formed crystals again, before final evaporation of the solution. At this stage, the urea produced reaches 99% by weight purity, at about 140 °C.

After concentration, the urea follows to the final granulation step (39) using a pre-cooled atmospheric air stream, which is generated by a blower (40). Urea for the production of fertilizers is marketed as grains of 2 mm to 4 mm in diameter. These grains are formed by spraying the molten urea onto previously formed "seeds", supported in a bed of air generated within a granulator. During the contact of the powdered urea with the cold air, the urea solidifies around the seeds, forming the grains of urea. This process was detailed by Schell (1978) and complemented by Isla (1993).

The granulated dry grains are classified through sieves arranged at the end of the granulator. Grains of dimensions above the specification are separated and subsequently comminuted and combined with the grains of dimensions below the specification for use as seeds of the granulation process. The final product is cooled with cold air and sent for bulk storage and subsequent commercialization.

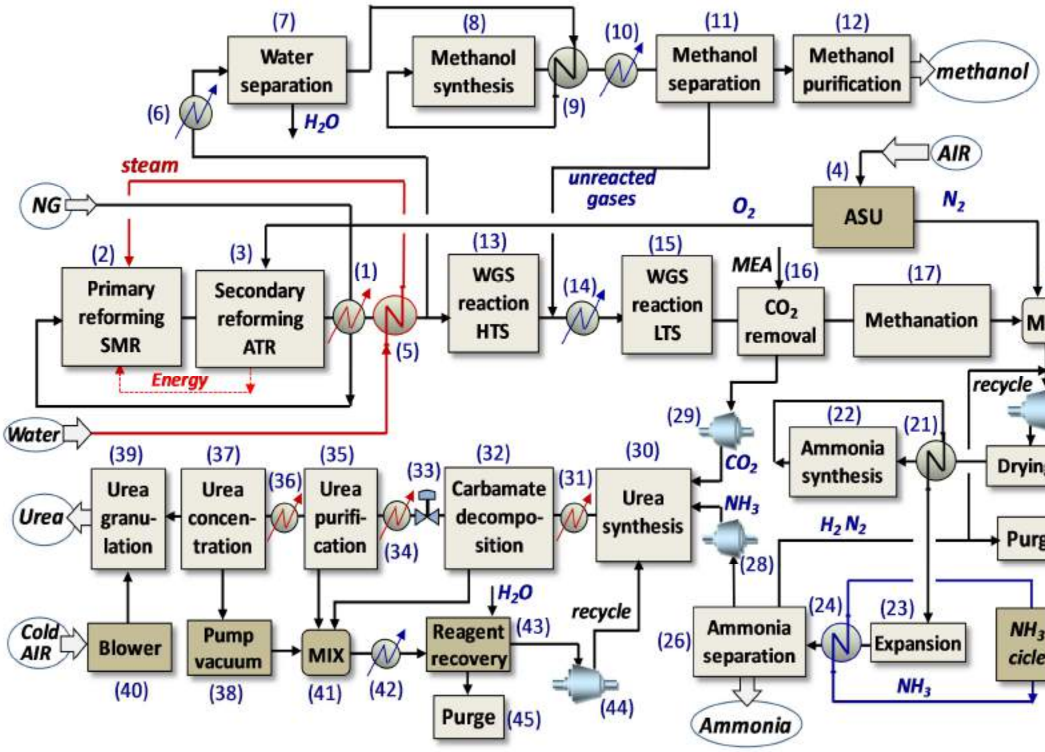
The vapor phase from the carbamate decomposition, purification and urea concentration sections is mixed in the vessel (41) and cooled in the heat exchanger (42). Thereafter, the vapor phase is removed to the reagent recovery section (43), where, by washing with water, recovery of the ammonia and CO_2 occurs, which are sent back to the synthesis reactor in a looping process as a recycle stream, through the compressor (44).

A small gas flow is purged (45) from the reagent recovery unit (43) in order to maintain the inert content of the reaction stream under operational control. This flow can also be sent to an alternative auxiliary unit for ammonia recovery. Figure 106 shows, in a simplified form, the consolidated block diagram of the industrial complex proposed in this study for the production of gasochemicals aiming at the supply of the Brazilian domestic market, according to the more traditional projects.

6.6 Consolidated block diagram

Figure 106 shows, in a simplified form, the consolidated block diagram of the industrial complex proposed in this study for the production of gasochemicals aiming at the supply of the Brazilian domestic market.

Figure 106 - Block diagram of the proposed industrial complex for the production of gasochemicals for the Brazilian market.



Source: The Author, 2017.

6.7 Analysis of the superstructure of the proposed industrial complex

In general, the configuration of the proposed complex adopts the most used and consecrated technologies available in the literature for each stage of the process. All proposed technologies can be found in the patents evaluated in Chapter 2, but none of them presents the same configuration as the proposal presented here. Thus, the contribution of this proposal is in the chosen set of technologies, so as to be the most appropriate for the Brazilian scenario.

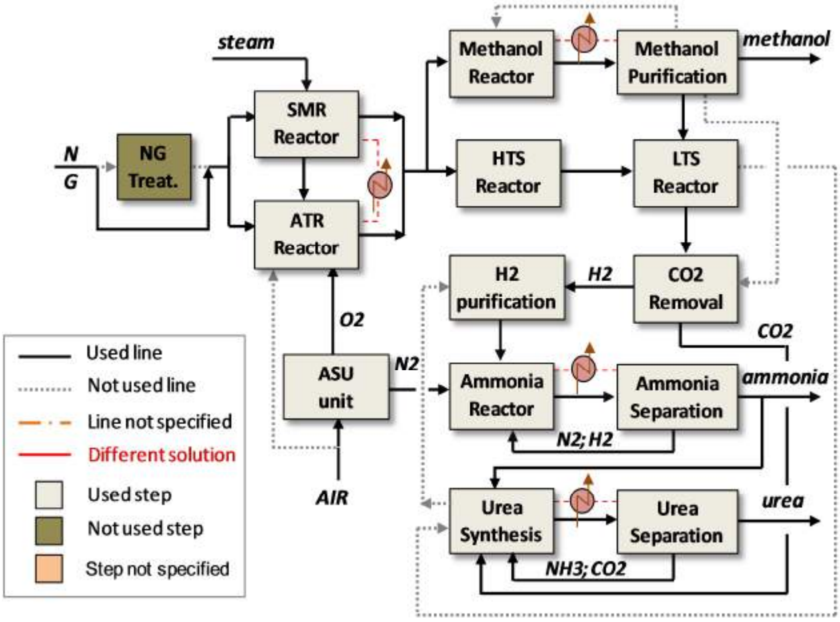
Following the reasoning adopted in Chapter 2, is presented a superstructure of the proposed complex for the production of gasochemicals from natural gas, to supply the Brazilian market. The initial treatment stage of natural gas was deactivated, due to the fact that there is no alternative feedstock besides the natural gas for the complex. Several patents evaluated in Chapter 2 presented this same solution.

The configuration of the reforming reactors SMR and ATR in series was adopted, as in most of the patents evaluated in Chapter 2. The use of an atmospheric air separation unit (ASU) was adopted, as are most of the treated processes that use natural gas as a source of hydrocarbons for the reforming step.

The synthesis gas division was adopted at the exit of the reforming stage, with part of the syngas following for the conventional treatment for ammonia production and part going directly to the methanol synthesis step, using only one passage in the conversion reactor. This solution was adopted in U.S. patent 2001/6333014-B1. U.S. patent No. 1968/3598527-A adopts the syngas delivery solution directly for the synthesis of methanol in a single passage through the reactor. But the difference is that there is no division of syngas.

Methanation technology was adopted for the final extinction of oxygenates from the syngas stream that feeds the ammonia reactor, as well as the vast majority of patents evaluated. In the same way, the conventional technology of CO_2 removal with monoethanolamine (MEA) was adopted. For the production of urea, the liquid phase conversion technology was adopted, which is the most efficient technology available currently. This choice follows the trend of the most recent patents, from the year 2000. Figure 107 presents the consolidated superstructure with the technologies chosen for the proposed solution.

Figure 107 - Superstructure of the proposed industrial complex for the production of gasochemicals for the Brazilian market.



Source: The Author, 2017.

6.8 Conclusions

The chosen technologies are configured in an integrated industrial complex, taking advantage of synergies between the production units, in order to maximize the economic result and to adapt to the specifics of the Brazilian domestic market.

The proposed complex does not use the sulphurous compounds removal step as well as the processes described in the patents studied which do not provide for the operation of the production units with different source of hydrocarbons load, like coal and biomass. This decision reduces the total cost of the industrial complex.

In the same way, the proposal presented uses the common solution of two reactors in series to compose the methane reform stage, the first being an SMR reactor and the second one, an ATR reactor.

Still as a common point to most of the patents studied, the proposed complex uses an atmospheric air separation unit. It should be noted that this solution is suitable for projects that only use natural gas as load of the industrial complex.

As the main differentiated technological solution adopted, in relation to the majority of patents studied, it is possible to highlight the step of removing oxygenated compounds from the syngas. In more conventional designs, syngas for the production of ammonia is traditionally treated in CO converters and then subjected to a methanation step in order to completely extinguish the oxygenated compounds.

In the proposed complex, part of the syngas generated is firstly sent to the methanol conversion reactor, where a part of the carbon oxides combines with the hydrogen to form the alcohol. This reactor operates without recycling. This conversion stage sensibly reduces the presence of oxygenated compounds, and consequently, reduces the intensity of the oxygen extinguishing step of the syngas for the production of ammonia.

Although this solution has been chosen to a greater or lesser extent by other patents, it can be considered that this technological solution is the most distinct item of the presented proposal, in relation to the majority of patents analyzed. Due to the way this solution is composed in the general configuration of the proposed complex, in addition to the use of this technology for the extinction of oxygenates, the proposal provides for the possibility of adjustment in the ammonia / methanol production ratio of the complex, in order to adapt to the possible market variations of these products.

This is possible because this proposal maintains a syngas flow directly feeding the stage of ammonia conversion and this flexibility allows more easily adjustment of the production profile of the complex. Then, the great distinction of this proposal is that it uses the extinction of oxygenates with the conversion of methanol in parallel with the direct feeding of part of the syngas to the production of ammonia. This gives a very great flexibility to the project, so that this adjustment can also be considered as an item of differentiation in relation to the projects studied.

The urea production step utilizes the most widespread technology in the most recent patents, which is the conversion of CO_2 and ammonia into liquid phase for the formation of the carbamate and in sequence, its dehydration with urea formation. This technology gives robustness to the configuration chosen, reducing any technological risks of the complex.

CONCLUSIONS

As discussed in Chapter 1, currently, the natural gas market is restricted to a narrow stretch of the Brazilian coast and cannot reach the interior of the country due to lack of infrastructure to move the product. Industrial projects by high demand for natural gas, such as the one proposed in this work, are especially suitable to serve as "anchor points", guaranteeing a level of consumption of the product that propitiates the remuneration and the expansion of the domestic gas market around them.

The natural gas consumption of a complex such as the one proposed in this paper has the condition to leverage the Brazilian natural gas market. The guaranteed minimum consumption functions as a "seed" that generates economic conditions enough to allow investment in logistics that to allow the product transport. A large consumer of natural gas can make possible the construction of the infrastructure necessary for gradual access to the most consumers farther away from the coast, thus contributing to the expansion of the Brazilian natural gas market.

The development of pre-salt gas reserves opens up an excellent opportunity for the development and expansion of the Brazilian natural gas market, ensuring medium and long-term supply of large-scale structuring projects, capable of leveraging the consumption of gas in the country and the internalization of the product. In the same way, the structuring of projects capable of consuming large quantities of natural gas can give a great boost to the Brazilian market, considerably reducing the price of the product in the domestic market. This is currently the main restriction to the development of the Brazilian natural gas market and its use as raw material in large chemical products production complexes.

The study of the various processes described in the patents for the production of gasochemical presented in Chapter 2 allowed a comprehensive technical overview on the advantages and disadvantages of the main technologies used in the combined production of ammonia, methanol and urea from natural gas through their conversion into synthesis gas. The use of natural gas as a raw material is practically unanimous. Some engineering solutions are consecrated and used by the great majority of the processes presented, e.g., two stages of natural gas reform and treatment and purification of the synthesis gas for the production of ammonia are very uniform. A superstructure for all evaluated patents was elaborated, being a basis for future optimization studies.

