

**DESIGN AND SIMULATION OF POWER-TO-LIQUID
PROCESSES BY UTILIZATION OF VACUUM RESIDUE
FROM OIL REFINERIES**

BY

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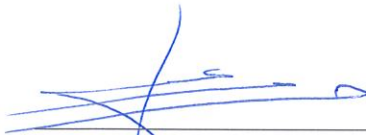
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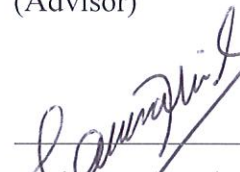

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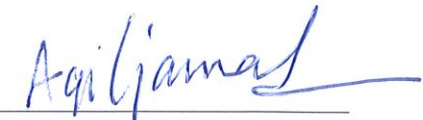



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[To my lovely parents]

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LIST OF ABBREVIATIONS

Nomenclature

ACC:	Annualized capital charge
ASME:	The American Society of Mechanical Engineers
ASU:	Air separation unit
CAGR:	Compound yearly growth rate
CAPEX:	Capital expenditure
CCUS:	Carbon Capture, Utilization, and Storage
CTM:	Coal-to-methanol
EOR:	Enhanced oil recovery
GJ:	Giga joule
IGCC:	Integrated gasification combined cycle
IPCC:	International Panel on Climate Change
LHHW:	Langmuir-Hinshelwood-Hougen-Watson
LHV:	Lower heating value
MW:	MegaWatt
OPEX:	Operating expenditure
PCA:	Paris Climate Agreement
PR:	Peng-Robinson
SN:	Stoichiometric number
SRTM:	Steam reforming to methanol
SRU:	Sulfur recovery unit
TAC:	Total annual cost
TCI:	Total capital investment
TRE:	Total energy requirement
VR:	Vacuum residue

VRTM: Vacuum residue to methanol

WGS: Water gas shift |

ABSTRACT

Full Name : [Al-Rowaili, Fayez Nasir]

Thesis Title : Design and Simulation of Power-to-Liquid Processes by utilization of Vacuum Residue from Oil Refineries

Major Field : [Chemical Engineering]

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The perpetual upsurge of global carbon emissions necessitates the utilization of fossil fuels in an ultra-cleaner and sustainable way. Gasification is a potential and promising technology that can convert the dirty fossil fuels to produce clean and environmentally friendly fuels in an economical manner. In this study, a novel work is introduced for the synthesis of clean fuel in less cost and less CO₂ emission. Vacuum residue is employed as a feedstock to produce high grade fuel. A vacuum residue to fuel (VRTM) process is simulated using Aspen Plus for a specific fuel production capacity with 99.9 wt.% purity. The developed VRTM process with sweet and sour shift were compared with the conventional SRTM process through energy, environmental and economic analysis. In other cases, VRTM integrated with methane dry reforming in parallel and sequence with gasification unit were compared. The performance of vacuum residue gasifier, natural gas reformer and the fuel synthesis reactor are validated against the plant data and the simulation results are found to be in good correlation. The results showed that the VRTM process offers a promising energy efficiency higher than the SRTM process. Also, the unit cost of fuel product from the VRTM process was observed to be lower compared to the SRTM process. In terms of environmental analysis, SRTM process emits less carbon emissions than the VRTM process. However, the VRTM process offers a high purity

captured CO₂ stream that can be utilized for another application that can further offset the fuel production cost

Keywords: Carbon dioxide capturing units, gasification process description, Dry methane Reforming, Methanol; vacuum residue gasification; economic analysis; process simulation |

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ملخص الرسالة

عنوان الرسالة: تصميم ومحاكاة عمليات تحويل الطاقة إلى سائل عن طريق استخدام البقايا الصلبة الناتجة من مصافي النفط

التخصص: هندسة كيميائية

تاريخ الدرجة العلمية: ديسمبر 2021

يستلزم التصاعد الدائم لانبعاثات الكربون العالمية استخدام الوقود الأحفوري بطريقة فائقة النظافة ومستدامة. التغويز هو تقنية محتملة وواعدة يمكنها تحويل الوقود الأحفوري الغير نظيف لإنتاج وقود نظيف وصديق للبيئة بطريقة اقتصادية. في هذه الدراسة ، تم تقديم فكرة عمل جديدة لإنتاج الميثانول بتكلفة أقل وانبعاثات أقل لثاني أكسيد الكربون مقارنة بالطريقة التقليدية لإعادة تشكيل الغاز الطبيعي البخار إلى ميثانول (SRTM). يتم استخدام البقايا الصلبة من مصفاة النفط كمادة أولية لإنتاج ميثانول عالي الجودة. يتم محاكاة عملية تحويل البقايا الصلبة من مصفاة النفط الى ميثانول (VRTM) باستخدام Aspen Plus بطاقة انتاجية محددة من الميثانول وبنقاوة 99.9% بالوزن. تمت مقارنة عملية VRTM المطورة بحالتي التحول الحلو و الحامض مع عملية SRTM التقليدية من خلال استهلاك الطاقة ، والتحليل البيئي والاقتصادي. في حالات أخرى ، تم دمج VRTM مع عملية إعادة تشكيل الميثان الجافة (DMR) بالتوازي والتسلسل مع وحدة التغويز. تم التحقق من صحة أداء وحدة التغويز لبقايا النفط الصلبة الناتجة من مصفاة النفط ، وحدة إعادة تشكيل الغاز الطبيعي (STMR) ومفعل تكوين الميثانول بالمقارنة ببيانات المصنع ووجدت نتائج المحاكاة تعطي نتائج دقيقة و صحيحة . أظهرت النتائج أن عملية VRTM توفر كفاءة طاقة واعدة أعلى من عملية SRTM. أيضًا ، لوحظ أن تكلفة 1 كغم لمنتج الميثانول من عملية VRTM أقل مقارنة بعملية SRTM. فيما يتعلق بالتحليل البيئي ، تصدر عملية SRTM انبعاثات كربون أقل من عملية VRTM. ومع ذلك ، توفر عملية VRTM ثاني أكسيد الكربون عالي النقاوة يمكن استخدامه في عمليات أخرى بحيث يساهم في تخفيض تكلفه الميثانول الكلية.

CHAPTER 1

INTRODUCTION

1.1 Background

Global communities depend largely on the burning of fossil fuels such as petroleum, natural gas, and coal for the generation of enormous demand for energy. A major byproduct of the burning of these fossil fuels (coal, natural gas, and petroleum) is a greenhouse gas (GHG) called carbon dioxide (CO₂). The uncontrolled discharge of this byproduct of fossil fuel combustion has resulted in the deposition of a very high amount of CO₂ into the atmosphere. It has caused global warming, acidification of the ocean bodies, harsh weather conditions, and the complete termination of natural species [1,2]. Within the last 19th century, the concentration of atmospheric carbon dioxide has rapidly and continuously increased approximately from 280 ppm within the last 1800s to more than 3890 ppm in 2019 [3][4]. Due to minimal mitigative attention so far received by the ever-increasing CO₂ in the atmosphere, the Inter-governmental Panel on Climate Change (IPCC) has foreseen the atmospheric carbon dioxide skyrocketing to a concentration of about 950 ppm in 2100 [5–7].

The excessive abundant atmospheric CO₂ has directly increased the mean temperature of the globe to about 1.9°C at 570 ppm atmospheric carbon dioxide concentrations by the absorption of longwave radiations [7]. Therefore, controlling both the emission and the concentration of atmospheric CO₂ is as important now as it has never been in the past and

requires undisturbed attention. Knowing that fossil fuels will retain their position as the major sources of global energy for a long period, reducing the anthropogenic carbon dioxide emissions by capturing them at the point at which they are generated (flue gases from the combustion of fossil fuels from power plants), will be an inevitable straightforward strategy. This ambitious strategy can be accomplished by utilizing efficient carbon capturing and storage technologies.

Stages such as purification, separation, compression, transportation, and processes of storage [8], are the major drawback of this technology because of the energy consumption associated with them. Without doubts, these energy-consumption stages are likely to be accompanied by further atmospheric carbon dioxide emissions, making the technology less effective in addressing the situation at hand. Moreover, different adsorbing materials for the CO₂ capture and storage have been developed but most of them have high regeneration temperatures and insufficient adsorption capacities which obstruct their advancement for “carbon capture and storage” techs [2,8–12]. Aside from “carbon capture and storage” technology, some other technology involves capturing and conversion of CO₂ into highly valuable chemicals and fuels. This technology performs as an anthropogenic cycle of carbon and is cleaner, sustainable, and efficient [13].

On the other hand, vacuum residue gasification involves the thermal transformation of the potential gaseous components of the refinery vacuum chamber to generate other products at some optimized conditions [14][15]. One of the technologies that increase the demand for the excess byproducts that are produced from the production process of quality petroleum products is the vacuum residue gasification tech [16][17]. It uses the Texaco type gasification process which is capable of sole gasification of liquid hydrocarbon fuel.

Resolving the imbalance between the consumption of light and heavy oil can prompt the expansion of the demand for heavy oil [16].

It is expected of this technology to also be a key alternative to maintain the stability of the domestic supply of energy and demand and resolve environmental issues not only because energy and electricity are produced with syngas, which is generated by gasifying a variety of raw materials that are solid or liquid, but also because new processes with poly-generation concepts that produce synthesize methanol and other important chemicals can be developed. Currently, over 200,000 bpd vacuum residue is produced from oil refineries in the Kingdom of Saudi Arabia. Some of them are supplied to use sulfur fuel oil or asphalt and others are supplied for improving the residue hydro-desulfurization process. The underlying principle of this technology is to transform heavy hydrocarbon with the high boiling point in crude oil, to light hydrocarbon under specified catalytic operation conditions.

1.2 Problem statement

The reduction of the amount of CO₂ (GHG) released into the atmosphere has become a major source of concern to the Ministry of Energy and the Kingdom of Saudi Arabia in general. It has called for research attention into how to minimize the release of this greenhouse gas into the atmosphere or better still convert them into more useful and environmentally harmless ultra clean fuel. In line with the Renewable Energy goals and policies of the Kingdom of Saudi Arabia and her vision 2030 on clean energy generation, this research work proposes novel modeling and simulation designs to optimize the utilization of the CO₂ component of the vacuum residue of the Saudi Arabia oil refineries to generate clean fuel. This study will be a complementary investigation of the

experimental reports and proof of theoretical validations. The simplified flow chart below shows the overall process of modeling and simulating the VR gasification and the production of robust clean fuel.

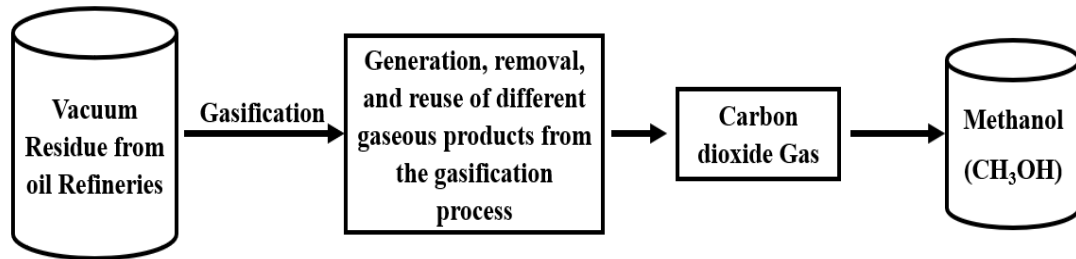


Figure 1-1 Flow chart for the overall process

1.3 Research motivations

- a) There is a need for an alternative energy source that will replace the fossil fuel energy source.
- b) The need to restore environmental sanity and discourage the discharge of greenhouse gas (carbon dioxide) into the atmosphere which can result in global warming.
- c) The need to queue into the clean energy generation policies of the Kingdom and to be part of the campaign against the environmental unsustainability of the Kingdom of Saudi Arabia.
- d) To expand the energy generation sector of the Kingdom and contribute towards job creation.
- e) The desire to see the maximum utilization of every material generated in the cause of crude oil refining.

The approaches that will be used to achieve the said objectives are reported under the research methodology.

1.4 Thesis structure

This thesis is organized as follows:

- ❖ Chapter 1 Background, problem statement, research motivations and thesis structure
- ❖ Chapter 2 Literature review.
- ❖ Chapter 3 summarizes the objectives of the present studies.
- ❖ Chapter 4 describes the methodology of the present studies. It contains the detailed description of modeling and simulations.
- ❖ Chapter 5 Techno-economic evaluation of methanol production via gasification of vacuum residue and conventional reforming routes
- ❖ Chapter 6 Eco-Technical study for Methanol Production through the gasification of vacuum residue process integrated with Methane Dry Reforming
- ❖ Chapter 7 Eco-Technical study for Methanol Production through the gasification of vacuum residue process integrated with Steam Dry Reforming
- ❖ Chapter 8 Conclusions and Recommendations |

CHAPTER 2 |

LITERATURE REVIEW

In this chapter, we provide an overview of the milestone attained so far in the catalytic waste biomass gasification. The chapter also covers theoretical studies in the form of thermodynamic and kinetic analysis of gasification of some model biomass compounds.

The Korea Institute of Energy Research recently investigated the gasification process of the vacuum residue by making use of an O₂-blown entrained-blown gasifier. The optimized experimental condition for their reaction were 1200-1250 °C temperature, 1.0 kg/cm² pressure, 0.8-1.2 oxygen/V.R ratio, and 0.4-0.7 steam/V.R ratio. The result of their experimental analysis revealed that the compositions of syngas (CO+H₂), cold gas efficiency, heating value, and the carbon conversion were 77-88%, 2300-2600 kcal/Nm³, 68-72%, and 95-99 respectively. It was also evident that their prediction of the vacuum residue gasification process with the equilibrium modeling gave predictable values which well agreed with the experimental data [16].

A. Ma'adhah et al. [18] reported a A. Ma'adhah et al. in the Kingdom of Saudi Arabia. In their report, they made it obvious that concerns such as environmental issues, flexibility, feedstock, and the upgrading of residue are among the key players in the problems confronting the global refining industries. They revealed that the present techniques of reducing the amount of refinery residues such as physical separations, hydrogen addition, and carbon rejection, also further generate vacuum residues of their own which will also

require to be utilized. They further confirmed that one excellent approach to completely utilize the residue and at the time yield to the demands of environmental sanity is the gasification or incomplete oxidation process.