This study allows us to conclude on the technical feasibility of producing these products in Brazil to supply its domestic market. The study of the nominal capacities that make feasible the production of methanol presented in Chapter 3 and ammonia production presented in Chapter 4, show that the quantities needed to supply the Brazilian domestic market can be economically served by the industrial complexes proposed with small discounts, either on the cost of the raw material and/or on project taxation. Supporting the technical data presented in the previous chapters, the economic feasibility study on the implementation of the complex presented in Chapter 5 validates the previous studies, considering the opportunity to substitute imports of the evaluated chemicals. Finally, Chapter 6 establishes the final proposal of this work, based on the studies carried out and in accordance with the needs of the Brazilian market.

The distinct economic behavior between the two products is evident. It is much easier to economically afford ammonia/urea production than methanol production. This differentiated behavior is explained by the higher value added to the molecule of ammonia and urea in the production units of these products. The cost of the ammonia and urea production units is higher, the operating cost and the energy expenditure as well, so that the cost of the raw material influences less the economic behavior of the project as a whole. In case of methanol (with the both much smaller CAPEX and OPEX), the cost of natural gas (raw material) influences much more the economic viability of the project.

Another issue that deserves to be highlighted is that, in the case of budget constraints, the project could be implemented in stages, with the synthesis gas generation unit and the ammonia production unit being constructed first and then in sequence, the urea. The methanol production unit could be postponed until a more favorable future for the unit's implementation. However, in this case it should not be forgotten that the (low) price of the methanol commodity will not stay at the current level forever and that a slight increase in the value of the alcohol molecule can bring completely different economic data, indicating the immediate production of the unit of production. According to the data obtained on the NPV of the methanol production unit presented in Chapter 3 and Appendix C, a 40% increase in the value of methanol in the international market would make the project feasible for all the attractiveness rates investigated in this study, even without any discount on the value of the raw material, or taxation of the complex.

In addition to the technical and economic issues discussed in the chapters presented, in summary and comprehensive, it should be emphasized that the possibility of replacing critical inputs for the national chemical industry, which they are currently imported in large quantities, may make the country less vulnerable to the policy of availability and prices stipulated by the international market. The substitution of imports of ammonia, methanol and urea by products produced in the country can give a very positive boost to the national chemical industry. This proposal is adequate to the current Brazilian scenario, which, on the one hand, has the availability of the large gas reserves of the pre-salt and, on the other hand, needs to reduce the country's great vulnerability which depends heavily on imports of basic chemicals products.

The most relevant academic contribution of this work is the model elaborated to estimate the CAPEX of projects based only on the cost of the main equipments is an interesting tool of comparison between industrial processes. This methodology can be easily used by other researchers interested in the analysis of economic processes, without the need to obtain economic data from companies, which are usually classified as confidential. Together with the use of the superstructure as a process flow diagram used for the comparison of industrial processes, this methodology offers an opportunity for a technical-economic analysis between processes of different production purposes.

On the other hand, the presentation of the technical summary of the main patents for the simultaneous production of gasochemicals brings an important scientific gain for researchers interested in processes of methanol, ammonia and urea co-production.

Complementing, there is also the prospect of turning Chapters 1 through 6 of this thesis into technical articles for being published in specialized magazines of the chemical engineering area.

As suggestions for future works, it is important to emphasize that the data used in this study need to be constantly reviewed in future studies. The review of the data may also consider other price scenarios and other sensitivity analyzes. As suggestions for future studies from this work, it is indicate economic comparisons of the methodology used (Towler and Sinnott) with other authors, as an example, Peter and Timerhaus, to give more robustness to the methodology developed in this work. Another important suggestion would be the realization of a simulation of the set of units proposed in this work, in order to show possible additional synergistic gains.

Another proposed research route would be the extension of the technical-economic studies for the production of carboxylic acids (formic acid and acetic acid), taking advantage of part of the CO2 currently discarded by the proposed project.

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APPENDIX A - Indexes for cost estimation

Appendix A presents indexes used for cost estimation. The cost estimated by the methodology used presents values in dollars based on the year of 2010 and equipment available in the American coast. Corrections are necessary to bring the estimated values for the year 2015 and equipment available in Brazilian ports. Appendix A presents the indexes and the factors used in this work. Table A1 presents the annual index of equipments price correction.

Table A1 - Annual Index of equipment price correction.

Nelson-Farrar Indexes				Location table	factor
EQUIPAMENTS	2013	2014	2015	USA Gulf coast	1.00
Pumps & compres	2,221	2,273	2,277	USA East coast	1.04
Electrical equip.	517	515	516	Mexico	1.03
Instruments	1,510	1,529	1,536	Brazil	1.14
Exchangers	1,293	1,305	1,305	China	1.12
Electrical equip.	1,318	1,334	1,338	Japan	1.26
Ovens	1,047	1,051	1,056	Australia	1.21

Source: Adapted from Nelson-Farrar Indexes, 2015 and Towler and Sinnott, 2013.

The estimation of the cost of implementation of the units (Construction & Assembly) was determined as a function of the total cost of the main equipment, through the application of cost factors, according to the methodology presented by Towler and Sinnott (2013). Table A2 shows the factors used to calculate the cost of each unit assembly item as a function of total cost of main equipments.

Table A2 - Cost factors for CAPEX estimation of units.

Cost construction and assembly of production units *(Based on the cost of main equipments of the unit)*	factor (%)
Detail design and engineering documents	0.20
BUILDINGS	
Land, wall/fence, gatehouse, sentry-house	0.15
Land leveling and containment basin	0.20
Inter.roads, sidewalks, adm.building, parking, urbaniz, lab.	0.15
Rainwater, gutters, dikes, passage and elevation boxes	0.10
Process. civil install. (equip. bases, control rooms, pipe ways)	0.15
ASSEMBLY OF PIPING AND EQUIPMENT	
Equipment assembly	0.30
Acquisition of piping	0.35

Piping accessories	0.15
Piping assembly	0.30
ELECTRICAL INSTALLATIONS	
Elect.Inst.(cables, panels, controlroom, emerg. generatator)	0.20
Substation and high voltage switches and circuit breakers	0.15
Control instrum. (sensors, transmitters, valves, panels, cables)	0.35
PLCs, IHM, control software, int.networks, no-breaks, panels	0.20
OTHER EQUIPMENT AND CONSUMABLE MATERIALS	
Secondary equipment and accessories	0.10
Safety equip. (tank, nets, pumps, hydrants, water cannons)	0.15
Catalysers, molecular sieves, membranes	0.20
Product storage tanks	0.15
Lubricants, filters, cartridges, consumables, chemical prod.	0.05
INSPECTION, TESTS, CONNECTIONS, COMMISSIONING	
Control loops tests and communication with internal network	0.10
Inspection and painting	0.20
Offsites (external connections)	0.20
Commissioning and pre-operation	0.15
CONTINGENCY, LICENSES AND INDUSTRIAL FACILITIES	
Contingency and Health, Safety and Environment - HSE	0.10
Restrictions and environmental licenses	0.10
Industrial facilities (considering apportionments)	0.30
TRAINING	
Training of operational, maintenance, inspection teams	0.07

Source: Adapted from Towler and Sinnott, 2013; insertions of items foreseen in the manual of engineering of the PETROBRAS.

APPENDIX B – Auxiliary tables used for cost estimation in chapter 3

Appendix B presents the auxiliary data tables used for calculating the cost of the main equipments of the synthesis gas generation and methanol production units investigated in Chapter 3. Below, is presented the auxiliary data tables used for calculating the cost of the main equipments of the synthesis gas generation units in Chapter 3.

Table B1 - Pump power and the pump cost as a function of the natural gas load of the synthesis gas generation unit.

NG load		Water Pump		cost		total
Pt.		vazão	power	pump	Motor	cost
	(t/h)	(m3/h)	(kw)	(US$*$10^3$)	(US$*$10^3$)	(US$*$10^3$)
1	31	34.55	57.91	9.84	25.08	34.92
2	38	43.20	72.40	10.25	28.52	38.76
3	48	53.00	90.17	10.70	32.38	43.08
4	60	67.52	113.20	11.36	36.95	48.31
5	75	84.41	141.50	12.11	42.09	54.19
6	94	105.90	177.50	13.03	48.06	61.09
7	118	132.20	221.60	14.14	54.74	68.90
8	147	165.10	276.70	15.51	62.39	77.90
9	183	206.30	345.80	17.18	71.17	88.34
10	229	257.50	431.60	19.20	81.13	100.33

Source: The Author, 2017.

Table B2 - Demanded thermal load, thermal exchange area and the cost of the heat exchangers as a function of the natural gas load of the synthesis gas generation unit.

Heat exchange area of each exchanger (m2)										
Load (t/h)		E-10	E-20	E-30	E-40	E-50	E-60	q-reat1	q-reat2	Total
1	31	0.28	9	2	6	30	88	45	45	226
2	38	0.35	11	3	8	38	110	56	56	283
3	48	0.44	14	3	10	47	137	70	70	352
4	60	0.55	17	4	12	59	172	86	86	437
5	75	0.69	22	5	15	74	215	108	108	549
6	94	0.86	27	7	19	93	270	135	135	688
7	118	1.08	34	8	24	116	337	169	169	859
8	147	1.35	43	11	30	145	421	214	214	1078
9	183	1.68	53	13	37	181	526	270	270	1353
10	229	2.10	67	17	46	226	657	338	338	1690

Exchangers cost (US$*million)										
Load (t/h)		E-10	E-20	E-30	E-40	E-50	E-60	q-reat1	q-reat2	Total
1	31	0.03	0.12	0.11	0.11	0.09	0.12	0.04	0.04	0.66
2	38	0.03	0.12	0.11	0.11	0.09	0.13	0.04	0.04	0.68
3	48	0.03	0.12	0.11	0.12	0.10	0.14	0.04	0,04	0.71
4	60	0.03	0.12	0.11	0.12	0.10	0.16	0.05	0.05	0.74
5	75	0.03	0.12	0.11	0.12	0.11	0.19	0.05	0.05	0.79
6	94	0.03	0.13	0.11	0.12	0.12	0.22	0.06	0.06	0.85
7	118	0.03	0.13	0.12	0.12	0.13	0.27	0.06	0.06	0.93
8	147	0.03	0.13	0.12	0.13	0.15	0.33	0.08	0.08	1.04
9	183	0.03	0.14	0.12	0.13	0,17	0.40	0.09	0.09	1.17
10	229	0.03	0.15	0.12	0.14	0.20	0.50	0.11	0.11	1.35

Source: The Author, 2017.

Table B3 - Pressure vessels weight and the total pressure vessels cost as a function of the natural gas load of the synthesis gas generation unit.

Load		Vessels weight			total	Vessels cost			cost
Pto.	GN	Vload	V.sulfur	V-20	weight	Vcarga	V.enxof.	V-20	
	(t/h)	(t)	(t)	(t)	(t)	(US$*$10^3$)	(US$*$10^3$)	(US$*$10^3$)	(US$*$10^6$)
1	31	17.35	8.81	6.50	33	162.84	194.17	77.89	0.43
2	38	19.71	97.76	71.65	37	180.00	209.82	83.53	0.47
3	48	22.21	10.79	78.64	41	197.93	226.03	89.35	0.51
4	60	24.88	11.86	85.95	45	216.60	242.805	95.36	0.55
5	75	27.69	12.98	9.36	50	236.01	260.13	101.56	0.60
6	94	30.64	14.15	10.16	55	256.13	277.99	107.94	0.64
7	118	33.76	15.38	10.98	60	276.97	296.40	114.50	0.69
8	147	37.01	16.65	11.84	66	298.50	315.33	121.24	0.74
9	183	40.42	17.97	12.74	71	320.73	334.79	128.16	0.78
10	229	43.98	19.35	13.66	77	343.63	354.76	135.26	0.83

Source: The Author, 2017.