This technique is one of the noncatalytic choices for the conversion and utilization of unmarketable high-sulfur heavy residues to a range of chemical viable products such as steam, electric power, hydrogen, and/or synthesis gas for chemicals production. In the Kingdom of Saudi Arabia, the inclusion of the cogeneration plant within the framework of the refinery is due to the demanding increase in electric power (about 10% yearly) and the excessive amount of heavy residues [18]. It is expected that the option of gasifying the heavy bottom (residue) will significantly contribute to the enhancement of the existing power capacity in the Kingdom. The already existing power capacity of over 28000 MW is expected to reach about 59000 MW by the end of 2050. The designed plant was expected to generate about 800 MW of electric power for both internal use and export and a 500 t/hr. HP steam [18]. It is expected that the global anthropogenic carbon dioxide emissions are to peak up to 40 Gt by the end of 2020 [19]. Climate change and the consequent global warming will continue to aggregate if these emissions are not mitigated which are a result of increasing demands for products and fuels produced from fossil sources. Conservatively, the greenhouse gas (Carbon dioxide) can be regarded as a starting material for chemical and industrial processes. The CO₂ gas can be used to produce different types of hydrocarbons such as CH₄, CH₃OH, and other higher alcohols and liquified fuels when it is synthesized with hydrogen gas in the presence of a catalyst. Judit Nyári et al [19] reported the barriers of techno-economic of industrial-scale methanol CCU-plant. They achieved this through the simulation model of a methanol plant using H₂ and CO₂ as feedstock in

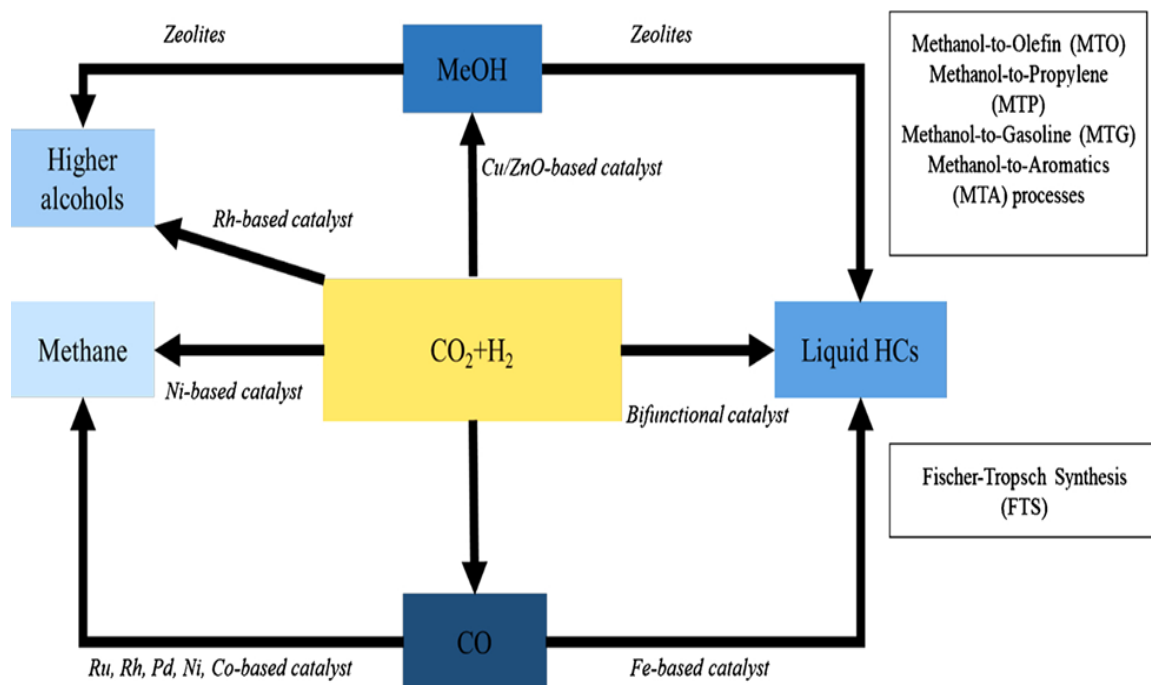


Figure 2-2. The pathways of CO_2 and H_2 catalytic conversion to different hydrocarbons [30].

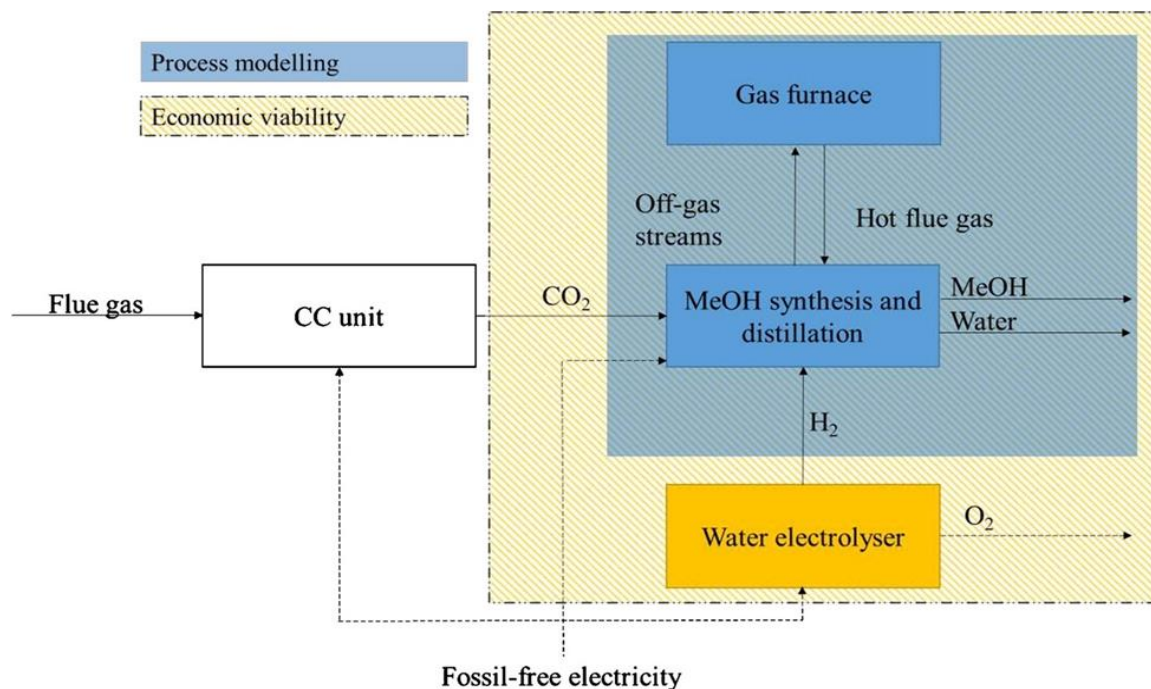


Figure 2-3. The boundary conditions of the methanol-CCU plants [30]

According to the authors [19], this is the first plant investigated at an industrial-scale comparable with fossil methanol plant units. The plant generated daily about 5 kt chemical-

grade methanol utilizable as a fuel and as feedstock for the chemical industry. The model of the kinetic, considering both carbon monoxide and carbon dioxide as a carbon source, achieved a net carbon dioxide conversion rate and close to stoichiometric raw material utilization. Under the present conditions of the market, the methanol plant is not attainable even at this scale. The high cost of hydrogen gas generated through water hydrolysis is the most remarkable cost parameter that is making the plant non-viable. A series of sensitivity analyses revealed that co-selling of oxygen by-products from the electrolyzer and lowering the hydrogen gas cost price have a significant factor in achieving a more competitive Levelized cost of methanol. These economic results are analyzed in-depth with previous studies to reveal the effect of different economic assumptions.

CHAPTER 3

RESEARCH OBJECTIVES

The general objective of this Ph.D. research project is to design and optimized modeling and simulation for the gasification of the vacuum residue from refineries in the kingdom of Saudi Arabia. This means to say that the data for the vacuum residue will be collated from designated refineries. However, the specific objectives of this doctorate research encompass the following:

- a) The development of base case (BC) refinery residue gasification to methanol product.
It will involve the validation of standalone refinery gasification,
- b) The validation of alternative refinery gasification technology,
- c) The validation of the novel integrated design,
- d) Techno-economic analysis of developed design, and
- e) Heat integration opportunities such as, integration between two distinct system DMR and VRTM, STMR and VRTM and other subsystem like CO₂ adsorption and WGSR.

CHAPTER 4

METHODOLOGY

4.1 Introduction

This section addresses the major approaches adopted to achieve the desired outcomes of this proposal

4.2 Modeling and Simulations

The modeling and simulation design for the methanol generation from the gasification of vacuum residue (heavy bottom) is explained in this section. The **Figure 4-1** below represent the different process designs of the modeling and simulation. This modeling and simulation will be performed using Aspen Hysys software and the data for the vacuum residue will be obtained from oil refinery within the Kingdom of Saudi Arabia.

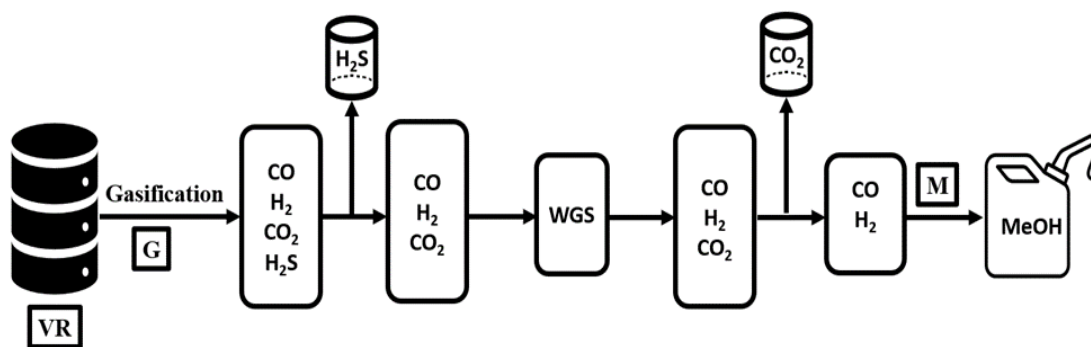


Figure 4-1. The process design of the base case (BC) production of methanol from the gasification of vacuum residue.

As shown in **Figure 4-2** the first modeling and simulation design for this research is the base case model where methanol is generated from the gasification of the heavy bottom

(vacuum residue). The vacuum residue will be gasified to carbon monoxide (CO), hydrogen gas (H₂), carbon dioxide (CO₂), and hydrogen sulfide (H₂S). The hydrogen sulfide (H₂S) gas of the gasification process will be removed, and the rest gases transferred to the water gas shift reactor (WGS) from where CO₂ will be removed with the final formation of syngas. In the end, the formation of methanol (M) from carbon dioxide is expected to take place.

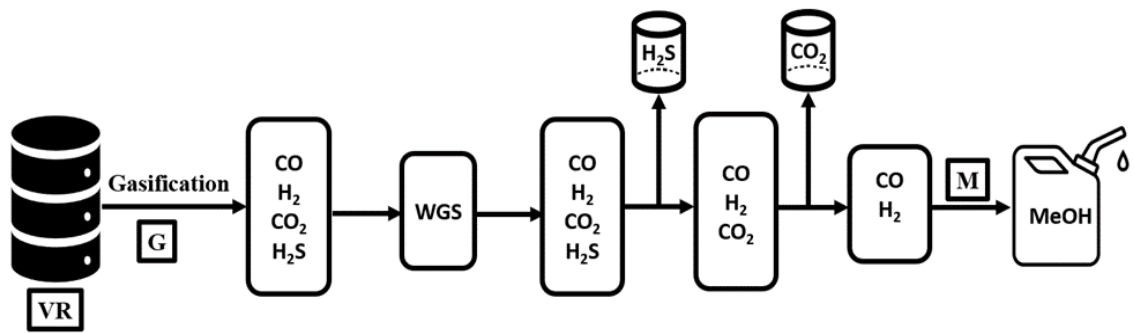


Figure 4-2. The process design of the base case (BC) production of methanol from the gasification of vacuum residue with the position of the WGS unit switched with the gasification product unit (see Figure 4.1).

The design process in **Figure 4-2** is similar to the design process in **Figure 4-1** except for the switched positions of the gasification products unit and the WGS unit. The switching of these units is to investigate the energy efficiency of the design process, the quality of the gasification products, and the purity of the gaseous products after the removal of H₂S and to compare the products of the two processes.

From the integrated base case process design in **Figure 4-3** the H₂S gas is removed immediately after the formation of the gaseous product from the vacuum residue formation. The CO, CO₂, and H₂ were recycled more than once to ensure improved purity before forming methanol with carbon dioxide. The water-gas shift reactor (WGS) is positioned

after the formation of methanol from where hydrogen gas and carbon dioxide will be formed. The carbon dioxide formed will be recycled via the dry reforming approach to generate syngas for further vacuum residue gasification. This is one of the novelties in this research proposal that will help to completely utilized excessively produced CO₂. It will help to avoid discharging carbon dioxide back into the atmosphere which in turn defeats the war against environmental degradation as a result of global warming. It is also expected that the recycling of the CO₂ via the dry reforming will improve the formation of methanol and increase yield.

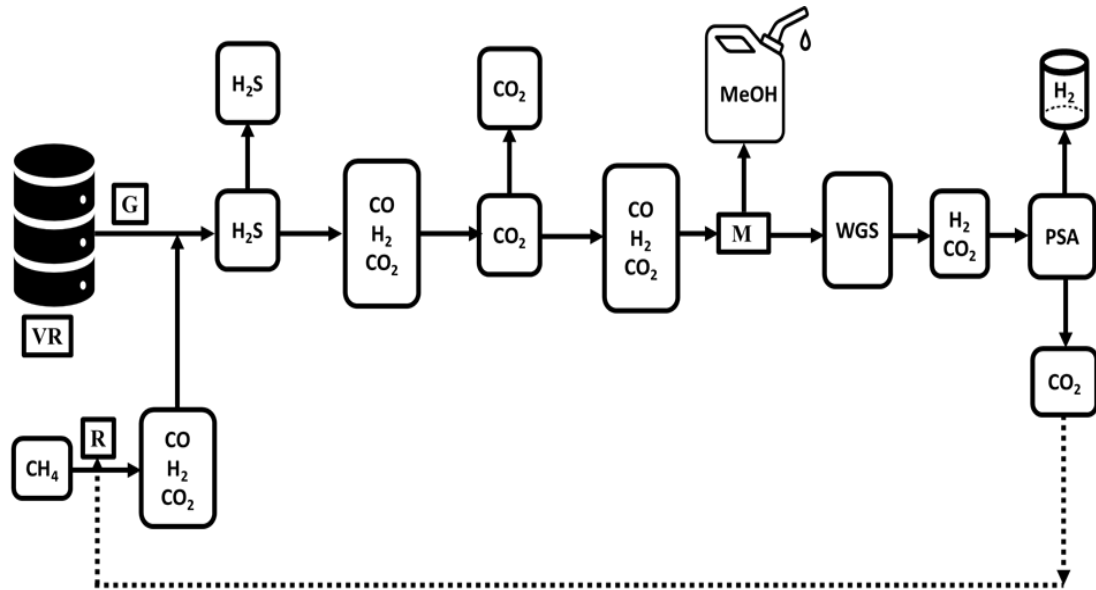


Figure 4-3. The integration of the two base case design processes (see Figure 4.1 and Figure 4.2) and the incorporation of the dry reforming unit

CHAPTER 5

Techno-economic evaluation of methanol production via gasification of vacuum residue and conventional reforming routes

5.1 Summary

The continuous rise of global carbon emissions demands the utilization of fossil fuels in a cleaner and sustainable way. Gasification is a potential technology that can convert the dirty fossil fuels for the production of clean and environment friendly fuels in an economical manner. In this study, vacuum residue is employed as a feedstock to produce high grade methanol. A vacuum residue to methanol (VRTM) process is simulated using Aspen Plus for a methanol production capacity of 90 t/h with 99.9 wt.% purity. The developed VRTM process is bench-marked with the conventional steam reforming to methanol (SRTM) process through energy, environmental and economic analysis. The performance of vacuum residue gasifier, natural gas reformer and the methanol synthesis reactor are validated against the plant data and the simulation results are found to be in good agreement. The results showed that the VRTM process offers a process energy efficiency of 49.5% which is 1.6 % higher than the SRTM process. The unit cost of methanol product from the VRTM process is \$ 317/tCH₃OH which is 14% lower compared to the SRTM process. In terms of environmental analysis, SRTM process emits less carbon emissions than the VRTM process. However, the VRTM process offers a high purity captured CO₂ stream that can be utilized for another application that can further offset the methanol production cost.

5.2 Introduction

The discharge of greenhouse gas into the atmosphere has seriously threatened the natural balance of the ecosystem and its minimization or circumvention has taken a pivotal position in the world's energy policies. It has been warned by the International Panel on Climate Change (IPCC) and other related climate policy agencies that if urgent action is not taken against the greenhouse emission, the climate will respond to mankind with severe droughts, famines, disease, and population displacement [20]. In response, the 2015 Paris Climate Agreement (PCA) targeted global warming to not exceed 2°C compared to the before-industrial era benchmark [21]. To achieve this important target, the wind and solar renewable forms of energy can be one of the best choices. However, their unstable supply has resulted in the flexibility requirement of the energy system. Despite the enormous improvement and the commercialization of renewables, fossil fuels are forecasted to be the main global energy source in the foreseeable future [22]. However, to enable the transition of fossil fuels to renewables, low carbon clean technologies must be involved.

Different potential techniques suitable for the reduction of CO₂ emissions have been improvised including carbon capture, utilization, and storage (CCUS); this undeniably offers a serene environment and improved economical profit. One of the potential CO₂ utilization approaches is the conversion of CO₂ to methanol which is a primary feedstock to produce many other value-added chemicals. This is because of the clean oxy-burning characteristics of methanol and the tendency to be blended with gasoline for use in automobiles. Because of its minimal emission, methanol is garnering rapid approval for use as a marine fuel against heavy fuel oil [23]. In addition, methanol has found wide range of applications in the production of biodiesel, as paints and resins solvent, anti-freezing

agent, and as denitrification wastewater [24,25]. Consequent to these appealing attributes, methanol has established a rapidly improving market value and demand. Its compound annual growth rate (CAGR) is predicted to grow at a 5.66 % for the period of 2019 - 2027 due to methanol-to-olefin industry [26].

Over time, different approaches and methods have been used to produce methanol [27–30]. The catalytic reaction of synthesis gas produced via steam reforming of natural gas is presently the most sought-after method of producing a large quantity of methanol [31]. Methanol production through direct hydrogenation of carbon dioxide (CO_2) has garnered enormous attention from researchers in the recent years due to the level of atmospheric CO_2 in prevalence. For example, Battaglia et al. [32] performed the techno-economic analysis for the methanol production by capturing the CO_2 from a power plant and generating H_2 from the water electrolysis system. The captured CO_2 and H_2 are then fed to the methanol synthesis section to produce 99.9 wt. % methanol product. The study explored the ways to recover heat through the thermal integration between various sections and reported savings for heating and cooling load as 81 % and 47 % respectively. Shi et al. [33] investigated the effect of mixed reforming of methane with and without carbon capture on the methanol synthesis plant, and compared the mixed reforming performance with that to the conventional steam reforming process. They found that the stoichiometric number and CO/CO_2 ratio have a positive impact on the syngas reactivity leading to a higher single pass conversion. Ahmed [34] studied the co-production of methanol and H_2 by integrating the gasification and reforming process. The study reported an energy efficiency improvement of 4.3 % for the integrated design compared to the standalone coal-to-methanol process. Ishaq and Dincer [35] proposed an integrated system for the co-

production of H_2 , ammonia and methanol. The proposed system was integrated with solar heat source that provides the steam to the reformers in the system as well as heat to the absorption cooling unit. The energy and exergy efficiencies for the proposed system were calculated as 66.83% and 68.55% respectively.

While significant efforts are underway to minimize the global carbon emissions, at the same time, decline in the crude oil prices has put the refiners under pressure to convert the bottom of the barrel into valuable products. Gasification is a feed-flexible technology that can produce high value clean fuels while utilizing dirty fossil-based feed stocks in a sustainable manner. It can resolve the imbalance between the consumption of light and heavy oil by enabling the expansion of heavy oil demand [16]. Vacuum residue from the oil refining process is one of the main candidates for the gasification technology that can produce clean energy or chemical feedstock such as syngas for the synthesis of other important chemicals. Compared to the gasification of other solid fuels, the gasification of heavy residues including vacuum residue has been scarcely investigated. Choi et al. [16] investigated the gasification of the vacuum residue experimentally to study the composition of raw syngas. They reported the optimized experimental conditions to be in the range of 1200 – 1250 °C temperature at 1.0 kg/cm² pressure. The result of their experimental analysis revealed that the compositions of syngas (CO+H₂), cold gas efficiency, heating value, and the carbon conversion were 77-88%, 2300-2600 kcal/Nm³, 68-72%, and 95-99 respectively [16]. Lazzaretto et al. [36] performed the pinch analysis of combined cycle using the heavy oil gasification to produce hydrogen and power. They reported the combined cycle efficiency to be in range of 49.1 to 50.7 % [36]. Motamedi et al. [37] performed the kinetic modeling of crude oil gasification for the production of hydrogen

gas. They reported the validation of the proposed kinetic model with that of the sawdust gasification [37]. Shahi et al. [38] conducted the parametric analysis to study the effect of a gasifying agent on heavy oil gasification. They reported that employing air-steam or oxygen-steam as a gasifying agent in a specific range can improve the hydrogen yield [38]. Shahraki and Motahari-Nezhad [39] simulated the gasification of high sulfur fuel oil to produce syngas by employing lime as a CO₂ sorbent. They investigated the effect of lime to fuel ratio on the CO₂ captured from the syngas. Ahmadi et al. [40] compared the gasification of three heavy oils in the IGCC plant for the power generation. They reported the energy efficiency of vacuum residue water slurry to be maximum at 45.7 %.

Currently, over 200,000 bpd vacuum residue is produced from oil refineries in the Saudi Arabia. Usually, the produced vacuum residue is sent to the delayed coker to produce heavy fuel oil and some of it ends up in the asphalt product. The handling and environmental concerns related to the vacuum residue products remains an issue. In addition, the strict environmental regulations enforced in the maritime industry on the usage of high sulfur heavy fuel oil means a decline in the demand of delayed coke products. One of the potential solutions is the conversion of refinery residue to the useful petrochemical products through gasification technology. Although gasification is a commercial technology with many operational plants around the world, however, little information on the gasification of vacuum residue has been reported in the literature. With increasing stringent industrial and environmental requirements in the oil business, ways to diversify the process technology are imminent. Therefore, the focus of this work is to design and simulate the methanol production process by the gasification of vacuum residue from an oil refinery. First a simulation model using a commercial process simulator is developed for the gasification

of vacuum residue to methanol (VRTM). In order to benchmark the performance of the VRTM process, the performance of the conventional methanol production processes, that is steam reforming to methanol (SRTM) is analyzed. For a fair comparison with the conventional methanol production route, the methanol production rate is assumed to be 90 tons/h with at least 99.9 wt. % purity for all the technologies assessed. The performance of the proposed VRTM process is compared to that of the conventional process in terms of technical, environmental and economic analysis.

5.3 Process description

5.3.1 Steam reforming to methanol (SRTM) process

The simplified flow diagram for the steam reforming process of natural gas to produce methanol is shown in **Figure 5-1**. The process contains hydrodesulphurization, steam synthesis, and distillation. The first stage of the process is the hydrodesulphurization of the natural gas which occurs in a fixed-bed reactor and at an increased temperature and pressure of about 300 to 400 °C and 30 to 130 atm respectively. This typically takes place in the presence of a catalyst comprising a cobalt and molybdenum-doped alumina. This process is followed by the steam-assisted reforming in a reformer vessel, producing synthesis gas (CO, H₂ and CO₂). Industrially, syngas is produced by steam reforming of natural gas over Ni-based catalyst with the process yielding a high enthalpy change as shown in Eq. 1. This shows that the process is highly endothermic and typically performed at a high pressure of 20 to 30 atm. Because equilibrium is not favored at high pressure, a large amount of steam is used for high methane conversion. The production of carbon dioxide at the expense of carbon monoxide is obtained when excess steam is used in the process. At this condition, the syngas produced will have an excessive amount of H₂,

leading to recycling and H₂ purging. The required syngas ratio (H₂/CO) can be achieved by adding CO₂ to the reformer feed.



The overall synthesis of methanol is exothermic and limited by equilibrium. It is typically favored by low pressure and temperature with commercial reactors with fixed bed operating at 50 to 100 atm and 230 to 270 °C, respectively [41]. Crude methanol (containing about 20% water content) from the synthesis chamber is fed into the distillation column, where over 99.9 wt.% pure methanol drawn-out is cooled down to 38 °C and sent to the storage.

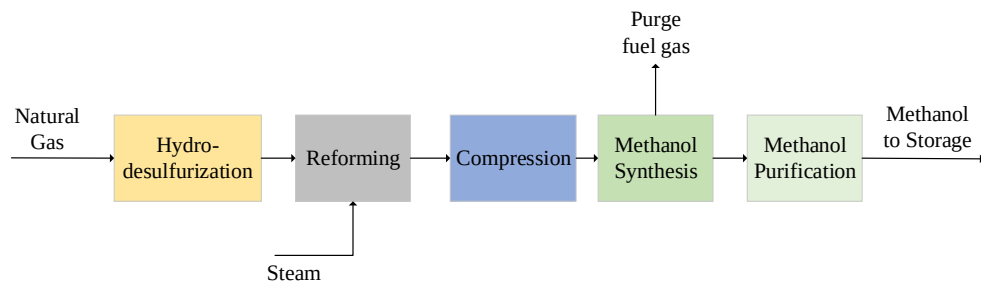
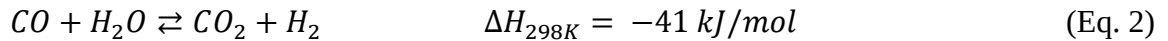


Figure 5-1. Block diagram of steam reforming to methanol (SRTM) process.

5.3.2 Vacuum residue to methanol (VRTM) process

The VRTM process is a versatile process where the vacuum residue feed, oxygen and steam are fed to the gasifier. The partial oxidation of vacuum residue takes place in the non-catalytic gasifier operated at high temperature and pressure to mainly produce H₂, CO, CO₂, H₂O, CH₄ and some impurities like H₂S, COS, NH₃, HCN and ash. One of the key design variables is the H₂/CO ratio whose value depend on the downstream application. The addition of steam to the gasifier acts as a moderator and enhances the WGS reaction to convert CO to H₂ in order to increase the syngas ratio. **Figure 5-2** shows the block

diagram for the vacuum residue to methanol process thru the gasification technology. The high temperature raw syngas leaving the gasifier is cooled down by recovering the sensible heat through effluent coolers to produce high pressure steam. The raw syngas also contains some unconverted carbon in the form of soot and particles of ash. The solid impurities including soot and ash are separated from the gas stream through a cyclone separator. The syngas is then fed to the scrubbing unit where a mixture of ammonia and water is used to wash out any remaining suspended solid particles. The gaseous impurities including H₂S, and COS are then removed from the syngas in the gas cleaning unit. The gas cleaning unit employs a physical solvent to efficiently remove more than 99.9 % of sulfur components present in the syngas. This is important to avoid the catalyst poisoning in the downstream methanol reactor where the allowed H₂S concentration range in the syngas is < 0.05 – 0.5 ppm [21]. The H₂/CO ratio of clean syngas is around unity which is not suitable to produce methanol. Therefore, in order to increase the H₂ content, WGS reaction is needed to convert the CO to H₂ as shown in Eq. (2).



Stoichiometric number (SN) is an important parameter which represents the feed composition for maximum conversion at the inlet of the methanol synthesis reactor as shown in Eq. (3).

$$SN = \frac{[H_2] - [CO_2]}{[CO] + [CO_2]} \quad (\text{Eq. 3})$$

The near optimal value of SN at the methanol synthesis reactor should be 2 or slightly higher which indicates the requirement of H₂ excess in the syngas [42]. The SN of the

sweet syngas at the outlet of gas cleaning unit is around 0.89 which represents the deficiency of H_2 in the syngas. Therefore, in order to achieve the required SN of 2 at the methanol synthesis section, the syngas stream at the outlet of the gas cleaning unit is split into two streams. A part of the syngas is directed to the WGS section for increasing the H_2 amount, while the other part of the split bypasses the WGS section. The syngas sent to the WGS unit passes through two-stage shift reactor where more than 99.5 % of CO is converted to the H_2 . The WGS reaction is exothermic in nature, hence intercooling is done between the two stages to control the temperature increase across the reactors. The additional CO_2 produced from the WGS reaction is then removed using the Rectisol process where methanol is employed as a physical solvent. The CO_2 removal rate is fixed as 98 % in this work to match the industrial syngas composition required at the methanol synthesis unit. The shifted gas from the WGS unit and the by-passed syngas stream are then mixed to have a syngas with SN of 2 and a H_2/CO ratio of 2.27. The syngas is first pressurized in a two-stage compressor to a final pressure of 100 bar before being fed to the methanol synthesis reactor at 230 °C. The reactor effluent stream leaves at 342 °C and is cooled down to allow the formation of heterogeneous phase so that the unreacted gas stream can be separated from the crude methanol. The unreacted syngas leaving at the top of the flash drum is sent back to the reactor with a small amount being purged to minimize the accumulation of inert in the loop. The crude methanol is sent to the distillation column where 99.9 wt.% pure methanol is produced from the top of the tower.