Table B4 - Reactors cost as a function of the natural gas load of the synthesis gas generation unit.

			primary reactor				secundary reactor			Total
NG load			acess.	corr.	reactor		acess.	corr.	reactor	reactors
		vol.	cost	factor	cost	vol.	cost	factor	cost	cost
pto	(t/h)	(m3)	(US$*$10^3$)		(US$*$10^6$)	(m3)	(US$*$10^3$)		(US$*$10^6$)	(US$*$10^6$)
1	31	20	523.17	4.20	2.20	20	523.17	4.20	2.20	43.95
2	38	25	610.39	4.20	2.56	25	610.39	4.20	2.56	51.27
3	48	30	694.17	4.20	2.92	30	694.17	4.20	2.92	58.31
4	60	35	775.18	4.20	3.26	35	775.18	4.20	3.26	65.12
5	75	40	853.91	4.20	3.59	40	853.91	4.20	3.59	71.73
6	94	45	930.69	4.20	3.91	45	930.69	4.20	3.91	78.18
7	118	50	1005.78	4.20	4.22	50	1005.78	4.20	4.22	84.49
8	147	55	1079.37	4.20	4.53	55	1079.37	4.20	4.53	90.67
9	183	60	1151.64	4.20	4.84	60	1151.64	4.20	4.84	96.74
10	229	65	1222.72	4.20	5.14	65	1222.72	4.20	5.14	102.71

Source: The Author, 2017.

Table B5 - Main equipment cost consolidation as a function of the natural gas load of the synthesis gas generation unit.

	Total cost of main equipments of syngas unit						TOTAL
Pt.	NG	SYNGAS	Pump	Exchan.	Vessel	Reactor	cost
	(t/h)	(t/h)			(US$*$10^6$)		
1	31	66	0.03	0.66	0.43	43.95	45.08
2	38	82	0.04	0.68	0.47	51.27	52.47
3	48	102	0.04	0.71	0.51	58.31	59.57
4	60	128	0.05	0.74	0.55	65.12	66.46
5	75	160	0.05	0.79	0.60	71.73	73.17
6	94	201	0.06	0.85	0.64	7818,00	79.73
7	118	251	0.07	0.93	0.69	84.45	86.17
8	147	313	0.08	1.04	0.74	90.67	92.52
9	183	391	0.09	1.17	0.78	96.74	98.78
10	229	488	0.10	1.35	0.83	102.71	105.00

Source: The Author, 2017.

Below is presented the auxiliary data tables used for calculating the cost of the main equipments of the methanol production units in Chapter 3.

Table B6 - Compressors power and the compressors cost as a function of the syngas load of the methanol production unit.

Pto.	Syngas (t/h)	Compressor power (kw) C-01	C-02	C-03	C-04	Total	Cost (US$*10^6)
1	31	1012	1602	204	203	3021	3.03
2	38	1266	2023	251	250	3789	3.39
3	48	1577	2495	319	318	4709	3.78
4	60	1978	3113	397	395	5883	4.23
5	75	2473	3886	508	506	7373	4.76
6	94	3091	4931	610	606	9238	5.37
7	118	3864	6083	788	784	11519	6.05
8	147	4838	7685	953	947	14423	6.84
9	183	6043	9445	1238	1232	17958	7.72
10	229	7543	11690	1558	1551	22342	8.72

Source: The Author, 2017.

Table B7 - Demanded thermal load, thermal exchange area and the cost of the heat exchangers as a function of the syngas load of the methanol production unit.

Pt.	Syngas (t/h)	**Heat exchange area of each exchanger (m2)** E-10	E-20	E-30	E-40	E-50	COND	REBOIL	resf. reator	Total Area
1	31	111	209	335	2.00	1.80	337	158	353	490
2	38	138	265	424	2.50	2.20	422	197	436	768
3	48	173	325	521	3.12	2.80	526	246	552	965
4	60	215	405	653	3.90	3.44	660	308	693	1321
5	75	273	504	812	5.00	4.41	826	386	873	2063
6	94	335	646	1034	6.00	5.28	1029	481	1065	2574
7	118	424	790	1271	7.70	6.83	1290	603	1361	3095
8	147	521	1007	1616	9.35	8.24	1610	752	1669	3525
9	183	662	1223	1977	12.10	10.74	2020	944	2144	3882
10	229	827	1509	2448	15.21	13.53	2521	1178	2696	4238

Pt.	Syngas (t/h)	**Exchanger Cost (US$*million)** E-10	E-20	E-30	E-40	E-50	COND	REBOIL	resf. reator	Total Cost
1	31	0.50	0.70	0.11	0.30	0.30	0.11	0.06	0.11	0.58
2	38	0.60	0.90	0.13	0.30	0.30	0.13	0.07	0.14	0.68
3	48	0.70	0.10	0.16	0.30	0.30	0.16	0.08	0.17	0.81
4	60	0.80	0.13	0.20	0.30	0.30	0.20	0.10	0.21	0.98
5	75	0.90	0.15	0.25	0.30	0.30	0.25	0.12	0.27	1.20
6	94	0.11	0.20	0.32	0.30	0.30	0.32	0.15	0.33	1.49
7	118	0.13	0.24	0.40	0.30	0.30	0.41	0.18	0.44	1.87
8	147	0.16	0.31	0.53	0.30	0.30	0.53	0.23	0.55	2.37
9	183	0.20	0.39	0.66	0.30	0.30	0.68	0.29	0.73	3.02
10	229	0.25	0.49	0.85	0.30	0.30	0.88	0.37	0.95	3.85

Source: The Author, 2017.

Table B8 - Pressure vessels weight and the total vessels cost as a function of the syngas load of the methanol production unit.

Load		Pressure vessels weight of methanol plant							total	Pressure vessels cost of methanol plant							Cost
Pt.	Syngas	Vload	V.sep.	Vflash	V-10	V-20	V-30	V-40	weight	Vload	V.sep.	Vflash	V-10	V-20	V-30	V-40	
	(t/h)	(t)								(US$*10^3)							(US$*10^6)
1	31	6.06	13.16	3.32	2.90	4.26	2.38	6.79	38.87	119.23	262.81	198.33	91.10	116.54	80.95	160.70	1.06
2	38	7.21	14.15	3.55	3.11	4.60	2.57	7.43	42.61	137.07	277.94	206.68	95.08	122.65	84.68	171.48	1.10
3	48	8.46	15.18	3.78	3.30	4.95	2.76	8.10	46.56	155.92	293.46	215.22	99.16	128.92	88.50	182.60	1.16
4	60	9.81	16.25	4.01	3.55	5.32	2.97	8.80	50.70	175.95	309.35	223.94	103.34	135.35	92.42	194.04	1.23
5	75	11.26	17.40	4.26	3.77	5.69	3.18	9.53	55.04	197.16	325.63	232.85	107.61	141.95	96.43	205.82	1.31
6	94	12.82	18.49	4.51	4.01	6.90	3.40	10.28	59.59	219.50	342.29	241.94	111.97	148.70	100.54	217.93	1.38
7	118	14.47	19.66	4.77	4.26	6.49	3.62	11.07	64.33	242.95	359.28	251.22	116.43	155.60	104.75	230.35	1.46
8	147	16.22	20.87	5.03	4.51	6.90	3.85	11.89	69.27	267.49	376.65	260.68	120.97	162.66	109.05	24.310	1.54
9	183	18.07	22.11	5.31	4.77	7.33	4.09	12.73	74.42	293.11	394.39	270.31	125.61	169.87	113.44	256.16	1.62
10	229	20.03	23.40	5.59	5.03	7.78	4.34	13.60	79.76	319.77	412.49	280.12	130.34	177.24	117.93	269.53	1.71

Source: The Author, 2017.

Table B9 - Reactor cost as a function of the syngas load of the methanol production unit.

Syngas Load		vol.	cost + acess.	corr. factor	reactor cost
pt.	(t/h)	(m3)	(US$)		(US$*10^6)
1	31	21	0.54	4.20	2.27
2	38	23	0.58	4.20	2.42
3	48	26	0.63	4.20	2.64
4	60	31	0.71	4.20	2.98
5	75	37	0.81	4.20	3.39
6	94	43	0.90	4.20	3.78
7	118	49	0.99	4.20	4.16
8	147	55	1.08	4.20	4.53
9	183	60	1.15	4.20	4.84
10	229	65	1.22	4.20	5.14

Source: The Author, 2017.

Table B10 – Towers cost as a function of the syngas load of the methanol production unit.

Load		Distillation Tower						Vessels						Total	
Syngas			hull		ntern		trays	Top and Bottom							
		dia.	weight	Cost	devic.			dia.	leng.	weight	Cost	intern.	acces.	Cost	weight
Pt.	(t/h)	(m)	(t)	(US$*10⁶)			(t)	(m)		(t)	(US$*10⁶)				(t)
1	31	2.30	66	0.44	0.22	0.04	0.20	1.70	2.10	4.12	0.08	0.01	0.79	1.58	71
2	38	2.50	72	0.47	0.24	0.05	0.24	1.80	2.30	4.72	0.09	0.01	0.86	1.72	77
3	48	2.70	79	0.50	0.25	0.06	0.28	1.80	2.30	4.86	0.10	0.01	0.92	1.84	84
4	60	2.90	85	0.54	0.27	0.06	0.32	1.90	2.40	5.22	0.10	0.01	0.98	1.96	90
5	75	3.10	91	0.57	0.29	0.07	0.37	2.00	2.40	5.59	0.11	0.01	1.04	2.09	97
6	94	3.30	98	0.60	0.30	0.08	0.42	2.00	2.50	5.75	0.11	0.01	1.11	2.21	104
7	118	3.50	104	0.64	0.32	0.09	0.47	2.10	2.60	6.29	0.12	0.01	1.17	2.34	111
8	147	3.80	114	0.69	0.34	0.11	0.56	2.20	2.80	7.04	0.13	0.01	1.27	2.55	121
9	183	4.10	124	0.74	0.37	0.12	0.65	2.30	2.90	7.64	0.13	0.01	1.37	2.74	132
10	229	4.40	134	0.79	0.39	0.14	0.75	2.40	3.00	8.27	0.14	0.01	1.47	2.94	143

Source: The Author, 2017.

Table B11 - Main equipment cost consolidation as a function of the syngas load of the methanol production unit.

Main equipments cost of methanol plant								
Pt.	NG	Syngas	Comp.	Exch.	Vessels	reactor	tower	Total
	(t/h)		(US$*10⁶)					
1	66	31	3.03	0.58	1.06	2.27	1.58	8.52
2	82	38	3.39	0.68	1.10	2.42	1.72	9.30
3	102	48	3.78	0.81	1.16	2.64	1.84	10.22
4	128	60	4.23	0.98	1.23	2.98	1.96	11.39
5	160	75	4.76	1.20	1.31	3.39	2.09	12.75
6	201	94	5.37	1.49	1.38	3.78	2.21	14.24
7	251	118	6.05	1.87	1.46	4.16	2.34	15.89
8	313	147	6.84	2.37	1.54	4.53	2.55	17.83
9	391	183	7.72	3.02	1.62	4.84	2.74	19.94
10	488	229	8.72	3.85	1.71	5.14	2.94	22.36

Source: The Author, 2017.

APPENDIX C – Data tables of npv results of the technical-economic study presented in chapter 3

Appendix C presents the data tables of the Net Present Value – NPV - results of the technical-economic study of the methanol production complex used in the elaboration of the graphs showed in this article. Table C1 presents the NPV results, considering 0%, 10% 15%, 20%, 25%, 30%, 32%, 35%, 32%, 35%, 38%, 40%, 42% and 45% of discount in raw material (Natural Gas) cost for the ten values of loads studied. These results do not consider any discount on the taxation of the complex.