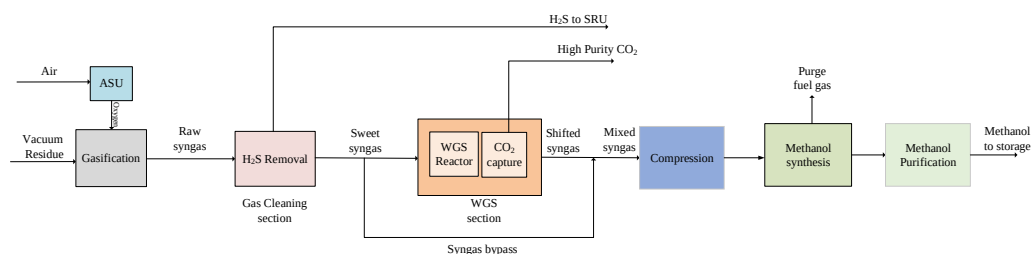


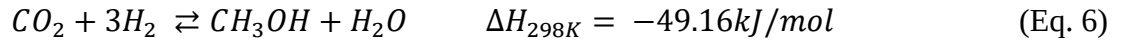
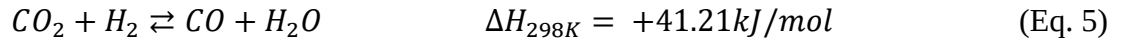
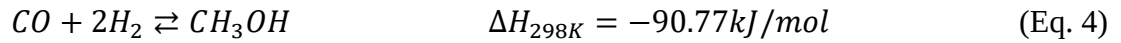
Figure 5-2. Block diagram of vacuum residue to methanol (VRTM) process – sweet shift

5.4 Simulation Methodology

The two technologies namely reforming and gasification are simulated and evaluated to produce methanol from natural gas and vacuum residue feedstocks, respectively. The methanol production rate and purity has been set as 90 tons/h and 99.9 wt. % respectively for both processes. The selection of components that correctly represent the actual compounds in the system is the foremost step before the simulation model development. The simulation has been performed using a commercial process simulator, Aspen Plus that contains a large database of the conventional components. All the components involved in the SRTM process exist as conventional components. The feed specification and composition for the reforming SRTM process are provided in the supplementary information. The thermodynamic package used to estimate the physical properties of components is Peng-Robinson (PR) equation of state.

Pre-heated natural gas stream and high pressure super-heated steam is fed to the reformer operating at 870 °C and 20 bar to produce the raw syngas. Calculator block tool in the Aspen Plus has been used to calculate the required steam molar flowrate which is three times that of the methane flowrate. The reformer effluent is initially cooled down by exchanging heat with the incoming feed stream. The raw syngas is then sent to the heat

recovery section, where the syngas passes through a series of heat exchangers to generate steam and finally leaves at 50 °C. The cooled syngas is then prepared for the methanol synthesis reactor by compressing it to 100 bar pressures through a two-stage compression train. The compression ratio for each compressor stage is calculated as 2.25. The compressed high-pressure syngas is then fed to the methanol synthesis reactor at 230 °C where the following reactions shown in Eq. (4 – 6) takes place to produce methanol and water.



Due to the exothermic nature of the reactions taking place in the methanol synthesis reactor, it is important to remove the heat generated from the reactor to avoid catalyst sintering caused by increasing temperatures. Various methanol reactor layouts have been employed in the industry including quench reactor, reactor with external cooling, isothermal reactor and others [21,43]. In this study, adiabatic quench reactor has been selected as the type of methanol synthesis reactor with five inter-stages each loaded with Cu-based catalyst. A part of the syngas enters the top of the reactor while the residual feed is entered at each inter-stage accomplishing quench. **Figure 5-3** shows the reactor layout used in Aspen Plus to simulate the five-stage methanol synthesis adiabatic quench reactor. Kinetic model proposed by Graaf et al. [44] has been adapted which considers the methanol formation from both CO and CO₂ in the syngas feed. Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetic model in the Aspen Plus is used to insert the following kinetics considered

in the methanol synthesis reactor as shown in Eq. (7 – 9). The numerical values for the kinetic parameters used in Aspen Plus can be found in literature [45].

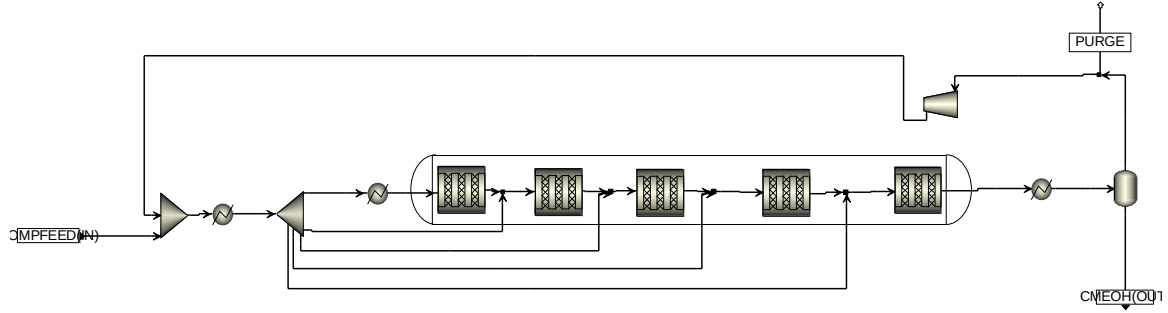


Figure 5-3. Five stage adiabatic quench reactor for methanol synthesis

$$r_A = k_A \frac{K_{CO} \left[f_{CO} f_{H_2}^{\frac{3}{2}} - f_{CH_3OH} / (K_A \sqrt{f_{H_2}}) \right]}{(1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2}) [\sqrt{f_{H_2}} + \left(\frac{K_{H_2O}}{\sqrt{K_H}} \right) f_{H_2O}]} \quad (\text{Eq. 7})$$

$$r_B = k_B \frac{K_{CO_2} [f_{CO_2} f_{H_2} - f_{H_2O} f_{CO} / K_B]}{(1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2}) [\sqrt{f_{H_2}} + \left(\frac{K_{H_2O}}{\sqrt{K_H}} \right) f_{H_2O}]} \quad (\text{Eq. 8})$$

$$r_C = k_C \frac{K_{CO_2} \left[f_{CO_2} f_{H_2}^{\frac{3}{2}} - f_{H_2O} f_{CH_3OH} / (f_{H_2}^{\frac{3}{2}} K_C) \right]}{(1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2}) [\sqrt{f_{H_2}} + \left(\frac{K_{H_2O}}{\sqrt{K_H}} \right) f_{H_2O}]} \quad (\text{Eq. 9})$$

The methanol synthesis reactor effluent contains the crude methanol along with unreacted syngas which is cooled down to separate the non-condensable vapor phase from the crude methanol. The vapor phase is compressed and recycled back to the reactor with a small amount purged to avoid inert accumulation while the crude methanol is sent to the purification section. The purification section employs two distillation columns to produce 99.9 wt. % methanol at the top of the second column which is sent to the methanol storage tank.

In the case of VRTM process, the vacuum residue feed is a blend of many heavy hydrocarbons and cannot be defined as a conventional component in Aspen Plus. Therefore, vacuum residue has been defined as a non-conventional component that relies on the built-in HCOLAGEN and DCOALIGT model for the calculation of enthalpy and density, respectively. The feed composition of the vacuum residue in terms of proximate, ultimate and sulfur analysis is provided in the supplementary information. With the help of the Fortran statement, a calculator block is installed to calculate the mass yield of individual species. In Aspen Plus, ULTANAL is defined as the ultimate analysis on a dry basis. The variable defined as the percent H₂O in the PROXANAL for vacuum residue is used to convert the ultimate analysis to a wet basis. The remaining eight variables (H₂O, Ash, and carbon, H₂, N₂, Cl₂, S and O₂) are defined as the individual component of various species in the RSTOIC block. Vacuum residue along with the high purity oxygen and steam is fed to the gasifier with the O₂/Feed mass ratio of unity. The raw syngas leaves the gasifier at 1300 °C with a H₂/CO ratio of unity. The heat energy available in the high temperature syngas is recovered through a series of heat exchangers generating high pressure steam. Cooled syngas is then sent to the gas cleaning unit where more than 99.9 % of H₂S is removed using the chilled methanol solvent. Design spec has been employed in to achieve the required purity by manipulating the solvent flowrate. Clean syngas at the outlet of gas cleaning unit is split into two streams, one pass through the WGS to increase the H₂ amount, second by-passing the WGS section. The split fraction is controlled by employing a Design Spec to maintain the required SN at the inlet of the methanol synthesis section. The syngas sent to the WGS section undergoes WGS reaction where a Calculator block is installed to manipulate the steam flow for achieving 99.5 % CO conversion. The by-passed syngas and

shifted syngas streams are then mixed that is sent to the 2-stage compression train to increase the syngas pressure to 100 bar. The compressed syngas is then sent to the methanol synthesis section as described earlier to produce methanol. The key specifications used for the two processes in the Aspen Plus models are shown in **Table 5-1**.

Table 5-1. Simulation specifications for Aspen Plus models

Unit/ system	Aspen Model	Parameters
SRTM process		
Gas Reforming	Reformer model: RGibbs	Temperature = 870 °C Pressure = 20 bar Feed ratio (Steam/ NG) = 2.90
VRTM Process		
ASU	-	(99.6%-O ₂ , 0.29%-Ar, 0.07%-N ₂) Energy 0.37 kWh/kg O ₂ [46]
VR Gasification	Gasifier model: RGibbs	Gasifier type = Entrained flow Gasifier Temperature = 1300°C, Pressure = 63 bar VR/O ₂ (wt./wt.) = 1.0 VR/Steam (wt./wt.) = 2.05 VR conversion = 99 %
Gas Cleaning	Absorber: RadFrac Stripper: RadFrac	H ₂ S removal: Rectisol (99.9%) CO ₂ removal: Rectisol (98.0%) Solvent regeneration: Thermal
Water Gas Shift	Shift model: REquil CO ₂ removal: RadFrac	High temperature shift = 343 °C Low temperature shift = 132 °C Steam:CO = 1.365 CO conversion ~99.5 % [47]
Methanol Section		
Gas Compression	Compr (Isentropic)	Compression stages: 2 Inter-stage cooling (T = 45 °C) Isothermal flash drum: 2 Compressor efficiency: ASME 80%
Methanol synthesis	Reactor model: RPlug (Fixed bed adiabatic quench reactor)	No. of reactor stages = 5 Temperature = 230°C Pressure = 100 bar

		Cu-based catalyst Catalyst density = 1940 kg/m ³ Bed voidage = 0.35
Methanol distillation	Radfrac	No. of columns = 2 MeOH product purity $\geq$ 99.9 wt. %

5.5 Model Validation

The simulation model reliability is an important step before the results can be analyzed or extended to changed operational conditions. Therefore, in order to ascertain the robustness of the developed models, validation has been performed with the design data. The reformer reactor and gasifier are the main equipment where the raw material is converted to the syngas product. The reformer takes natural gas as the feed, while vacuum residue is the feed for the gasifier. The syngas producing reactors (reformer and gasifier) are the one of the first equipment in the process flowsheets. Therefore, validating these reactors is of an utmost importance. **Figure 5-4** shows the validation of reformer and gasifier respectively, in terms of the syngas composition produced from each of these reactors. The result shows that there is a good agreement between the plant data and the simulation results. The temperature and pressure conditions for the reformer used for the purpose of validation are 870 °C and 20 bar respectively, while the conditions used for the gasifier are 1300 °C and 63 bar respectively.

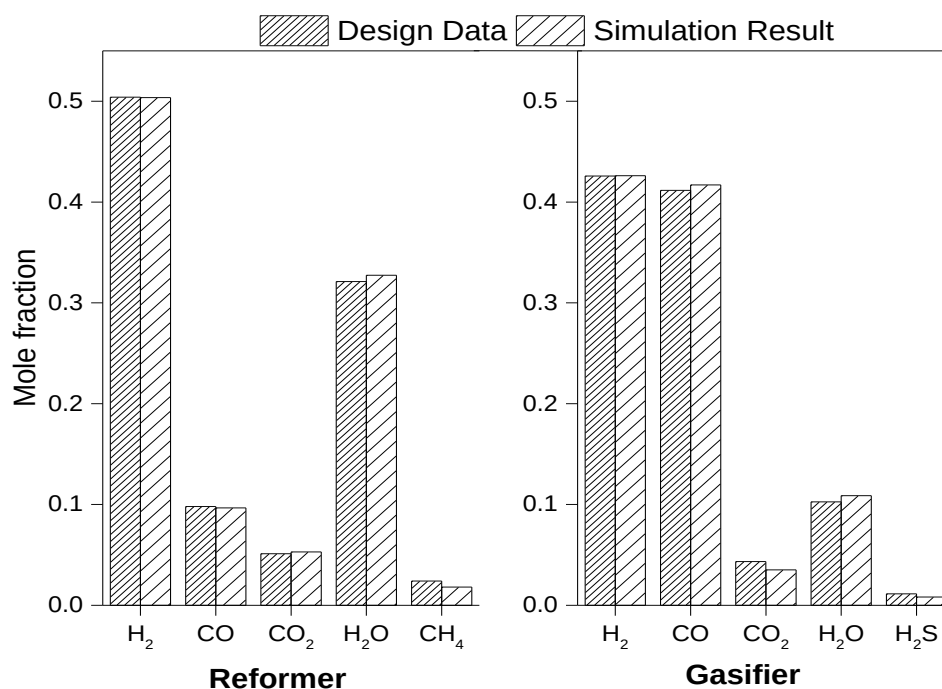


Figure 5-4. Validation of syngas composition at the reformer and gasifier outlet for the SRTM and VRTM processes respectively

5.6 Results and Discussions

The merits and competency of the two designs have been evaluated in terms of energy analysis, environmental performance, and economics.