Table C1 - NPV results for several discount values in the cost of the raw material cost.

load	NPV (2017) (US\$*10^6) discount: raw material: 0% discount: taxation: 0%			NPV (2017) (US\$*10^6) discount: raw material: 10% discount: taxation: 0%			NPV (2017) (US\$*10^6) discount: raw material: 15% discount: taxation: 0%			NPV (2017) (US\$*10^6) discount: raw material: 20% discount: taxation: 0%		
(t/h)	TMA 8%	TMA 10%	TMA 12%	TMA 8%	TMA 10%	TMA 12%	TMA 8%	TMA 10%	TMA 12%	TMA 8%	TMA 10%	TMA 12%
31	-406.79	-368.18	-337.75	-279.98	-264.28	-251.16	-216.65	-212.37	-207.89	-153.32	-160.46	-164.62
38	-478.92	-432.65	-396.19	-320.60	-302.87	-288.02	-241.43	-237.98	-233.94	-162.18	-173.02	-179.79
48	-553.13	-498.69	-455.86	-355.91	-337.03	-321.12	-257.25	-256.16	-253.72	-163.76	-179.53	-189.85
60	-640.56	-575.58	-524.59	-393.09	-372.74	-355.53	-269.35	-271.31	-270.99	-161.19	-182.65	-197.09
75	-737.38	-660.19	-599.76	-427.77	-406.40	-388.24	-273.02	-279.55	-282.51	-148.99	-177.89	-197.77
94	-868.37	-772.78	-698.24	-480.06	-454.48	-432.94	-285.95	-295.37	-300.33	-137.35	-173.57	-198.81
118	-983.01	-872.00	-785.60	-498.14	-474.56	-454.34	-255.62	-275.76	-288.65	-90.10	-140.09	-175.57
147	-1,132.78	-1,000.14	-897.17	-527.38	-503.90	-483.53	-241.00	-269.15	-287.91	-34.44	-99.84	-146.79
183	-1,282.84	-1,128.57	-1,009.05	-526.43	-508.56	-492.28	-195.54	-237.33	-266.22	62.61	-25.73	-89.85
229	-1,483.50	-1,298.65	-1,155.78	-539.39	-524.78	-510.77	-147.15	-203.27	-242.80	175.09	60.87	-22.65

load	NPV (2017) (US\$*10^6) discount: raw material: 25% discount: taxation: 0%			NPV (2017) (US\$*10^6) discount: raw material: 30% discount: taxation: 0%			NPV (2017) (US\$*10^6) discount: raw material: 32% discount: taxation: 0%			NPV (2017) (US\$*10^6) discount: raw material: 35% discount: taxation: 0%		
(t/h)	TMA 8%	TMA 10%	TMA 12%	TMA 8%	TMA 10%	TMA 12%	TMA 8%	TMA 10%	TMA 12%	TMA 8%	TMA 10%	TMA 12%
31	-104.01	-120.04	-130.93	-60.78	-84.61	-101.40	-43.48	-70.43	-89.58	-17.56	-49.18	-71.87
38	-105.74	-126.75	-141.23	-51.71	-82.47	-104.32	-30.09	-64.75	-89.56	2.32	-38.18	-67.41
48	-96.43	-124.34	-143.85	-29.16	-69.20	-97.89	-2.24	-47.13	-79.49	38.18	-14.00	-51.88
60	-76.74	-113.43	-139.40	7.71	-44.21	-81.71	41.50	-16.51	-58.62	92.16	25.01	-24.01
75	-43.36	-91.31	-125.61	62.32	-4.68	-53.41	104.54	29.93	-24.56	167.94	81.90	18.75
94	-4.87	-64.97	-108.30	127.61	43.62	-17.79	180.64	87.09	18.44	260.16	152.26	72.77
118	75.36	-4.46	-62.52	240.89	131.22	50.56	307.10	185.49	95.79	406.35	266.84	163.60
147	172.19	69.53	-5.63	378.75	238.84	135.49	461.38	306.58	191.95	585.37	408.21	276.66
183	32.,71	185.83	86.48	578.86	397.43	262.85	682.11	482.07	333.39	836.95	608.99	439.17
229	497.27	324.95	197.46	819.44	589.04	417.57	948.36	694.71	505.65	1,141.68	853.17	637.72

load	NPV (2017) (US\$*10^6) discount: raw material: 38% discount: taxation: 0%			NPV (2017) (US\$*10^6) discount: raw material: 40% discount: taxation: 0%			NPV (2017) (US\$*10^6) discount: raw material: 42% discount: taxation: 0%			NPV (2017) (US\$*10^6) discount: raw material: 45% discount: taxation: 0%		
(t/h)	TMA 8%	TMA 10%	TMA 12%	TMA 8%	TMA 10%	TMA 12%	TMA 8%	TMA 10%	TMA 12%	TMA 8%	TMA 10%	TMA 12%
31	8.42	-27.88	-54.12	25.66	-13.75	-42.34	42.97	0.43	-30.52	68.95	21.73	-12.77
38	34.80	-11.56	-45.22	56.42	6.16	-30.45	78.03	23.87	-15.69	110.44	50.45	6.46
48	78.53	19.07	-24.32	105.45	41.14	-5.93	132.37	63.21	12.47	172.78	96.33	40.08
60	142.81	66.53	10.60	176.60	94.23	33.68	210.40	121.93	56.77	261.05	163.45	91.38
75	231.34	133.86	62.07	273.57	168.48	90.91	315.85	203.14	119.80	379.19	255.05	163.07
94	339.61	217.39	127.05	392.64	260.86	163.28	445.61	304.27	199.46	525.12	369.45	253.79
118	505.66	348.25	231.45	571.87	402.52	276.69	638.02	456.74	321.88	737.33	538.15	389.73
147	709.30	509.79	361.32	791.93	577.53	417.78	874.57	645.26	474.24	998.56	746.89	558.94
183	991.86	735.96	545.00	1,095.11	820.59	615.54	1,198.36	905.23	686.08	1,353.20	1,032.15	791.87
229	1,335.00	1,011.63	769.80	1,463.86	1,117.26	857.83	1,592.72	1,222.88	945.87	1,786.04	1,381.34	1,077.94

Source: The Author, 2017.

Table C2 presents the NPV results, considering 10% of discount in taxation of complex and 10% 15%, 20%, 25%, 30% and 35% of discount in raw material (Natural Gas) cost for the ten values of loads studied.

Table C2 - NPV results for several discount values in the cost of the raw material, considering 10% of discount in taxation of complex.

load (t/h)	NPV (2017) ($\mathrm{US\$}{*}10^{6}$) discount: raw material: 10% discount: taxation: 10%			NPV (2017) ($\mathrm{US\$}{*}10^{6}$) discount: raw material: 15% discount: taxation: 10%			NPV (2017) ($\mathrm{US\$}{*}10^{6}$) discount: raw material: 20% discount: taxation: 10%		
	TMA 8%	TMA 10%	TMA 12%	TMA 8%	TMA 10%	TMA 12%	TMA 8%	TMA 10%	TMA 12%
31	-260.70	-248.48	-237.99	-197.37	-196.57	-194.72	-134.08	-14.68	-151.47
38	-296.50	-283.12	-271.56	-217.33	-218.23	-217.48	-143.21	-157.47	-166.83
48	-325.84	-312.38	-300.58	-227.18	-231.51	-233.18	-180.40	-198.42	-210.25
60	-355.37	-341.82	-329.76	-231.64	-240.40	-245.22	-134.86	-161.07	-179.11
75	-380.60	-367.74	-356.01	-225.84	-240.88	-250.28	-115.82	-150.70	-175.11
94	-421.24	-406.27	-392.76	-229.63	-249.21	-261.85	-95.84	-139.54	-170.45
118	-424.41	-414.12	-403.97	-204.74	-234.06	-253.89	-37.64	-97.09	-139.73
147	-435.35	-428.46	-420.69	-177.22	-216.87	-244.34	31.39	-45.88	-101.82
183	-411.02	-413.96	-413.43	-114.99	-171.30	-211.18	145.72	42.39	-33.07
229	-395.31	-406.68	-412.34	-46.15	-120.48	-173.79	279.28	146.27	48.54

load (t/h)	NPV (2017) ($\mathrm{US\$}{*}10^{6}$) discount: raw material: 25% discount: taxation: 10%			NPV (2017) ($\mathrm{US\$}{*}10^{6}$) discount: raw material: 30% discount: taxation: 10%			NPV (2017) ($\mathrm{US\$}{*}10^{6}$) discount: raw material: 35% discount: taxation: 10%		
	TMA 8%	TMA 10%	TMA 12%	TMA 8%	TMA 10%	TMA 12%	TMA 8%	TMA 10%	TMA 12%
31	-90.42	-108.90	-121.65	-46.77	-73.12	-91.83	-3.12	-37.34	-62.01
38	-88.64	-112.74	-129.56	-34.08	-68.02	-92.28	20.48	-23.29	-55.00
48	-74.93	-106.72	-129.16	-6.99	-51.03	-82.75	61.01	4.71	-36.29
60	-49.58	-91.16	-120.84	35.71	-21.26	-62.58	120.99	48.65	-4.31
75	-9.15	-63.27	-102.24	97.58	24.22	-29.32	204.24	111.65	4.55
94	37.95	-29.87	-79.04	171.75	79.79	12.36	305.60	189.51	103.81
118	130.03	40.43	-25.04	296.61	176.90	88.63	463.71	313.86	202.79
147	240.,05	125.16	40.74	448.66	296.15	183.26	657.33	467.19	325.82
183	406.36	256.04	145.00	667.07	469.74	323.11	927.72	683.39	501.18
229	604.64	412.97	270.82	930.01	679.66	493.11	1,255.69	946.66	715.68

Source: The Author, 2017.

Table C3 presents the NPV results, considering 20% of discount in taxation of complex and 10% 15%, 20%, 25%, 30% and 35% of discount in raw material (Natural Gas) cost for the ten values of loads studied.

Table C3 - NPV results for several discount values in the cost of the raw material, considering 20% of discount in taxation of complex.

load (t/h)	NPV (2017) ($\text{US\$}*10^{6}$) discount: raw material: 10% discount: taxation: 20%			NPV (2017) ($\text{US\$}*10^{6}$) discount: raw material: 15% discount: taxation: 20%			NPV (2017) ($\text{US\$}*10^{6}$) discount: raw material: 20% discount: taxation: 20%		
	TMA 8%	TMA 10%	TMA 12%	TMA 8%	TMA 10%	TMA 12%	TMA 8%	TMA 10%	TMA 12%
31	-241.43	-232.68	-224.82	-178.1	-180.77	-181.55	-120.66	-133.69	-142.31
38	-272.40	-263.37	-255.10	-193.24	-198.48	-201.01	-126.32	-143.63	-155.30
48	-295.77	-287.74	-280.04	-197.11	-206.87	-212.63	-121.69	-145.05	-161.10
60	-317.65	-310.90	-303.99	-194.20	-209.71	-219.65	-124.95	-152.95	-172.34
75	-333.43	-329.07	-323.78	-189.73	-211.28	-225.61	-82.02	-122.99	-152.02
94	-362.42	-358.05	-352.57	-188.64	-215.61	-233.85	-53.53	-104.87	-141.55
118	-350.68	-353.68	-353.59	-152.91	-191.57	-218.47	15.81	-53.28	-103.21
147	-343.32	-353.02	-357.82	-112.19	-163.57	-199.91	98.45	9.09	-56.00
183	-296.07	-319.74	-334.90	-32.88	-104.00	-155.09	230.38	111.79	24.77
229	-271.75	-305.40	-327.92	56.80	-36.09	-103.46	385.41	233.27	121.05

load (t/h)	NPV (2017) ($\text{US\$}*10^{6}$) discount: raw material: 25% discount: taxation: 20%			NPV (2017) ($\text{US\$}*10^{6}$) discount: raw material: 30% discount: taxation: 20%			NPV (2017) ($\text{US\$}*10^{6}$) discount: raw material: 35% discount: taxation: 20%		
	TMA 8%	TMA 10%	TMA 12%	TMA 8%	TMA 10%	TMA 12%	TMA 8%	TMA 10%	TMA 12%
31	-76.58	97.56	-112.20	-32.50	-61.43	-82.08	11.58	-25.30	-51.97
38	-71.22	-98.47	-117.66	-16.13	-53.30	-80.01	38.97	8.14	-42.37
48	-53.03	-88.76	-114.19	15.58	-32.53	-67.33	84.24	23.76	-20.41
60	-21.90	-68.48	-101.93	64.22	2.11	-43.10	150.33	72.70	15.74
75	25.69	-34.70	-78.43	133.47	53.64	-4.80	241.18	141.93	68.79
94	81.57	5.88	-49.25	216.67	116.62	43.05	351.84	227.41	135.40
118	184.56	85.05	12.08	353.40	223.39	127.39	522.07	361.70	242.67
147	309.16	181.81	87.96	519.81	354.47	231.87	730.52	527.19	375.82
183	493.58	327.53	204.58	756.84	543.32	384.44	1,020.04	759.06	564.26
229	713.97	502.58	345.51	1,042.52	771.89	569.97	1,371.13	1,041.25	794.48

Source: The Author, 2017.