5.6.1 Energy Analysis

A detailed energy analysis has been performed to ascertain the performance of the two methanol production technologies. Vacuum residue gasification is an exothermic process where significant amount of high-quality energy is available. The high temperature syngas stream leaving the gasifier is utilized to produce steam, a part of which is consumed back in the process while the remaining steam may be utilized to produce power. The quality of raw syngas produced from the gasifier is not suitable in terms of H₂/CO ratio for the methanol production, hence, further downstream processing is required consuming additional energy. On the other hand, reforming is an endothermic process operating at

more than 850 °C requiring substantial energy input. The syngas produced from the reformer has high SN and can be directly fed to the methanol synthesis section without any further syngas ratio manipulation. **Figure 5-5** shows the energy consumption in terms of utilities for the two designs. The results show that the methanol production thru SRTM process requires the highest energy with more than 50 % of the energy demand attributed to the heating utilities. The energy required by the cooling duties is also substantial and accounts for around 45 % of the total energy consumption. Electricity consumption mainly by the pumps and compressors contribute to less than 4 % of the total energy demand. In the case of VRTM, the cooling utilities are the highest energy consuming service with 57.5 % of the total energy requirement. High cooling utilities consumption is mainly linked to the Rectisol process, where low temperature methanol solvent is employed for the removal of acid gases. In addition, thermal solvent regeneration system also consumes significant amount of energy. In the case of VRTM, high purity oxygen supply to the gasifier contributes around 5 % of the energy consumption. The results show that the heating duty and electricity requirement for the VRTM is 41.8 % and 29.1 % less compared to the SRTM process. On the other hand, the cooling requirement for the VRTM is 7.3 % higher compared to the SRTM process. The overall energy requirement of the SRTM is 14.9 % higher in comparison to the VRTM process.

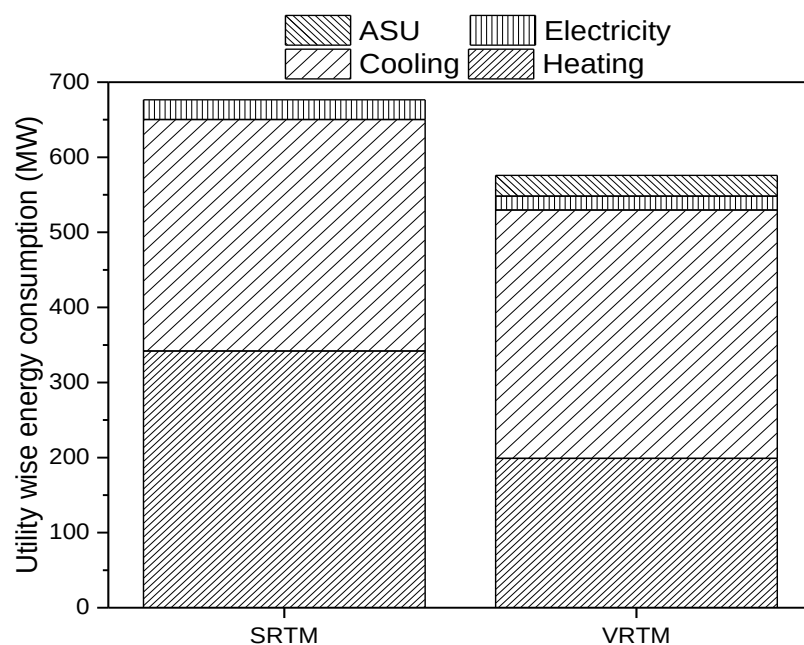


Figure 5-5. Total energy consumption in terms of the required utilities

Figure 5-6 shows the section-wise energy break down for the two methanol production technologies. In the case of SRTM, reformer and methanol synthesis sections are the most energy consuming sections contributing around 30.9 % and 33.3 % of the total energy consumption, respectively. In the case of VRTM, WGS and methanol synthesis sections each contribute approximately 33 % of the energy demand. However, it should be noted that the energy consumption of CO₂ capture unit is included in the WGS section. In general, methanol synthesis section appears to be the most energy consuming part of the plant because of its severe operating conditions of temperature and pressure, 230 °C and 100 bar respectively. In addition, the carbon single pass conversion of methanol synthesis reactor is 18.3% which requires larger downstream separation equipment and huge recycle stream to send the unreacted feed back to the reactor.

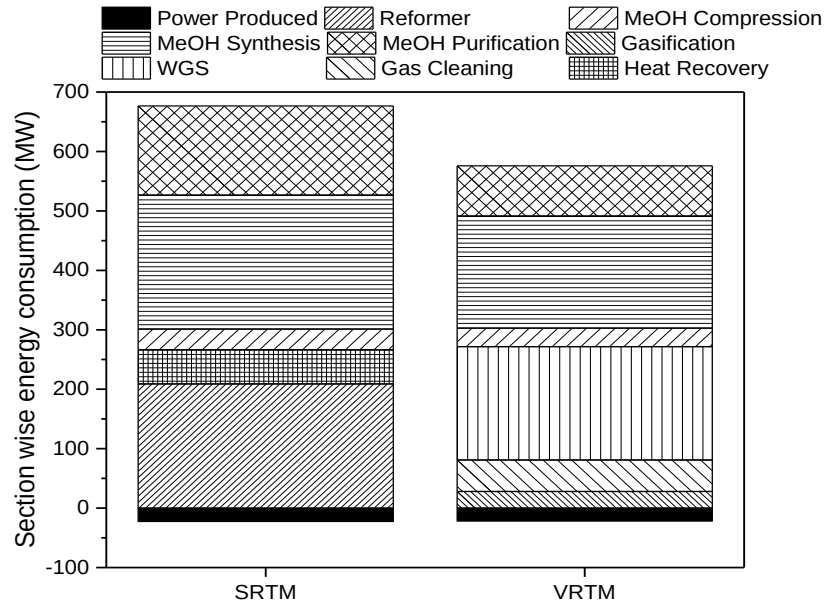


Figure 5-6. Section-wise total energy consumption for the SRTM and VRTM processes. The results also reveal that the heat energy extracted from the hot syngas can produce 22.6 MW and 21.8 MW of power from the SRTM and VRTM processes respectively. One of the commonly employed indicators to gauge the performance of any process based on the first law of thermodynamics is energy efficiency as defined by Eq. (10).

$$\text{Energy Efficiency} = \frac{\text{Energy content in MeOH} + \text{Heat and Power}}{\text{Feed heating value} + \text{Energy Consumed}} \times 100 [\%] \quad \text{Eq. (10)}$$

Energy efficiency has been calculated for the two processes using the lower heating value (LHV) for the vacuum residue, natural gas, and methanol as 39.9, 52.2 and 23 MJ/kg respectively. The results show that the efficiency for SRTM process is 1.6 % lower compared to the VRTM process for the same amount and quality of methanol product. The energy efficiency for the SRTM and VRTM has been calculated as 47.9 % and 49.5 % respectively.

5.6.2 Environmental Metrics

In order to assess the impact of fossil fuel-based methanol production on the environment, two key performance indicators namely carbon emissions and carbon efficiency are investigated for the SRTM and VRTM processes. Carbon emission is defined as the amount of carbon emitted to the atmosphere per unit mass of methanol product produced from the process as shown in Eq. (11).

$$\text{Carbon emission} = \frac{\text{Total carbon released } (\frac{\text{kg}}{\text{hr}})}{\text{Methanol production } (\frac{\text{kg}}{\text{hr}})} \quad \text{Eq. (11)}$$

Carbon emissions for the two processes have been calculated as shown in **Table 5-2**.

Table 5-2 Results summary in terms of energy, environment, and economic parameters.

	SRTM Process	Sweet Shift VRTM Process	Sour Shift VRTM Process
Total energy requirement (MW)	676.5	575.8	686.3
Energy efficiency (%)	47.9	49.5	45.7
Specific emission (kg CO ₂ /kg MeOH)	0.08	1.25	1.25
Carbon efficiency (%)	87	50	50
Direct CAPEX (M\$)	33.8	18.6	22.8
Indirect CAPEX (M\$)	21.5	12.5	14.9
OPEX (M\$/y)	257.6	223.2	242.3
Annualized CAPEX (M\$/y)	5.9	3.3	4.0
TAC (M\$/y)	263.5	226.5	246.3
MeOH cost (\$/t)	368	317	344

The results show that the SRTM process emits relatively small amount of emissions compared to the VRTM process. The carbon emissions from the VRTM process are approximately 15.5 times higher compared to the SRTM process on a mass basis. This is

because the carbon captured in the VRTM process is considered as emissions in this study. However, it should be noted that the carbon captured in the VRTM process is 99.2 mol. % CO₂ and may be considered as a by-product useful for another application such as enhanced oil recovery (EOR) or chemical manufacturing. In the case of high purity CO₂ captured stream considered as a by-product and not as emissions, the carbon emissions for the VRTM process can be reduced by 80 %.

Carbon efficiency is another important parameter that reflects the conversion of carbon present in the feed to the product. It is defined as the ratio of carbon content in the methanol product to the carbon present in all the components of the feed stream as shown in Eq. (12).

$$\eta_C = \frac{Carbon_{MeOH}}{Carbon_{feed}} [\%] \quad \text{Eq. (12)}$$

Table 5-2 shows the carbon efficiency of the two processes. The results show that the carbon efficiency of the SRTM process is 37 % higher compared to the VRTM process. This is attributed to the quality of the raw syngas produced at the outlet of the reformer with high H₂/CO ratio as already discussed. The raw syngas produced from the gasifier has lower H₂/CO ratio requiring WGS reactions which result in the conversion of CO to CO₂. Since the SN value at the inlet of the methanol synthesis section is set as 2, in the case of VRTM process the additional CO₂ produced from the WGS section is captured and hence significant amount of carbon present in the feed is lost in the captured CO₂ stream causing lower carbon efficiency.

5.6.3 Economic Analysis

The energy analysis performed in the previous section showed that VRTM process consumes around 100 MW less compared to the SRTM process for the methanol

production capacity of 90 t/hr. However, the findings reported in energy analysis alone are not sufficient to conclude the comparative performance of the two processes. Therefore, a detailed economic analysis has been performed to investigate the economic feasibility of the methanol production processes. The economic analysis includes the estimation of capital expenditure (CAPEX) and annual operating expenditure (OPEX). The CAPEX includes the direct and indirect cost. The costs associated with the direct CAPEX includes equipment cost, materials required for installation (piping, instrumentation and electrical, insulation, painting, fireproofing, foundation and structures) and the labor cost to install the equipment and materials. The indirect CAPEX contains freight, insurance, taxes and permits costs, construction overhead, contractor engineering expenses and contingencies. **Table 5-2** shows the CAPEX breakdown in terms of direct and indirect costs. The results show that the direct CAPEX contributes around 60%, while the indirect costs add approximately 40% of the total CAPEX. An insight into the CAPEX estimation reveals that equipment cost is 35 % and 38 % of the total CAPEX for the SRTM and VRTM processes, respectively.

The OPEX calculation include the feed cost, utilities, labor and supervisory costs, maintenance, plant overhead and general and administrative costs. The cost of vacuum residue and natural gas is taken as 47.6 \$/bbl and 10 \$/1000 ft³ respectively, while the price for the high purity oxygen is taken as 25 \$/t [48]. **Table 5-2** shows the OPEX for the two methanol production processes. The results show that the price of raw material is the largest factor contributing to the OPEX followed by the utilities cost. Raw materials and utility costs range between 72 – 77 % and 21 – 25 % of the total OPEX respectively for the two processes. The results show that the SRTM process requires an extra 19.5 M\$ per year than

the VRTM process for the utilities cost. This is due to the high electricity consumption in the SRTM process is attributed to the compressor power, where the syngas is compressed from 20 bar to 100 bar before feeding it to the methanol synthesis reactor. Syngas compressors in the SRTM process consumes 7.5 MW more power compared to the VRTM process. In addition, the heating load in the case of SRTM process is also high because of the endothermic reactions taking place in the reformer. The results show that the SRTM process requires an additional 34.4 M\$ per year of OPEX compared to the VRTM process.

CAPEX has been converted to the annualized capital charge (ACC) assuming a project life of 30 years and an interest rate of 10% using the relation shown in Eq. (13).

$$ACC = \frac{[i(1+i)^n]}{[(1+i)^n - 1]} \times CAPEX \quad (\text{Eq. 13})$$

Table 5-2 shows the TAC in terms of annualized CAPEX and OPEX for the two processes. The results show that the TAC for the VRTM is 14 % less compared to the SRTM process. Since the methanol production rate is fixed for both the design, the TAC translates into the product cost of 368 \$ and 316 \$ per ton of methanol for the SRTM and VRTM process, respectively.

5.6.4 Effect of soar shift in VRTM process

Due to the presence of sulfur components such as H₂S and COS in the raw syngas, two concepts exist related to the positioning of the WGS section, a sweet shift and sour shift. The VRTM process explained earlier is based on the sweet shift, which means that all the sulfur components are removed prior to feeding the syngas in the WGS reactor. The common catalysts employed in the case of sweet shift is Fe- and Cu-based for the high temperature and low temperature shifts, respectively [49]. The presence of sulfur in the

syngas can poison the sweet shift catalyst, requiring the removal of sulfur-based components before the WGS section. The sour shift, on the other hand, employs CoMo-based catalysts which are tolerant to the presence of sulfur in the syngas. There is an economic trade-off between the applications of sweet versus sour shift. In the case of sweet shift, the removal of acid gases upstream of the WGS system require smaller equipment (reduced CAPEX) due to the reduced stream flowrate. On the other hand, the sour shift requires less steam consumption (reduced OPEX) due to the presence of water vapors present in the raw syngas. Few studies in the past have compared the application of sweet and sour shift in the IGCC based power generation plant. Zhang and Ahn [49] reported that the sweet shift requires 4.6 times more steam compared to the sour shift. Erin and Yang [50] reported that the larger shift reactors can increase the CAPEX of WGS section by 30 %. In this study, comparative energy and economic analysis has been performed to investigate the effect of sour shift on the VRTM process. **Figure 5-7** shows the block flow diagram for the VRTM process based on the sour shift while maintaining all the stream specification requirements discussed previously at the inlet of methanol synthesis reactor.

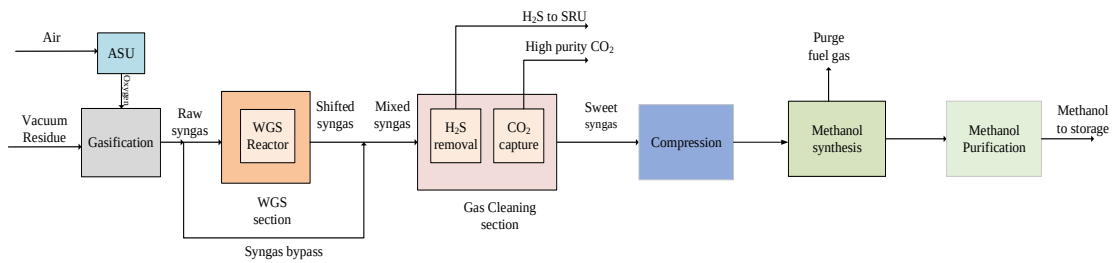


Figure 5-7. Block diagram of vacuum residue to methanol (VRTM) process – sour shift

The raw syngas leaving the gasification section is split into two streams, where one stream enters the WGS section while the other stream bypasses the WGS section. The split fraction is manipulated to have the same hydrogen content in the syngas at the inlet of methanol

synthesis section as in the case of sweet shift VRTM process. The shifted syngas from the WGS section is then mixed with the bypassed syngas which is sent to the gas cleaning section. Rectisol process is employed in the gas cleaning section where 99.9 % H_2S is removed from the syngas to meet the downstream methanol synthesis catalyst requirement. Syngas free of sulfur compounds is then sent to the CO_2 capture unit where physical solvent flowrate is manipulated to maintain the $\text{SN} = 2$ at the inlet of methanol synthesis section to have consistency with the sweet shift VRTM process for a fair evaluation.

The results show that due to the presence of water vapors in the raw syngas directly fed to the WGS reactor, the steam requirement in sour shift case is reduced by 20 % compared to the sweet shift. CO_2 capture rate in the gas cleaning section is found to be 86.3% in order to maintain the required SN at the methanol synthesis reactor. **Table 5-2** shows the comparison of sweet versus sour shift VRTM process. The results clearly show the merits of sweet shift VRTM process in comparison to the sour shift process.

5.6.5 Effect of feed cost

The economic analysis showed that the price of raw material is the largest cost contributor to the annual OPEX ranging between 72 – 77 %. However, the price trend for the crude oil and industrial natural gas shows a highly fluctuating pattern due to many other factors such as economic growth, supply, demand, geographics, and others. Therefore, a sensitivity analysis has been performed to study the effect of raw material price on the methanol price. **Figure 5-8** shows the variation in the calculated methanol price as the price of industrial natural gas and vacuum residue is varied $\pm 40\%$. The result shows that the feed cost has a huge impact on the methanol product cost. The unit cost of methanol product can vary $\pm$

30.3% and ± 28.2 % when the vacuum residue and natural gas price is varied ± 40 % respectively.

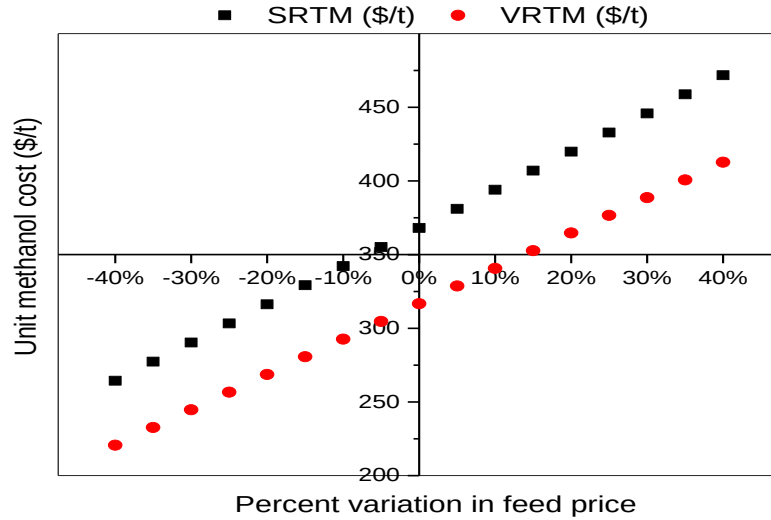


Figure 5-8. Effect of change in feed price on the production cost of methanol product

5.7 Conclusions

In view of limiting the increase of global carbon emissions and to enable fossil fuels utilization in a sustainable manner, this study investigated the vacuum residue to methanol (VRTM) production process in terms of energy, environmental and economic aspects. The proposed VRTM process is compared with the conventional methanol production process from the steam reforming of methane (SRTM). A comprehensive simulation model with a methanol production rate of 90 t/h with 99.9 wt.% purity was developed in Aspen Plus to analyze the process performance of the VRTM and SRTM processes. The major findings of this study are summarized here:

- The proposed VRTM is a potential process to produce clean fuel like methanol. This process can enable the utilization of bottom of the oil barrel to convert it to a petrochemical useful in many downstream applications.
- The developed VRTM process is competitive and feasible in comparison to the conventional SRTM process. The overall energy requirement of the VRTM is 14.9 % lower in comparison to the SRTM process. The heating load and electricity for the VRTM process is 41.8% and 29.1% less, respectively compared to the SRTM process. Specific methanol production energy requirement reported in the literature ranges between 33.4 – 37.2 GJ per ton of methanol product. The results for VRTM process show the specific energy consumption of 24.2 GJ per unit ton of methanol product which clearly demonstrates the process viability.
- The carbon emissions for the VRTM process are significant compared to the SRTM process. This is due to the consideration of captured CO₂ as emissions in this study. However, the specific carbon emissions from VRTM process can be reduced to 0.24 kg/kg CH₃OH if the captured high purity CO₂ is considered as byproduct useful for another application. The results also revealed the carbon efficiency for the SRTM and VRTM process to be 87% and 50% respectively.
- This study performed a detailed economic analysis, and the results show that the VRTM process requires a TAC of M\$ 227 in comparison to M\$ 263 for the SRTM process, offering an annual cost saving of M\$ 37. For a production rate of 90 t/h, this translates to the methanol product cost of \$ 317/tCH₃OH for VRTM process in contrast to \$

368/tCH₃OH for the SRTM process. However, the product cost is a strong function of raw materials cost which contributes around 70 – 75% to the TAC.

- Comparison has been made between the sweet and sour shift VRTM process to investigate the effect of WGS section location on the process performance and cost. The location of WGS section has no effect on the carbon emissions, however, the sweet shift VRTM process offers higher efficiency and lower product cost compared to the sour shift VRTM process.
- The profitability of the VRTM process can be further enhanced by integrating it with the renewable energy source. For example, the energy requirements in ASU and WGS sections of the VRTM process can be omitted with the integration of VRTM process with solar-powered water electrolysis process

CHAPTER 6

Eco-Technical study for Methanol Production through the gasification of vacuum residue process integrated with Methane Dry Reforming

6.1 Summary

The continuous rise in global carbon emissions, demands the utilization of fossil fuels in a cleaner and sustainable way. Owing to emission in various forms, our environment and the air we breathe in are contaminate, necessitating the need for alternative means. Gasification is a potential technology that can convert CO₂ to produce clean and environmentally friendly methanol fuel in an economical manner. Therefore, this study proposed and analyzed critically two different routes for the production of high purity methanol from vacuum residue while minimizing the carbon emissions. The first route (Case I) studied the gasification of heavy vacuum residue (VR) in sequence with dry methane reforming (DMR). Whereas, the second pathway investigated the gasification of VR in parallel integration with DMR (Case II). The two process were compared, and the methanol production in terms of CO₂ emissions, energy efficiency, energy consumption, and environmental and economic impacts are herein presented. Aspen Plus for a methanol production capacity of 38 t/h with 99.9 wt. % purity was employed for the two vacuum residue to methanol (VRTM) processes. The results showed that Case II offers a process energy efficiency of 49.5% which is higher than the Case I by almost 5%. The unit cost of methanol product for Case II is 342.2 \$/t of methanol which is almost 7% lower compared to Case I. In terms of environmental analysis, both cases have comparably low carbon emissions of around 0.95 kg of CO₂/kg of methanol produced with high purity that can be used for further downstream production of other products or application of industrial use.

6.2 Introduction

The continuous rise in global population and anthropogenic activities have resulted in massive acceleration in energy demand. According to BP energy outlook 2020, the global energy demands across the globe is projected to keep on growing for a period [51]. Consequently, prompting natural imbalance of ecosystem because of discharge of greenhouse gas into the atmosphere. CO₂, predominant among the greenhouse gases has been fast tracking at a global scale [52]. The root cause of CO₂ emissions is the combustion of fossil fuels and perhaps is released either directly or indirectly as non-sustainable sources of energy. By far, the rate of emission of CO₂ indirectly is greater than the direct sources. In either way, there is increase in greenhouse gases, which causes rise in earth temperature thus leading to climatic issues [53,54]. At present, the main fossil fuels accessible to overwhelm the high-energy gap includes natural gas, crude oil, and coal [53,55]. Natural gas has been reported to exhibit high-energy efficiency but with minimum greenhouse gas emission [56]. On the other hand, coal is abundantly available in nature and a 2013 survey conducted showed an estimated of 890 billion tonnes of coal reserves accessible around the globe [57]. Coal consumption, in various industrial applications such as power and hydrogen (H₂) production are anticipated to increase from 2012 to 2040 with an average increase of 0.6% per annum [58]. However the combustion of coal, contributes a considerable quantity of CO₂ to the atmosphere per unit of heat energy, further than combustion of other fossil fuels [55,59–61]. The IPCC (International Panel on Climate Change) and PCA (Paris Climate Agreement) have caution against detrimental effects associated with rise in temperature [20,51]. Therefore, to achieve minimal global temperature and control global warming [21] substantial renewable energy source is

essential. Even so the unsymmetrical supply of energy from these sources cannot compete with the requirement. Fossil fuels are speculated to be the main energy source [22]. Nonetheless there must be improvement in terms of technologies or process to make the use of fossil fuels safer and effective utilization of the energy resources while decreasing the emission of greenhouse gas.

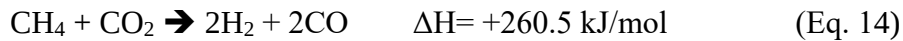
They are numerous inherent technologies developed and employed for the decrease of CO₂ emissions that are promising, economical and environment friendly. The conversion of CO₂ to valuable industrial chemical such as methanol has fascinated a fresh rebirth of attention [62]. Methanol exhibit wide range of applications such as excellent additive or substitute for gasoline in an inner combustion engine because of its high-octane rating and similarly it is utilized as a modifier in diesel engines as well as methanol fuel cells [63]. Methanol blended with gasoline can be used as fuel as it retains clean burning characteristics. In addition, methanol is not only an ideal energy carrier but also a chemical building block and intermediate for the synthesis of commodity and specialty products [64,65]. Moreover, it has various applications in petrochemical industry as paints, solvents and anti-freezing agent [24,25]. Consequently, heavy fuel is getting replaced with methanol [23]. Thus the demand and market value of methanol has greatly been improved due to its captivating uses [62]. Due to the applications of methanol in olefin industry, the methanol compound annual growth rate has been estimated to grow by 5.66% during the period of 2019-2027 [26].

Now with the passage of time many methods and techniques have been employed to produce methanol [27–30]. Methanol can be produced by various methods. One of such processes is gasification of waste materials like plastics, feed stocks, fossil fuel based waste

and heavy residues. Apart from being the major purpose to minimize the global carbon emissions, the decrease in crude oil prices has economically put pressure on refiners to convert the bottom products into valuable products. Gasification can produce high value clean fuels by using waste fossil-based feed stock in a sustainable manner. It can create stability between light and heavy oil by increasing the heavy oil demand [16]. The experimental investigation of Choi et al. [16] shows composition of raw syngas in gasification of vacuum residue. The experimental conditions reported are 1200°C – 1250 °C temperature at 1.0 kg/cm² pressure. The outcome of this investigation says 77-88% of syngas, 2300-2600 kcal/nm³ cold gas efficiency, 68-72% heating value and 95-99% carbon conversion [16]. The kinetic modeling of crude oil was performed by Motamedi et al. [37] for the production of hydrogen prior to methanol. The study of effect of gasifying agent on heavy oil gasification was carried out by Shahi et al. [38]. The results of their analysis say that employing air or oxygen as gasifying agent in a specific range can improve hydrogen yield [37]. The gasification of carbonaceous feed is carried out at temperature higher than 700°C. In the course of gasification, cracking (thermal decomposition) of heavy residue takes place. All of these are conventional means of methanol production by gasification.

In spite of the traditional processes this research employs progressing approach for production of methanol by using heavy oil residues. In which gasification of heavy residues from oil refinery integrated with Methane Dry Reforming is being studied. The conventional processes cannot be continued in future, due to their higher carbon dioxide emissions. This research is focusing on the integration of Methane Dry Reforming (DMR) accompanying gasification and water gas shift processes. The literature shows that the

syngas (Carbon monoxide and hydrogen) is produced by the reaction of methane and carbon dioxide in DMR as shown in equation (14) [66].



Methane is fed in Dry Methane Reformer (DMR) which on reaction with carbon dioxide produces syngas. Dry Methane reformer is different than conventional steam reformer as indicated by name it works on moisture free basis. The conversion of carbon monoxide into carbon dioxide and hydrogen takes place in Water Gas Shift (WGS) unit.

The carbon dioxide produced at this stage is absorbed by the CO₂ capturing unit, limiting possible greenhouse gas output, which is the primary objective of this study since oil refinery region gives about 4% of all greenhouse gases. The methanol is produced in the next unit process by the synthesis section where the conversion of hydrogen to methanol is taken place. The methanol synthesis reaction takes place at 250 °C and 45 bar.

The study proclaims that the use of thermal energy has been reduced by both capturing and utilization of carbon dioxide together so far making design environment friendly. In addition to this, the studies given by Ishaq and Dincer (2021) [67] show that multi stage water gas reactor integrating with DMR is predicted to have a higher conversion of carbon monoxide into carbon dioxide and hydrogen. The two CO₂ capturing units installed in this process make the entire operation emitting less CO₂ into the open environment. The next assessment is to analyze the parallel and sequence processes with dry reforming.

Though, Gasification is an industrial process with many operational plants yet insufficient information has been reported about the gasification of vacuum residue in literature.

Therefore, the aim of this study is to provide substantial information about the production of methanol by heavy residues

6.3. Process description

6.3.1 Vacuum Residue to Methanol (VRTM)

There are two proposed routes for the VRTM process to take place. The first process of gasification of heavy residue is in sequence with DMR as illustrated in **Figure 6-1**. In this series configuration, gasification of heavy residue is achieved first and followed by CO₂ capturing and H₂S removal in the gas cleaning unit afterwards. Subsequently, the stream goes in sequence to the DMR and WGS section. Overall in the sequence process route, two CO₂ capturing units are installed. The first which is bridged between gasifier and DMR and the second installed right after WGS unit as shown in **Figure 6-1**.