Table C4 presents the NPV results, considering 30% of discount in taxation of complex and 10% 15%, 20%, 25%, 30% and 35% of discount in raw material (Natural Gas) cost for the ten values of loads studied.

Table C4 - NPV results for several discount values in the cost of the raw material, considering 30% of discount in taxation of complex.

load	NPV (2017) (US\$*10^6) discount: raw material: 10% discount: taxation: 30%			NPV (2017) (US\$*10^6) discount: raw material: 15% discount: taxation: 30%			NPV (2017) (US\$*10^6) discount: raw material: 20% discount: taxation: 30%		
(t/h)	TMA 8%	TMA 10%	TMA 12%	TMA 8%	TMA 10%	TMA 12%	TMA 8%	TMA 10%	TMA 12%
31	-222.16	-216.88	-211.65	-158.83	-164.97	-168.38	-106.98	-122.48	-132.97
38	-248.30	-243.61	-238.63	-169.14	-178.72	-184.55	-109.11	-129.52	-143.54
48	-265.71	-263.09	-259.49	-169.32	-184.03	-193.64	-100.05	-127.30	-146.32
60	-279.94	-279.99	-278.22	-167.69	-187.98	-201.54	-80.67	-116.65	-142.09
75	-286.26	-290.40	-291.55	-153.33	-183.91	-202.79	-47.58	-94.76	-128.49
94	-303,60	-309.84	-312.39	-146.85	-181.35	-205.30	-10.44	-69.54	-112.10
118	-276.95	-293.24	-303.22	-100.12	-148.30	-182.41	70.25	-8.65	-66.01
147	-258.68	-283.65	-299.99	-45.93	-109.26	-154.64	166.76	65.08	-9.33
183	-214.96	-253.25	-279.43	50.79	-35.42	-97.93	316.60	182.47	83.68
229	-170.04	-222.03	-258.44	161.69	49.89	-31.80	493.50	321.86	194.89

load	NPV (2017) (US\$*10^6) discount: raw material: 25% discount: taxation: 30%			NPV (2017) (US\$*10^6) discount: raw material: 30% discount: taxation: 30%			NPV (2017) (US\$*10^6) discount: raw material: 35% discount: taxation: 30%		
(t/h)	TMA 8%	TMA 10%	TMA 12%	TMA 8%	TMA 10%	TMA 12%	TMA 8%	TMA 10%	TMA 12%
31	-62.48	-86.00	-102.56	-17.97	-49.52	-72.15	26.53	-13.04	-41.75
38	-53.48	-83.20	-105.53	2.15	-38.32	-67.53	57.78	7.28	-29.52
48	-30.72	-70.47	-98.95	38.55	-13.70	-51.63	107.88	43.13	-4.26
60	6.28	-45.38	-82.68	93.23	25.90	-23.27	180.19	97.17	36.13
75	61.18	-5.61	-54.19	170.00	83.58	20.16	278.76	172.73	94.46
94	126.09	42.37	-18.83	262.39	154.09	74.29	398.86	265.96	167.53
118	240.62	131.00	50.38	411.06	270.70	166.82	581.43	410.35	283.22
147	379.52	239.47	136.02	592.21	413.81	281.33	804.96	588.20	426.68
183	582.35	400.30	265.23	848.17	618.18	446.84	1,113.92	836.01	628.39
229	825.23	593.78	421.53	1,156.97	865.70	648.17	1,488.77	1,137.67	874.85

Source: The Author, 2017.

Table C5 presents the NPV results, considering 0% of discount in taxation and raw material of complex and 20%, 30% and 40% of increase of the revenue of the complex for the ten values of loads studied.

Table C5 - NPV results for increase of 20%, 30% and 40% of the revenue of the methanol production unit.

load	NPV (2017) ($\text{US\$}*10^{6}$) discount: raw material: 0% discount: taxation: 0% revenue increase: 20%			NPV (2017) ($\text{US\$}*10^{6}$) discount: raw material: 0% discount: taxation: 0% revenue increase: 30%			NPV (2017) ($\text{US\$}*10^{6}$) discount: raw material: % discount: taxation: 0% revenue increase: 40%		
(t/h)	TMA 8%	TMA 10%	TMA 12%	TMA 8%	TMA 10%	TMA 12%	TMA 8%	TMA 10%	TMA 12%
31	-130.21	-141.52	-148.84	-46.80	-73.15	-91.85	36.61	-4.78	-34.86
38	-138.19	-153.36	-163.41	-33.90	-67.87	-92.16	70.39	17.62	-20.90
48	-136.00	-156.77	-170.88	-5.86	-50.10	-81.97	124.22	56.53	6.90
60	-126.14	-153.92	-173.15	37.13	-20.09	-61.60	200.35	113.69	49.90
75	-104.62	-141.20	-167.46	99.51	25.81	-28.00	303.64	193.13	11.46
94	-84.90	-130.57	-162.97	169.63	78.06	10.92	424.21	286.79	184.84
118	-21.02	-83.46	-128.37	298.07	178.09	89.63	617.10	439.59	307.59
147	52.27	-28.76	-87.55	450.54	297.69	184.54	848.75	624.10	456.60
183	176.32	67.48	-12.16	675.78	476.88	329.06	1,175.24	886.28	670.29
229	318.10	178.09	75.06	941.60	689.17	501.03	1,565.10	1,200.24	927.00

Source: The Author, 2017.

APPENDIX D – Auxiliary tables used for cost estimation in chapter 4

Appendix D presents the auxiliary data tables used for calculating the cost of the main equipments of the synthesis gas generation and ammonia production units investigated in Chapter 4. Below, is presented the auxiliary data tables used for calculating the cost of the main equipments of the synthesis gas generation units in Chapter 4.

Table D1 - Pump power and the pump cost as a function of the natural gas load of the synthesis gas generation unit.

		PUMPS - nominal flow, demanded power and cost									
Natural Gas load		water pump				MEA pump				consolidated data	
		data		cost		data		cost			
		flow	power	pumps	motors	flow	power	pumps	motors	power	cost
pt.	(t/h)	(m^3/h)	(kw)	(US\$*10^3)		(m^3/h)	(kw)	(US\$*10^3)		(kw)	(US\$*10^3)
1	45	83	140	12.06	41.79	227	309	17.99	66.55	449	138.39
2	67	125	210	13.85	52.99	397	541	24.55	93.74	751	185.13
3	89	167	280	15.58	62.79	430	586	25.79	97.25	866	201.41
4	133	250	420	18.92	79.78	432	588	25.84	97.44	1008	221.98
5	178	334	559	22.15	94.61	1082	1472	69.51	262.61	2031	448.88
6	222	417	699	25.29	108.00	1344	1829	79.31	298.69	2528	511.29
7	267	501	839	37.84	159.57	1624	2211	99.05	375.76	3050	672.67
8	311	584	979	41.08	174.79	1751	2384	104.23	392.93	3363	713.03
9	356	668	1119	44.29	189.24	1756	2391	104.42	393.62	3510	731.57
10	400	751	1259	47.46	202.95	1758	2393	104.49	393.81	3652	748.71
11	445	834	1398	50.59	215.97	1759	2394	104.51	393.91	3792	764.98
12	489	918	1538	63.24	269.52	1760	2395	104.57	394.00	3933	831.33
13	534	1001	1678	66.43	283.81	1762	2397	104.64	394.20	4075	849.08

Source: The Author, 2017.

Table D2 – Demanded thermal load, thermal exchange area and the cost of the heat exchangers as a function of the natural gas load of the synthesis gas generation unit.

Heat exchange area of each exchanger (m^2)												
Load (t/h)		E-10	E-20	E-30	E-40	E-50	E-60	E-70	E-80	E-90	E-100	Total
1	44	0.30	9	7	68	12	42	215	135	58	30	577
2	67	0.40	13	11	103	18	64	323	237	87	45	899
3	89	0.50	17	15	137	24	85	430	257	115	59	1140
4	133	0.80	26	22	205	36	127	646	257	172	89	1582
5	178	1.10	35	29	274	48	170	861	645	231	119	2413
6	222	1.40	43	37	342	60	212	1076	801	289	149	3011
7	267	1.60	52	44	411	73	255	1291	968	347	178	3621
8	311	1.90	61	51	479	85	297	1506	1044	404	208	4137
9	356	2.20	69	58	548	97	340	1722	1047	461	238	4581
10	400	2.50	78	66	616	109	382	1937	1048	518	268	5024
11	445	2.70	87	73	685	121	425	2152	1048	575	297	5465
12	489	3.00	95	80	753	133	467	2367	1049	632	327	5907
13	534	3.30	104	88	822	145	510	2583	1049	689	357	6349
Exchanger cost (US$ million)												
Load (t/h)		E-10	E-20	E-30	E-40	E-50	E-60	E-70	E-80	E-90	E-100	Total
1	44	0.03	0.03	0.03	0.04	0.03	0.04	0.08	0.06	0.04	0.04	0.42
2	67	0.03	0.03	0.03	0.05	0.03	0.04	0.10	0.08	0.05	0.04	0.05
3	89	0.03	0.03	0.03	0.06	0.04	0.05	0.13	0.09	0.05	0.04	0.55
4	133	0.03	0.04	0.03	0.07	0.04	0.06	0.20	0.09	0.07	0.05	0.67
5	178	0.03	0.04	0.04	0.09	0.04	0.07	0.26	0.20	0.08	0.05	0.90
6	222	0.03	0.04	0.04	0.11	0.04	0.08	0.34	0.25	0.09	0.06	1.07
7	267	0.03	0.04	0.04	0.13	0.04	0.09	0.41	0.30	0.11	0.07	1.26
8	311	0.03	0.04	0.04	0.15	0.05	0.10	0.49	0.33	0.13	0.07	1.56
9	356	0.03	0.04	0.04	0.17	0.05	0.11	0.57	0.33	0.14	0.08	1.56
10	400	0.03	0.05	0.04	0.19	0.05	0.12	0.65	0.33	0.16	0.09	1.70
11	445	0.03	0.05	0.04	0.21	0.05	0.13	0.73	0.33	0.18	0.10	1.85
12	489	0.03	0.05	0.05	0.23	0.06	0.14	0.82	0.33	0.19	0.10	2.00
13	534	0.03	0.05	0.05	0.25	0.06	0.16	0.90	0.33	0.21	0.11	2.15

Source: The Author, 2017.

Table D3 – Pressure vessels weight and the total pressure vessels cost as a function of the natural gas load of the synthesis gas generation unit.

Load		Unit pressure vessels weight calculation						total weight	Unit pressure vessels cost calculation						Cost (US$)
pt	NG (t/h)	Vload	V.enxof	V-10	V-20	V-30	V-40		Vload	V.enxof.	V-10	V-20	V-30	V-40	
					(t)						(US$*$10^3$)				(US$*$10^6$)
1	44	24.88	11.87	10.70	8.60	6.78	9.51	72	216.60	242.81	224.59	95.36	80.27	102.81	0.96
2	67	27.69	12.99	11.55	9.36	7.42	10.27	79	236.01	260.13	237.96	101.56	85.66	108.60	1.03
3	89	30.64	14.16	12.44	10.16	8.09	11.60	87	256.13	277.99	251.68	107.94	91.21	115.07	1.10
4	133	33.75	15.38	13.35	10.98	8.79	11.87	94	276.97	296.40	265.75	114.50	96.93	121.43	1.17
5	178	37.01	16.65	14.30	11.84	9.51	12.71	102	298.50	315.33	280.17	121.25	102.81	127.95	1.25
6	222	40.40	17.97	15.28	12.74	10.27	13.58	110	320.73	334.79	294.93	128.16	108.86	134.63	1.32
7	267	43.98	19.35	16.29	13.66	11.06	14.48	119	343.63	354.76	310.04	135.26	115.07	141.47	1.40
8	311	47.69	20.77	17.34	14.62	11.87	15.41	128	367.21	375.24	325.48	142.53	121.43	148.45	1.48
9	356	51.55	22.24	18.42	15.61	12.71	16.37	137	391.456	396.24	341.25	149.96	127.95	155.59	1.56
10	400	55.56	23.77	19.53	16.64	13.58	17.35	146	416.35	417.73	357.36	157.57	134.63	162.88	1.65
11	445	57.21	25.34	20.67	17.69	14.48	18.37	154	426.50	439.72	373.80	165.35	141.47	17.03	1.72
12	489	58.89	26.97	21.84	18.78	15.41	19.42	161	436.74	462.20	390.56	173.29	148.45	177.89	1.79
13	534	60.57	28.65	23.05	19.90	16.37	20.49	169	447.09	485.17	407.65	181.40	155.59	185.62	1.86

Source: The Author, 2017.