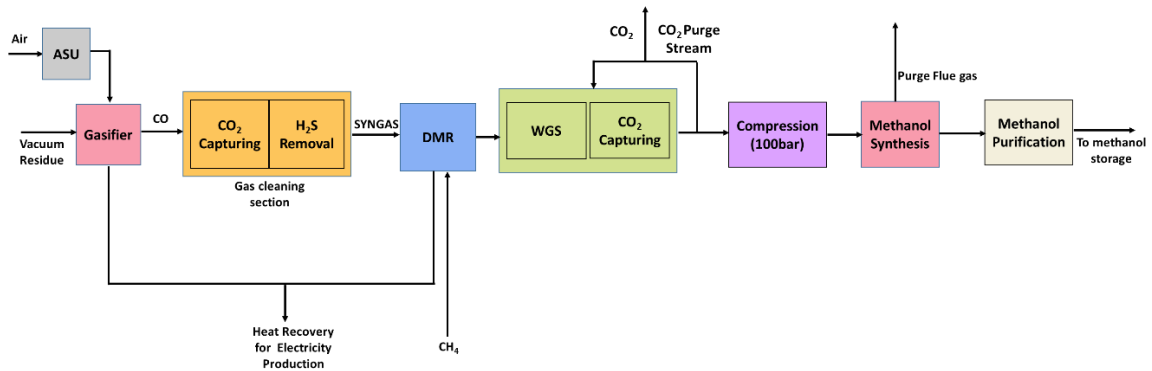


Figure 6-1. Process flow diagram for Methanol production with DMR in Sequence.

In the second VRTM process route **Figure 6-2** the combination is similar to sequence route, however, unlike in the sequence process, the DMR section in this process is in parallel arrangement with gasifier and WGS unit. This process is more efficient as compared to

sequence, because syngas production is enhanced by parallel arrangement resulting in more methanol production.

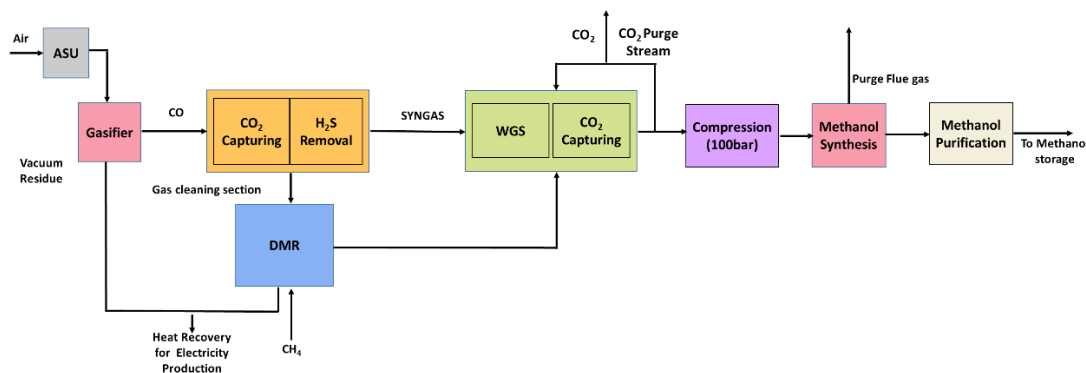
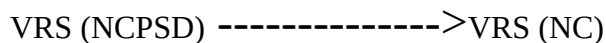


Figure 6-2. Process flow diagram for Methanol production with DMR in parallel.

Generally, irrespective of the route, in VRTM process, vacuum residue (a non-conventional solid available with particle size distribution / components attributes) is used as the source of feeds. Consequently this feed is transformed into its individual elemental constituents.



6.3.1.1 Gasifier Unit

products from gasifier largely comprises of H_2 , CO , CO_2 , H_2O , CH_4 , N_2 and impurities (H_2S , COS , NH_3 , HCN and ash). Among many other parameters, syngas ratio (H_2/CO) is a crucial design variable

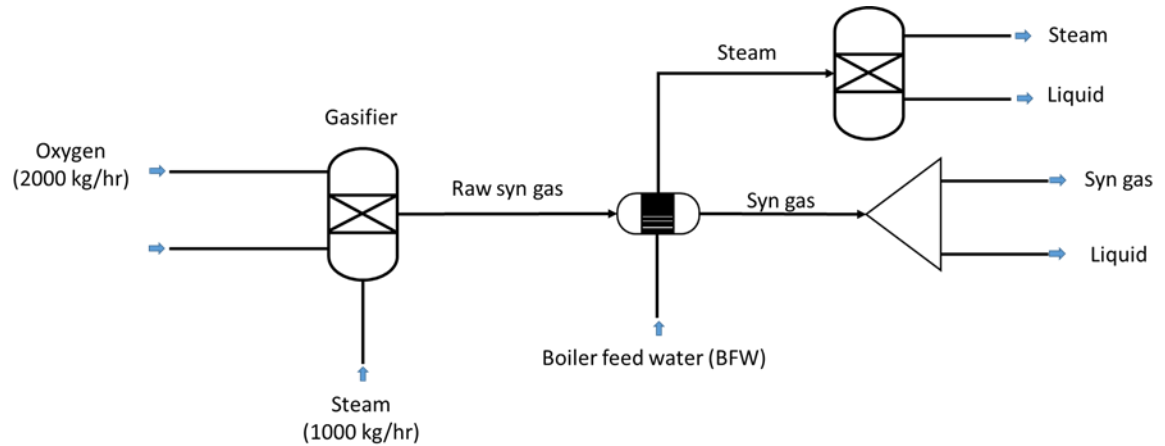


Figure 6-3. Gasification system.

6.3.1.2 Heat Recovery System

The raw syngas is at high temperature and pressure and the energy generated can be used to operate turbines and also to produce steam in HRSG section (Heat recovery steam generation section) **Figure 6-4**. In addition to producing electric power through two turbines, the heat recovery system also produced 10 bar steam through exchanging heat with raw water.

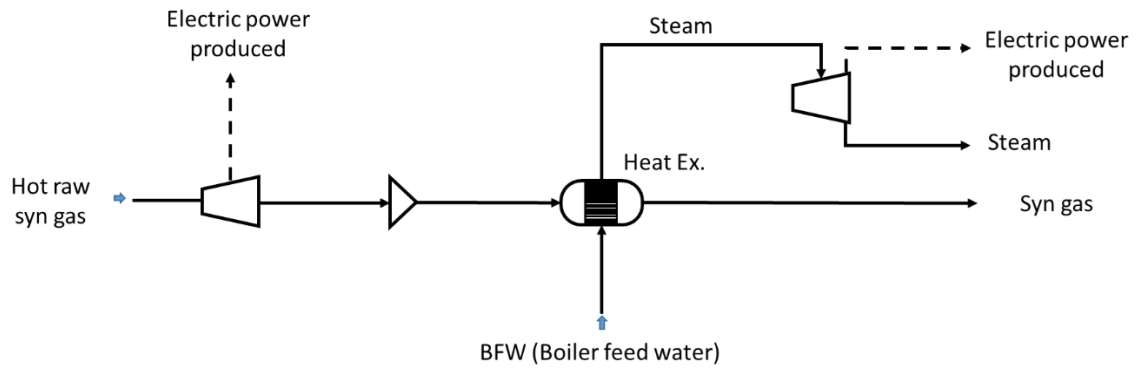


Figure 6-4. Heat recovery system.

6.3.1.3 Dry Methane Reforming

In the dry methane reformer **Figure 6-5**, the methane gas is introduced into the reformer from the bottom. The two gases, methane and carbon dioxide then react in the reformer to yield CO and H₂ gases as shown in the equation (15) [67]:

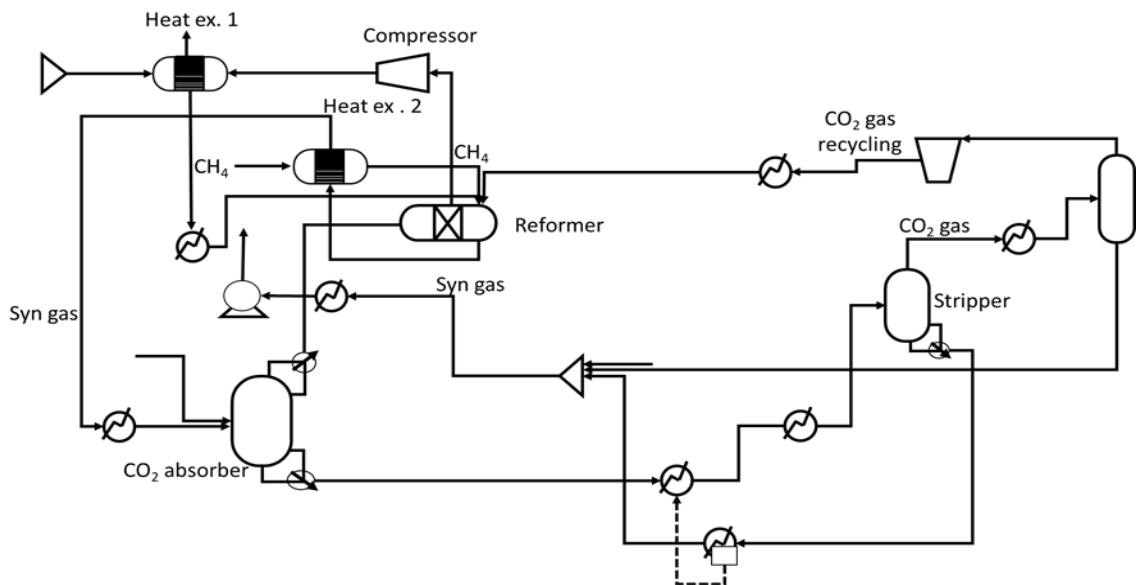
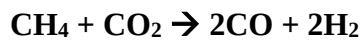


Figure 6-5. Dry methane reformer (DRM) system.



Eq. (15)

The reaction in the dry methane reformer is endothermic reaction. DRM is used when a mixture of carbon monoxide and hydrogen is essential. DMR contains CO₂ capture unit to optimize the process. As shown in **Figure 6-5**, DRM contains CO₂ capture unit to optimize the process. Essentially, the main reaction taking place in the reformer reactor is that, the reformer receives in fresh feed of methane (natural gas) and carbon dioxide. Furthermore, stripped CO₂ from the produced syn-gas is also recycled back to the reformer to minimize CO₂ emissions. The produced syngas is cooled down before entering the CO₂ removal section where 11 stage absorber column using fresh feed of amine solvent eliminate CO₂ and 10 stages regeneration column used to regenerate the solvent is modeled based on the amount of CO₂ and feed conditions to be recovered. Removed CO₂ is recycled to reformer to enhance reaction process as CO₂ is main reactant in the reformer. Finally, the pure syngas, which mainly contain CO and H₂, is passed through the water gas shift (WGS) unit.

6.3.1.4 Cleaning Unit (H₂S removal)

Immediately after cooling, the raw synthetic gas from the gasifier is sent to gas cleaning section which comprises of two sub-sections, solid impurities removal and gaseous impurities removal section as illustrated in **Figure 6-6**. In the first section, the cyclone separator installed (**Figure 6-6**), separates the solid impurities and the ash from the main gas stream. In the subsequent step, the gas stream is fed to a scrubber where mixture of ammonia and water is used to wash out any remaining solid impurities left out in cyclone separator.

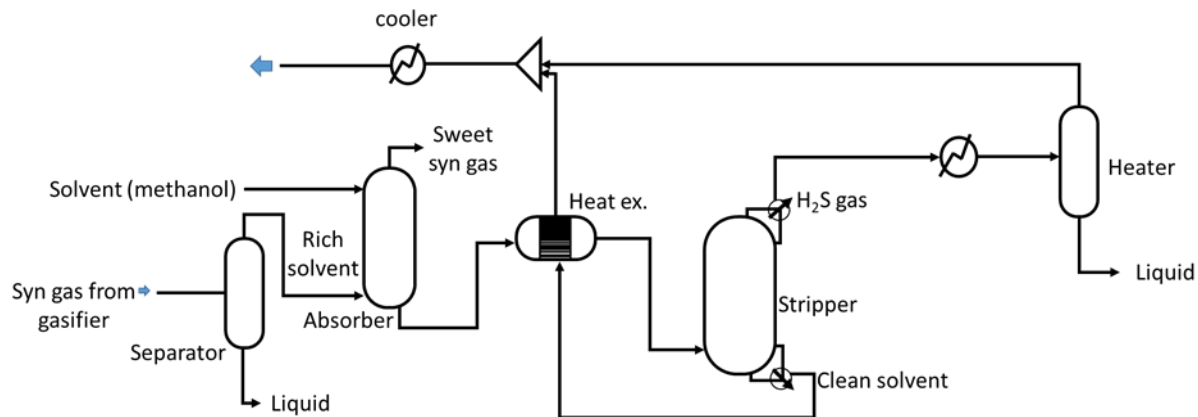
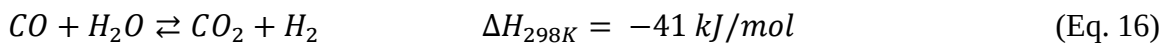


Figure 6-6. H₂S removal unit

Upon removal of solid impurities, gaseous impurities such as COS and H₂S are also separated and removed from the syngas. To achieve this, a suitable physical solvent is employed in the cleaning unit which is able to remove 99.9% Sulfur impurities from syngas. The permissible range for H₂S concentration is < 0.05-0.5ppm. Furthermore, the removal of sulfur at this stage is significant as it deactivates the catalyst used in methanol reactor due to catalyst poisoning. At this stage, the sweet syngas ratio is less than 1 which is not sufficient to produce methanol but can be supplemented by increasing H₂ production through shift reactors in WGS section.

6.3.1.5 Water Gas Shift Reaction

In the WGS section **Figure 6-7**, the H₂/CO is adjusted which is enhanced by the DMR unit prior to WGS. Consequently, Water Gas Shift reaction convert CO to H₂ as illustrated by the equation (16).



Besides, the Stoichiometric Number (SN) is an important parameter which represents the feed composition for maximum conversion at the inlet of methanol synthesis reactor. The

optimum value of SN should be 2 which indicates that there should be excess of H_2 in the syngas. Therefore, the mainstream after gas cleaning unit is divided into two sub-streams. A part of it goes to WGS section **Figure 6-7** where amount of H_2 is increased whereas the other part bypasses the WGS section. As depicted in **Figure 6-7**, the syngas in WGS section is passed through two stage shift reactors which converts 99.5% of CO into H_2 . The nature of this reaction is exothermic. Thus, in order to control the temperature; intercooling is done between the stages of reactor. The gas stream from WGS and bypassed stream are then mixed where the syngas ratio is around 2.27 and SN value is 2.