Table D4 – Reactors cost as a function of the natural gas load of the synthesis gas generation unit.

NG Load		Primary reactor				Secondary reactor				HTS reactor				LTS reactor				Methanador reactor				Total
pt.	(t/h)	vol. (m^3)	acces. cost (*)	corr. factor	reactor cost (*)	vol. (m^3)	acces. cost (*)	corr. factor	reactor cost (*)	vol. (m^3)	acces. cost (*)	corr. factor	reactor cost (*)	vol. (m^3)	acces. cost (*)	corr. factor	reactor cost (*)	vol. (m^3)	acces. cost (*)	corr. factor	reactor cost (*)	reactors cost (*)
1	44	35	0.78	4.20	3.26	35	0.78	4.20	3.26	15	0.43	1.68	0.72	15	0.43	1.68	0.72	12	0.37	1.68	0.63	8.59
2	67	40	0.85	4.20	3.59	40	0.85	4.20	3.59	20	0.52	1.68	0.88	20	0.52	1.68	0.88	14	0.41	1.68	0.69	9.62
3	89	45	0.93	4.20	3.91	45	0.93	4.20	3.91	25	0.61	1.68	1.03	25	0.61	1.68	1.03	17	0.47	1.68	0.79	10.66
4	133	50	1.01	4.20	4.22	50	1.01	4.20	4.22	30	0.69	1.68	1.17	30	0.69	1.68	1.17	20	0.52	1.68	0.88	11.66
5	178	55	1.08	4.20	4.53	55	1.08	4.20	4.53	34	0.76	1.68	1.28	34	0.76	1.68	1.28	24	0.59	1.68	1.00	12.61
6	222	60	1.15	4.20	4.84	60	1.15	4.20	4.84	38	0.76	1.68	1.28	38	0.76	1.68	1.28	28	0.66	1.68	1.11	13.55
7	267	65	1.22	4.20	5.14	65	1.22	4.20	5.14	41	0.87	1.68	1.46	41	0.87	1.68	1.46	31	0.71	1.68	1.19	14.39
8	311	70	1.29	4.20	5.43	70	1.29	4.20	5.43	44	0.92	1.68	1.54	44	0.92	1.68	1.54	34	0.76	1.68	1.28	15.21
9	356	75	1.36	4.20	5.72	75	1.36	4.20	5.72	47	0.96	1.68	1.61	47	0.96	1.68	1.61	37	0.81	1.68	1.36	16.02
10	400	80	1.43	4.20	6.01	80	1.43	4.20	6.01	50	1.01	1.68	1.69	50	1.01	1.68	1.69	40	0.85	1.68	1.43	16.82
11	445	85	1.50	4.20	6.29	85	1.50	4.20	6.29	53	1.05	1.68	1.76	53	1.05	1.68	1.76	43	0.90	1.68	1.51	17.62
12	489	90	1.56	4.20	6.57	90	1.56	4.20	6.57	56	1.09	1.68	1.84	56	1.09	1.68	1.84	46	0.95	1.68	1.59	18.40
13	534	95	1.63	4.20	6.84	95	1.63	4.20	6.84	59	1.14	1.68	1.91	59	1.14	1.68	1.91	50	1.01	1.68	1.69	19.20

*(*): $(\text{US}\$*10^6)$* Source: The Author, 2017.

Table D5 - Main equipment cost consolidation as a function of the natural gas load of the synthesis gas generation unit.

	NG	Main equipments cost					Total
Pt.	load (t/h)	compr.	pumps	exch.	vessels	reactors	cost
		$(\text{US}\$*10^6)$					
1	44	3.00	0.14	0.42	0.96	85.89	90.41
2	67	3.67	0.18	0.50	1.03	96.23	101.62
3	89	4.26	0.20	0.55	1.10	106.56	112.67
4	133	5.27	0.22	0.67	1.17	116.60	123.92
5	178	6.15	0.45	0.90	1.25	126.14	134.89
6	222	6.95	0.51	1.07	1.32	135.48	145.34
7	267	7.69	0.67	1.26	1.40	143.86	154.87
8	311	8.37	0.71	1.41	1.48	152.10	164.08
9	356	9.02	0.73	1.55	1.56	160.23	173.10
10	400	9.64	0.75	1.71	1.65	168.24	181.99
11	445	10.23	0.76	1.86	1.72	176.16	190.73
12	489	10.80	0.83	2.00	1.79	183.98	199.40
13	534	11.35	0.85	2.15	1.86	191.96	208.17

Source: The Author, 2017.

Below is presented the auxiliary data tables used for calculating the cost of the main equipments of the ammonia production units in Chapter 4.

Table D6 - Compressors power as a function of the syngas load of the ammonia production unit.

Syngas load		Compression demanded Power of ammonia unit (kw)										Total
Pt.	(t/h)	C-10	C-20	C-30	C-40	C-50	C-60	C-70	C-80	C-90	C-100	(Mw)
1	12	1967	1775	2350	2371	2477	2499	4943	2496	2195	1959	25.03
2	19	2950	2662	3524	3556	3715	3748	7414	3744	3292	2939	37.54
3	25	4031	3637	4760	4803	5018	5062	10010	5056	4389	3919	50.69
4	37	6164	5567	7218	7283	7609	7676	15180	7667	6653	5939	76.96
5	50	8210	7419	9621	9708	10140	10230	20240	10220	8916	7960	102.66
6	62	9843	8884	11750	12860	12390	12500	24730	12490	10970	9797	126.21
7	75	12260	11080	14400	14530	15180	15320	30290	15300	13440	12000	153.80
8	87	14240	12790	16700	16860	17610	17770	35140	17740	15430	13780	178.06
9	100	16620	14820	19230	19400	20270	20450	40440	20420	17150	15310	204.11
10	112	18270	16280	21360	21560	22520	22720	44930	22690	19200	17140	226.67
11	125	20340	18130	23760	23980	25050	25270	49980	25240	21400	19100	252.25
12	137	22610	20160	26290	26530	27720	27960	55300	27930	23660	21120	279.28
13	150	24470	21820	28560	28820	30110	30380	60080	30340	25790	23020	303.39

Source: The Author, 2017.

Table D7 - Compression cost as a function of the syngas load of the ammonia production unit.

Syngas load		Compression cost (US$*million)										Total
Pt.	(t/h)	C-10	C-20	C-30	C-40	C-50	C-60	C-70	C-80	C-90	C-100	
1	57	2.47	2.36	2.69	2.70	2.75	2.77	3.87	2.76	2.60	2.47	27.45
2	86	3.00	2.85	3.27	3.28	3.35	3.37	4.78	3.37	3.16	2.99	33.41
3	115	3.49	3.32	3.80	3.82	3.90	3.92	5.61	3.92	3.65	3.44	38.86
4	172	4.34	4.12	4.71	4.73	4.84	4.87	7.03	4,86	4.51	4.26	48.27
5	229	5.04	4.78	5.49	5.52	5.65	5.67	8.25	5.67	5.27	4.96	56.30
6	287	5.56	5.26	6.11	6.42	6.29	6.32	9.23	6.32	5.89	5.54	62.95
7	344	6.26	5.92	6.83	6.87	7.03	7.07	10.35	7.06	6.58	6.18	70.16
8	402	6.79	6.40	7.41	7.45	7.63	7.67	11.26	7.67	7.10	6.67	76.06
9	459	7.39	6.94	8.02	8.06	8.26	8.30	12.20	8.29	7.52	7.70	82.04
10	516	7.79	7.31	8.50	8.55	8.76	8.80	12.96	8.79	8.01	7.52	86.99
11	574	8.27	7.76	9.02	9.07	9.30	9.34	13.77	9.34	8.51	7.99	92.37
12	631	8.78	8.23	9.55	9.60	9.84	9.89	14.60	9.88	9.00	8.45	97.82
13	688	9.17	8.60	10.01	10.06	10.31	10.37	15.31	10.36	9.45	8.87	102.51

Source: The Author, 2017.

Tables D8, D9 and D10 present respectively the calculation of the thermal load, thermal exchange area and cost of the exchangers of the ammonia production unit as a function of the nominal SYNGAS load of the unit.

Table D8 – Demanded thermal exchange load as a function of the nominal syngas load of the ammonia production unit.

Load		Demanded thermal load													
equipament		E-10	E-20	E-30	E-40	E-50	E-60	E-70	E-80	E-90	E-100	E-110	E-120	E-130	Total thermal load
DTML (°C)		10	17	14	14	14	14	21	69	32	25	7	24	37	
U (kj/°C.m2.h)		12000	12000	12000	12000	12000	12000	12000	12000	12000	12000	12000	12000	12000	
pt.	(t/h)	(Gj/h)	(Gj/h)	(Gj/h)	(Gj/h)	(Gj/h)	(Gj/h)	(Gj/h)	(Gj/h)	(Gj/h)	(Gj/h)	(Gj/h)	(Gj/h)	(Gj/h)	(Gj/h)
1	57	6	7	10	9	9	9	18	132	44	14	34	4	44	340
2	86	9	10	12	13	14	14	27	199	65	21	51	6	67	507
3	115	12	13	17	17	18	18	36	268	90	29	68	8	89	684
4	172	18	20	25	26	28	28	55	406	137	44	102	13	135	1039
5	229	24	27	34	35	37	37	73	542	183	59	137	17	181	1386
6	287	29	33	41	43	45	45	89	662	218	72	169	21	222	1691
7	344	35	41	50	53	55	56	110	811	273	88	207	26	272	2077
8	402	44	47	58	61	64	65	127	941	315	106	237	30	313	2408
9	459	56	55	67	71	74	74	146	1083	365	126	264	33	347	2762
10	516	62	60	75	78	82	83	163	1203	401	140	295	37	389	3068
11	574	69	67	83	87	91	92	181	1338	446	156	329	41	433	3414
12	631	77	74	92	97	101	102	200	1481	496	172	364	46	480	3780
13	688	83	80	100	105	110	110	217	1609	537	187	397	50	522	4107

Source: The Author, 2017.

Table D9 – Thermal exchange area as a function of the nominal syngas load of the ammonia production unit.

load		Heat exchange area of each equipment (m2)													total
pt.	(t/h)	E-10	E-20	E-30	E-40	E-50	E-60	E-70	E-80	E-90	E-100	E-110	E-120	E-130	area
1	57	50	32	63	51	53	53	71	161	113	47	406	15	99	1216
2	86	76	48	75	77	79	80	107	241	169	71	609	23	149	1804
3	115	104	66	101	104	107	108	145	325	231	96	812	30	199	2428
4	172	157	101	154	158	162	163	220	493	354	147	1231	45	301	3686
5	229	207	135	205	211	216	217	293	657	472	195	1650	61	404	4923
6	287	252	162	250	258	264	265	358	803	564	237	2031	75	497	6016
7	344	306	201	307	315	323	325	438	983	705	292	2488	92	609	7386
8	402	384	232	356	366	375	377	508	1141	813	350	2857	106	699	8563
9	459	488	269	409	421	431	434	585	1313	943	418	3174	117	777	9780
10	516	539	296	455	468	479	482	650	1459	1035	463	3555	131	870	10882
11	574	598	330	506	521	533	537	723	1623	1153	515	3961	146	969	12114
12	631	662	366	560	576	590	594	800	1796	1281	571	4381	162	1072	13410
13	688	716	397	608	626	641	645	869	1951	1387	619	4775	176	1168	14578

Source: The Author, 2017.

Table D10 – Total exchangers cost as a function of the nominal syngas load of the ammonia production unit.

Load		Exchangers cost (US$*million)													Total
pt.	(t/h)	E-10	E-20	E-30	E-40	E-50	E-60	E-70	E-80	E-90	E-100	E-110	E-120	E-130	Cost
1	57	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.06	0.05	0.04	0.13	0.03	0.05	0.65
2	86	0.04	0.04	0.04	0.04	0.05	0.05	0.05	0.08	0.07	0.04	0.19	0.03	0.06	0.79
3	115	0.05	0.04	0.05	0.05	0.05	0.05	0.06	0.10	0.08	0.05	0.25	0.04	0.07	0.95
4	172	0.06	0.05	0.06	0.06	0.06	0.06	0.08	0.15	0.11	0.06	0.39	0.04	0.10	1.29
5	229	0.07	0.06	0.07	0.08	0.08	0.08	0.10	0.20	0.15	0.07	0.54	0.04	0.13	1.65
6	287	0.09	0.06	0.08	0.09	0.09	0.09	0.11	0.25	0.17	0.08	0.68	0.04	0.15	1.99
7	344	0.10	0.07	0.10	0.10	0.10	0.10	0.14	0.31	0.22	0.10	0.86	0.05	0.19	2.43
8	402	0.12	0.08	0.11	0.12	0.12	0.12	0.16	0.36	0.25	0.11	1.01	0.05	0.21	2.82
9	459	0.15	0.09	0.13	0.13	0.13	0.13	0.18	0.42	0.29	0.13	1.15	0.05	0.24	3.22
10	516	0.16	0.10	0.14	0.14	0.15	0.15	0.20	0.47	0.32	0.14	1.31	0.06	0.27	3.61
11	574	0.18	0.11	0.16	0.16	0.16	0.16	0.22	0.53	0.36	0.16	1.49	0.06	0.30	4.05
12	631	0.20	0.12	0.17	0.18	0.18	0.18	0.25	0.59	0.41	0.17	1.67	0.06	0.33	4.52
13	688	0.22	0.12	0.19	0.19	0.20	0.20	0.27	0.65	0.44	0.19	1.87	0.07	0.37	4.95

Source: The Author, 2017.

Table D11 - Pressure vessels weight as a function of the nominal syngas load of the ammonia production unit.

load		Pressure vessels weight of ammonia production unit (t)													Total
Pt.	(t/h)	Vsieve	Vload	V-10	V-20	V-30	V-40	V-50	V-60	V-70	V-80	V-90	Vflash	Vsep.	weight
1	57	18.52	8.79	14.84	12.20	13.18	14.84	10.98	9.86	7.59	2.44	1.97	11.87	3.93	131
2	86	19.39	9.27	15.53	12.84	13.90	15.53	11.59	10.49	8.19	2.57	2.08	12.43	4.16	138
3	115	20.28	9.76	16.25	13.49	14.64	16.25	12.20	11.13	8.81	2.70	2.20	13.00	4.39	145
4	172	21.19	10.27	16.98	14.15	15.41	16.98	12.84	11.79	9.45	2.83	2.32	13.58	4.63	152
5	229	22.12	10.79	17.72	14.84	16.19	17.72	13.49	12.48	10.11	2.97	2.44	14.18	4.88	160
6	287	23.07	11.32	18.49	15.53	16.98	18.49	14.15	13.18	10.80	3.11	2.57	14.79	5.14	168
7	344	24.04	11.87	19.27	16.25	17.80	19.27	14.84	13.90	11.50	3.25	2.70	15.41	5.40	175
8	402	25.03	12.43	20.06	16.98	18.64	20.06	15.53	14.64	12.23	3.40	2.83	16.05	5.66	184
9	459	26.05	13.00	20.87	17.72	19.50	20.87	16.25	15.41	12.99	3.54	2.97	16.70	5.93	192
10	516	27.08	13.58	21.70	18.49	20.37	21.70	16.98	16.19	13.76	3.70	3.11	17.36	6.21	200
11	574	28.13	14.18	22.54	19.27	21.27	22.54	17.72	16.98	14.56	3.85	3.25	18.03	6.50	209
12	631	29.20	14.79	23.40	20.06	22.18	23.40	18.49	17.80	15.38	4.01	3.40	18.72	6.79	218
13	688	30.29	15.41	24.27	20.87	23.12	24.27	19.27	18.64	16.22	4.17	3.54	19.42	7.09	227

Source: The Author, 2017.

Table D12 - Pressure vessels cost as a function of the nominal syngas load of the ammonia production unit.

load		Pressure vessels cost of ammonia production unit (US$*10^6)													Total
Pt.	(t/h)	Vsieve	Vload	V-10	V-20	V-30	V-40	V-50	V-60	V-70	V-80	V-90	Vflash	Sep.	cost
1	57	1.01	0.14	0.14	0.12	0.18	0.20	0.16	0.15	0.12	0.06	0.05	0.43	0.19	2.95
2	86	1.04	0.14	0.15	0,13	0.19	0.21	0.17	0.15	0.13	0.06	0.05	0.44	0.20	3.07
3	115	1.08	0.15	0.15	0.13	0.20	0.22	0.17	0.16	0.14	0.06	0.05	0.46	0.21	3.18
4	172	1.12	0.15	0.16	0.14	0.21	0.22	0.18	0.17	0.14	0.06	0.06	0.47	0.22	3.30
5	229	1.16	0.16	0.17	0.14	0.22	0.23	0.19	0.18	0.15	0.06	0.06	0.49	0.22	3.42
6	287	1.20	0.16	0.17	0.15	0.22	0.24	0.19	0.18	0.16	0.07	0.06	0.50	0.23	3.54
7	344	1.24	0.17	0.18	0.15	0.23	0.25	0.20	0.19	0.17	0.07	0.06	0.52	0.24	3.67
8	402	1.28	0.18	0.18	0.16	0.24	0.26	0.21	0.20	0.17	0.07	0.06	0.54	0.25	3.80
9	459	1.32	0.18	0.19	0.17	0.25	0.26	0.22	0.21	0.18	0.07	0.06	0.55	0.26	3.92
10	516	1.36	0.19	0.19	0.17	0.26	0.27	0.22	0.22	0.19	0.07	0.07	0.57	0.26	4.05
11	574	1.41	0.19	0.20	0.18	0.27	0.28	0.23	0.22	0.20	0.08	0.07	0.59	0.27	4.18
12	631	1.45	0.20	0,21	0.18	0.28	0.29	0.24	0.23	0.21	0.08	0.07	0.60	0.28	4.32
13	688	1.49	0.21	0.21	0.19	0.29	0.30	0.25	0.24	0.22	0.08	0.07	0.62	0.29	4.45

Table D13 – Cost and volume of the reactor as a function of the nominal syngas load of the ammonia production unit.

Reactor cost of ammonia production unit by load variation unit													
Pt.	1	2	3	4	5	6	7	8	9	10	11	12	13
Load (t/h)	57	86	115	172	229	287	344	402	459	516	574	631	688
vol. (m3)	18	20	22	25	28	31	35	40	45	50	55	60	65
Cost (US$*10^6)	1.91	2.05	2.19	2.39	2.59	2.79	3.04	3.35	3.65	3.94	4.23	4.51	4.79

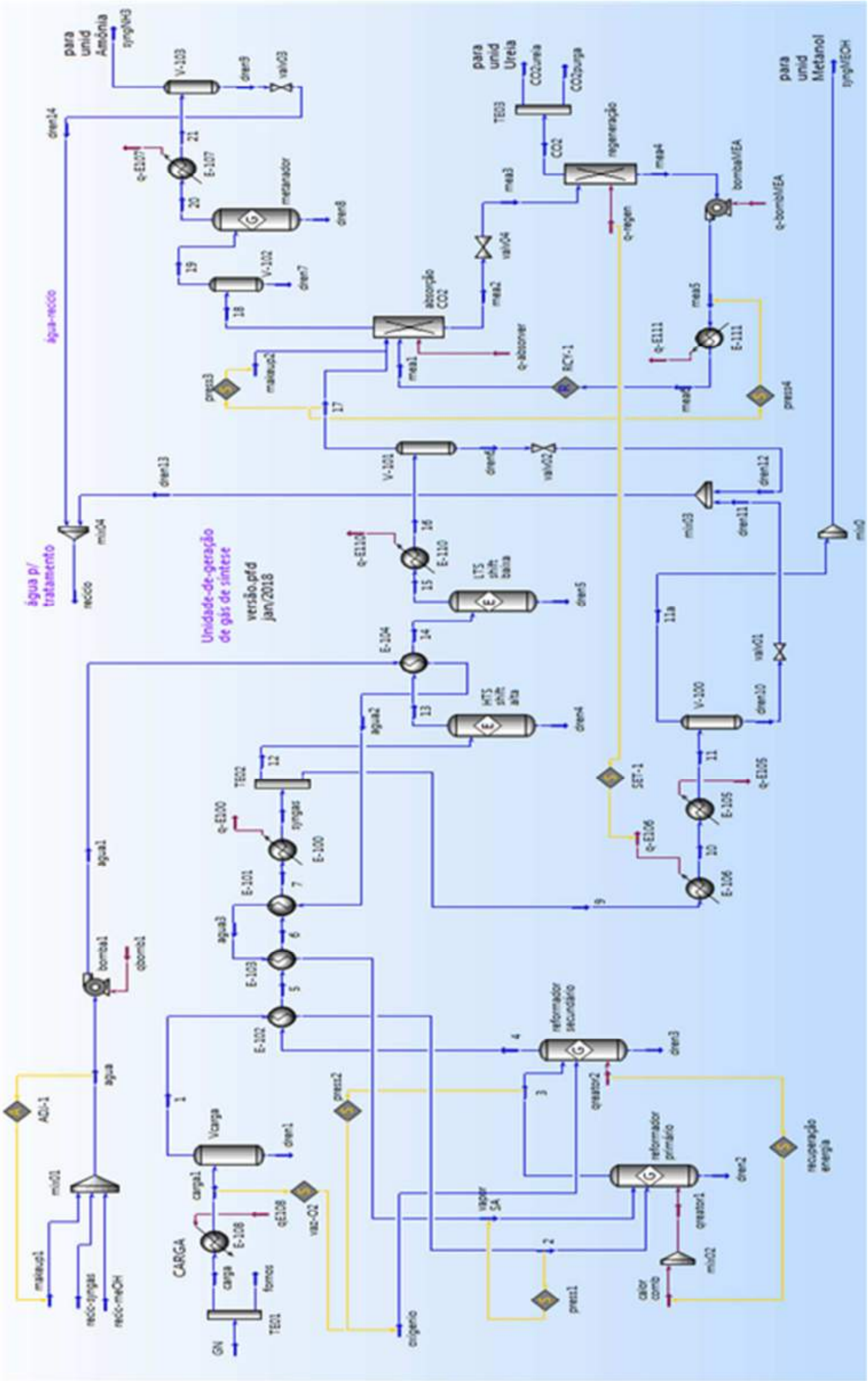
Table D14 – Main equipment cost consolidation as a function of the nominal syngas load of the ammonia production unit.

	LOAD		Compressors		Exchangers			Pressure vessels		Reactor		Total
Pt.	Nat. Gas (t/h)	syngas (+N2) (t/h)	power (Mw)	total cost (*)	thermal load (Gj/h)	exchange area (m^2)	total cost (*)	Total weight (t)	Total cost (*)	vol. reator (m^3)	total cost (*)	equip. cost (*)
1	44	57	25	27.45	340	1216	0.65	131	2.95	18	1.91	32.96
2	67	86	38	33.41	507	1804	0.79	138	3.07	20	2.05	39.32
3	89	115	51	38.86	684	2428	0.95	145	3.18	22	2.19	45.18
4	133	172	77	48.27	1039	3686	1.28	152	3.30	25	2.39	55.25
5	178	229	103	56.30	1386	4923	1.62	160	3.42	28	2.59	63.93
6	222	287	126	62.95	1691	6016	1.93	168	3.54	31	2.79	71.21
7	267	344	154	70.16	2077	7386	2.33	175	3.67	35	3.04	79.19
8	311	402	178	76.06	2408	8563	2.68	184	3.80	40	3.35	85.88
9	356	459	204	82.04	2762	9780	3.03	192	3.92	45	3.65	92.64
10	400	516	227	86.99	3068	10882	3.36	200	4.05	50	3.94	98.35
11	445	574	252	92.37	3414	12114	3.75	209	4.18	55	4.23	104.53
12	489	631	279	97.82	3780	13410	4.13	218	4.32	60	4.51	110.79
13	534	688	303	102.51	4107	14578	4.50	227	4.45	65	4.79	116.26

(*): (US$*10^6) Source: The Author, 2017.

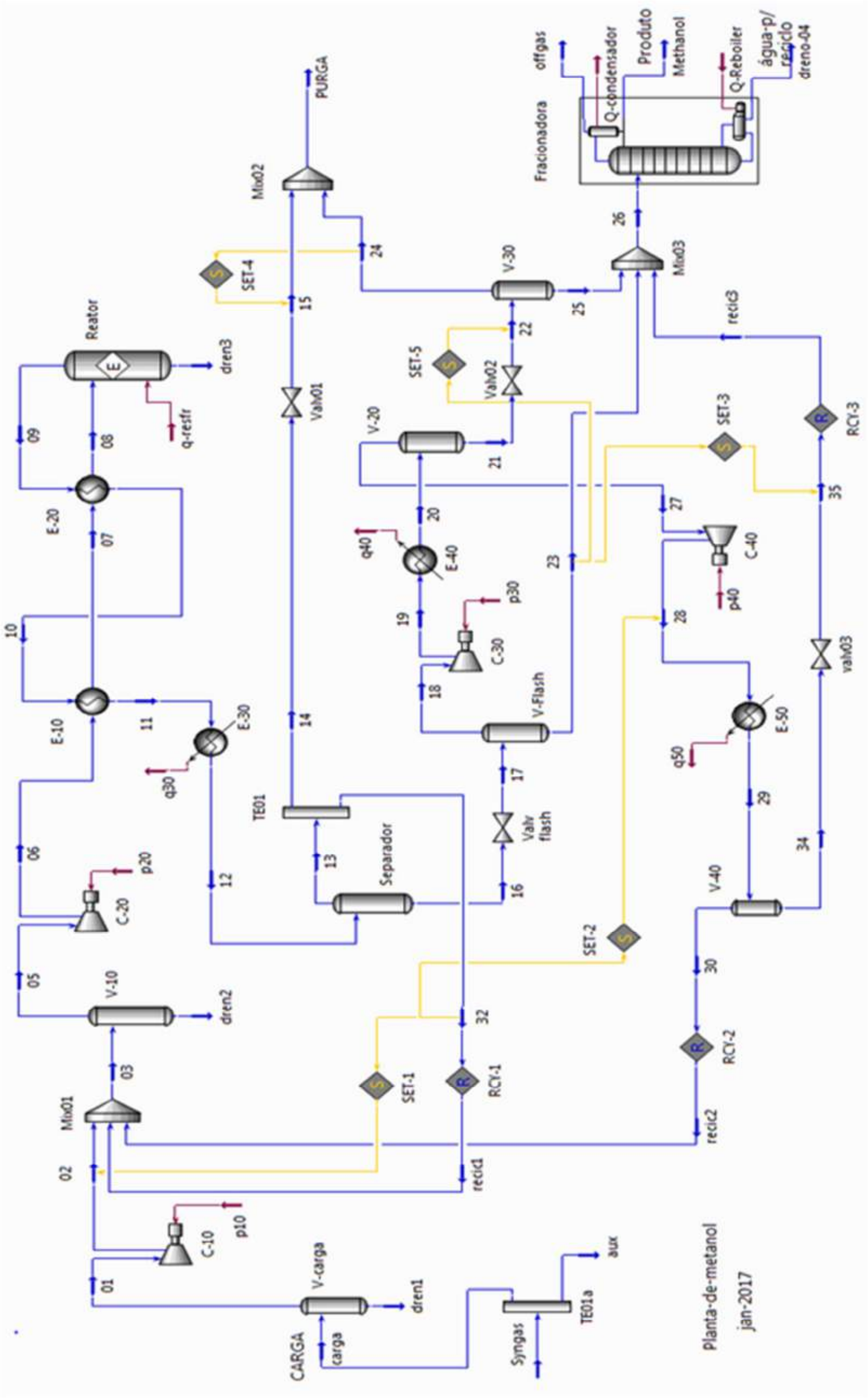
APPENDIX E – Process flow diagram – pfd of production units as implemented in the simulation software

Figure E1 - Process Flow Diagram – PFD of syngas plant as implemented in the simulation software.



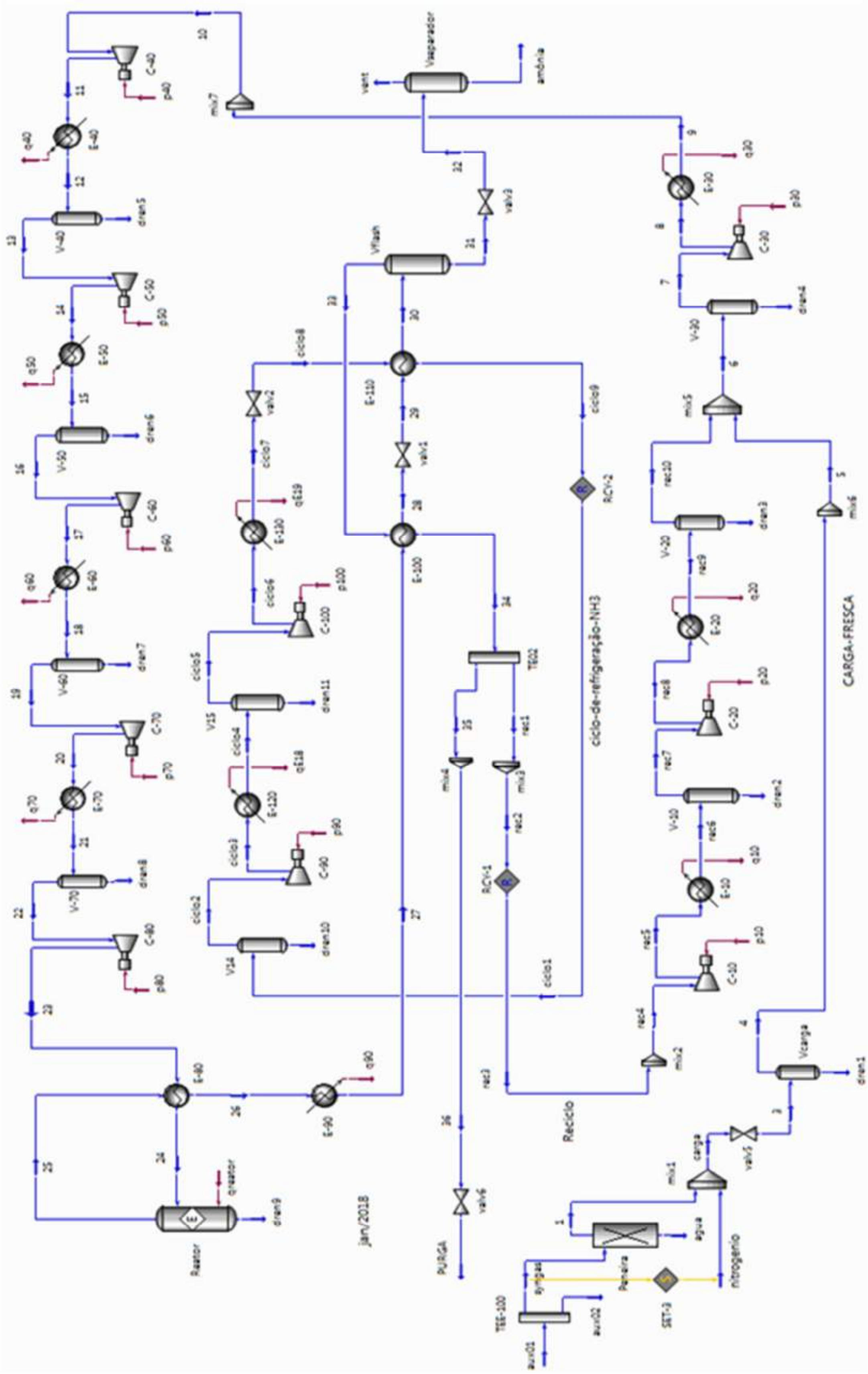
Source: Hysys simulation, 2017.

Figure E2 - Process Flow Diagram – PFD of methanol plant as implemented in the simulation software.



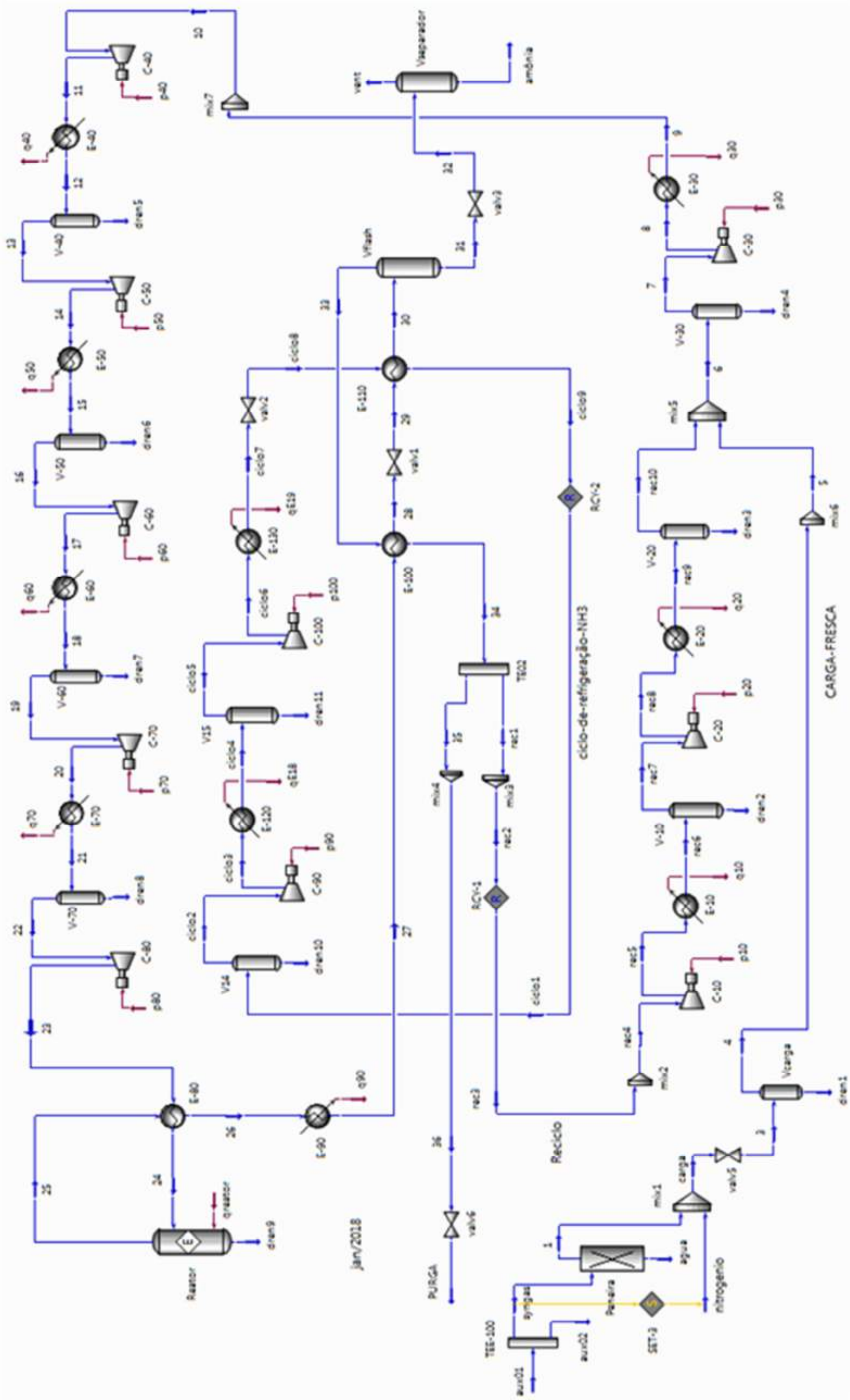
Source: Hysys simulation, 2017.

Figure E3 - Process Flow Diagram – PFD of ammonia plant as implemented in the simulation software.



Source: Hysys simulation, 2017.

Figure E4 - Process Flow Diagram – PFD of urea plant as implemented in the simulation software.



Source: Hysys simulation, 2017.