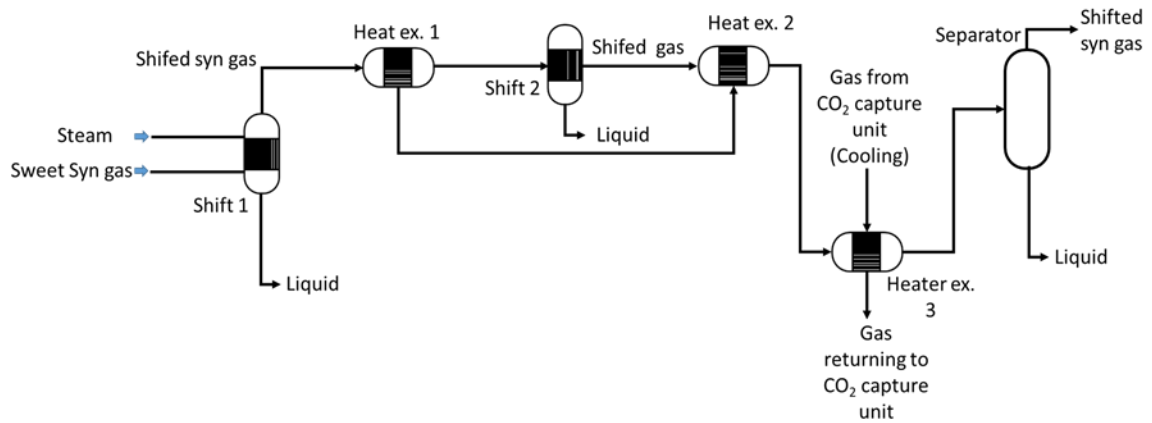


Figure 6-7. Water gas shift reaction system (WGS).

6.3.1.6 CO₂ Absorption

The WGS section is followed by CO₂ absorption section **Figure 6-8** an appropriate physical solvent is employed to absorb CO₂ from the syngas. About 50% of stripped gas from CO₂ stripper **Figure 6-8** is purged and the remaining fraction is recycled to DMR-reformer reactor to produce more syn-gas.

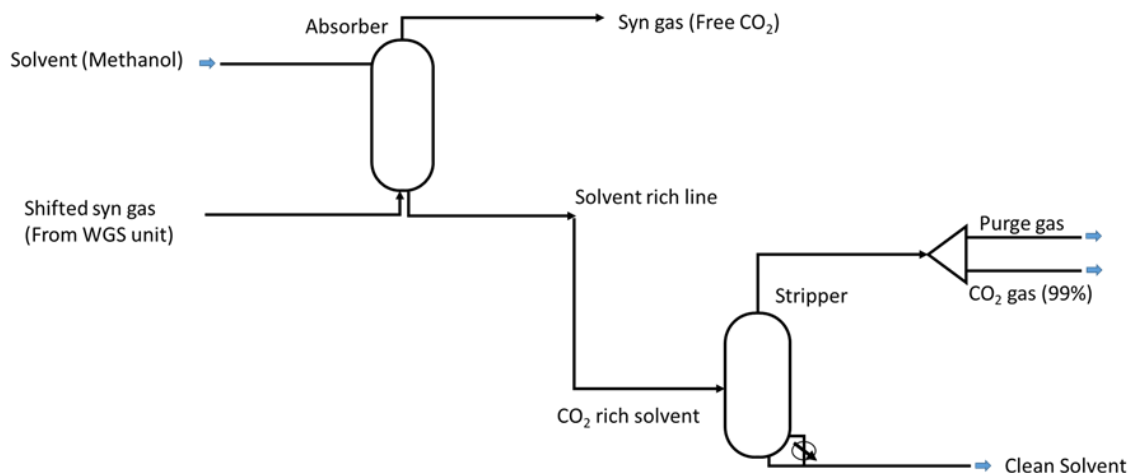


Figure 6-8. CO₂ adsorption system

6.3.1.7 Pre-Methanol Synthesis (Syn. Gas Compression)

The desirable reaction pressure in methanol synthesis reactor is 100 bar **Figure 6-9**. In order to achieve this pressure, syngas stream is pressurized to 100 bar by three stage compressors supported by inter-stage cooling.

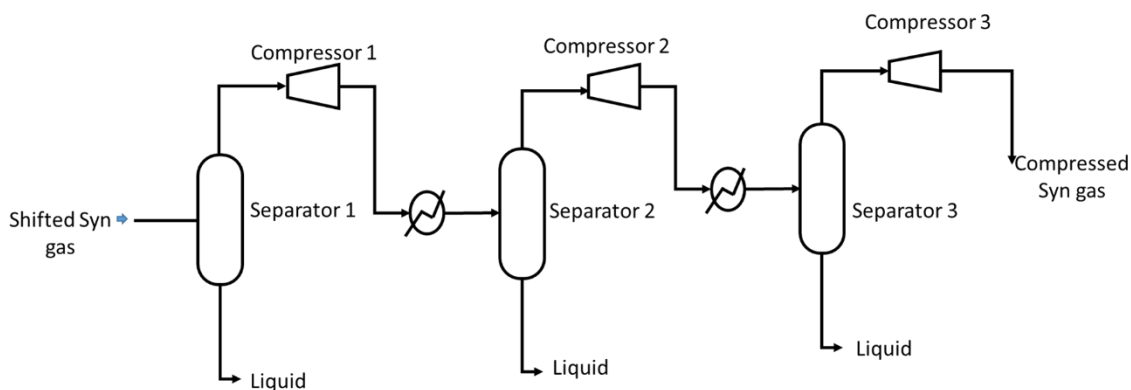


Figure 6-9. Methanol compression plant (methanol preparation)

6.3.1.8 Methanol synthesis

Compressed gas from compression plant is then fed to series of five plug flow reactors

Figure 6-10. The temperature is maintained at 230°C at inlet of first reactor. The effluent stream leaves at 280°C which is cooled down and unreacted gas stream recycled after

separation. The separation takes place in a flash drum where crude methanol is separated from unreacted syngas which is sent back to reactor with a small amount being purged to avoid the accumulation of inert.

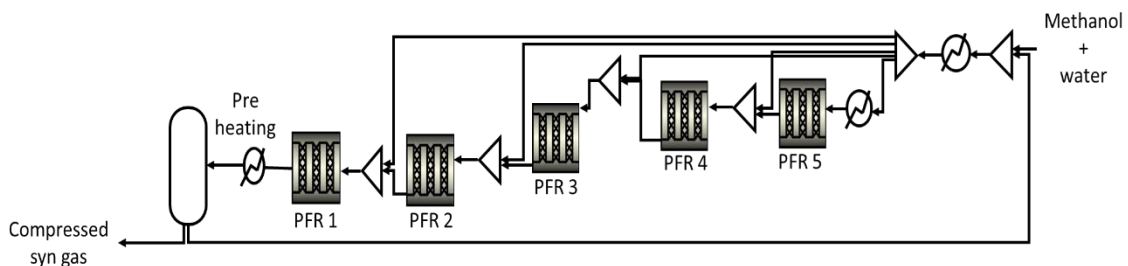


Figure 6-10. Five stage plug flow reactors for methanol synthesis

The final stage of the process is purification of methanol **Figure 6-11**. Which is done by distillation operation where 99.9% pure methanol is produced, leaving from the top of column

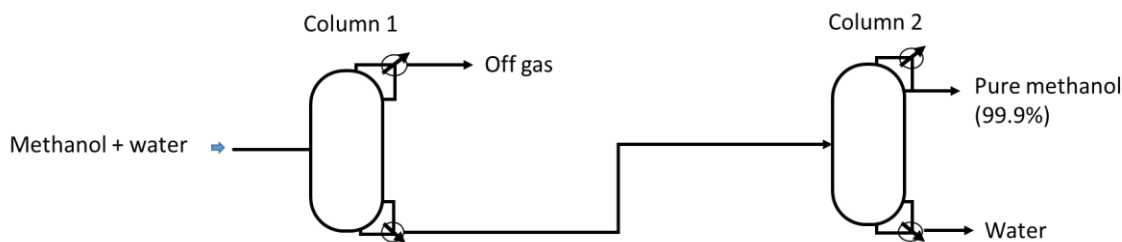
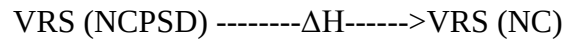


Figure 6-11. Methanol purification unit

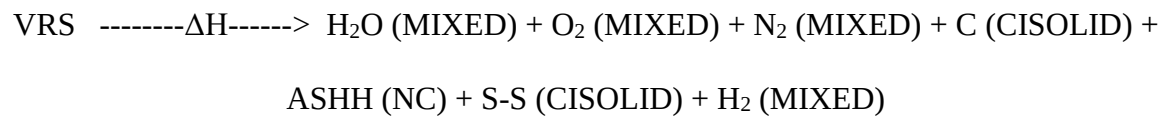
6.3.2 Simulation Methodology

In VRTM process, the vacuum residue feed is a mixture of many heavy hydrocarbons which cannot be defined as conventional component in Aspen Plus. Consequently, vacuum residue has been termed as unconventional components consisting built in HCOLAGEN and DCOALIGT model for thermodynamic calculations. The feed composition of vacuum

Residue is simulated in terms of ultimate, proximate and sulfur analysis. The mass yield of each specie is calculated by a calculation block with the help of FORTRAN statement. The Ultimate analysis on dry basis is defined as ULTANAL. The variable defined as the percent H₂O in the PROXANAL for vacuum residue is used to convert the ultimate analysis to a wet basis. The remaining eight variables (H₂O, Ash, C, H₂, N₂, Cl₂, S and O₂) are defined as the individual component of various species in the RSTOIC block. Following reaction takes place in first RSTOIC block



This is a conversion process and endothermic in nature, extent of conversion is about 95% . Extent of reaction is a function of residence time which is a function of PSD, gasifier volume and slurry flow. In 2nd RSTOIC block Feed is converted in its elemental constituents by following reaction.



This reaction is also defined as conversion process and endothermic in nature, extent of conversion is about 99%. Mainly two-unit processes namely, reforming integrated with gasification, are simulated, and assessed to produce methanol from vacuum residues. The purity of methanol is 99.9 wt. % and rate of production is approximately X 35.2 tons/h for this process. The simulation of the process is performed by a software, Aspen plus V11 which has large existing database for components. The components appearing in the process are present in the database. The input instructions and parameters for feed are added for the VRTM process. Peng-Robinson (PR) equation of state is used as

thermodynamic package to determine physical properties of components. The overall process simulation flow is presented in **Figures 6-1 and 6-2**.

To make the process simplified and understandable overall simulation is divided into below sub sections:

- Gasification and Solids Impurities Removal Section (GASFR)
- HRSG (Energy Recovery) (HRSG)
- Gas Cleaning (Gas Sweetening or H₂S Removal) (CLEANING)
- WGS Section (WGS)
- CO₂ Removal Section (CO₂)
- DMR Section (DMR)
- MeOH synthesis section have 3 Subsections as shown in **Figure 6-12**.
- Compression Section (COMP)
- MeOH Synthesis Section (SYN)
- MeOH Purification Section (PURE-SEC)

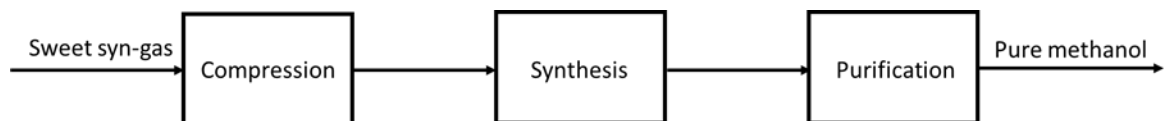


Figure 6-12. Process Flow Diagram MeOH Synthesis Section

The Natural gas and air are fed to DMR at higher temperature and pressure. As for, the production of syngas operating conditions of DMR are 950 °C and 4 bar. The reformer is RGibbs reactor and set to calculate phase and chemical equilibrium simultaneously. The requisite air molar flow rate is X about 1.12 times - of methane molar flow rate and can be calculated by Calculator block tool in the Aspen. The effluent stream coming out of the

reformer is at higher temperature and it is cooled down by heat exchanger (HeatX block) employed to pre heat the feed. The RadFrac column block is used as absorber (with no condenser and reboiler) to absorb CO₂. Stripper is also a RadFrac column block equipped with reboiler. This stripper is acting as regenerator for the absorbent used to absorb CO₂ from Syngas produced in DMR.

Similarly, in VR gasification section RGibbs reactor block is being used as gasifier. Calculator block can be used to fix steam oxygen and VR flow rate ratio in gasifier. Component Separator block (sep) is implemented as cyclone separator to separate solid impurities from Raw syn gas produced from VR gasification.

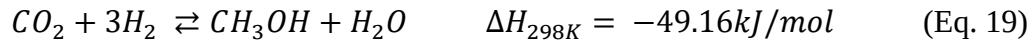
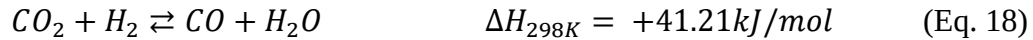
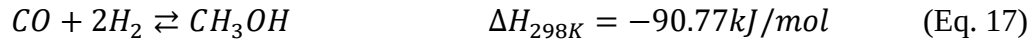
The produced syngas from gasifier and DMR is sent to heat recovery unit (HRSG). High pressure raw syngas is employed to drive turbine. Isentropic turbine model has been used in simulation with specified fixed discharge pressure which is equal to syngas pressure from DMR. Mixed syngas from both sources then passed through the heat exchangers to extract heat from syngas and to reduce temperature from 379 °C to 200 °C. Excess heat is used in boiler to produce HP steam from BFW. HeatX block with specified fixed outlet temperature and countercurrent flow option has been used as boiler.

Gas cleaning and sweetening section is comprised of absorber and absorbent regenerator RadFrac column block has been used for both unit operations. Configuration of columns is similar to as used in DMR section to absorb CO₂. Here the chilled methanol solvent removes the 99.9% of H₂S.

After Cleaning Syngas enters in WGS section where H_2/CO ratio is enhanced in series of 2 shift reactors. REquil reactor block is used as shift reactor with specified temperature approach of reaction.

Separated cooled gas stream from pre flash separator of WGS is fed to CO_2 absorption section. Process and equipment block of CO_2 separation section is same as that of CO_2 absorption of DMR.

Before route to MeOH synthesis this gas stream from CO_2 section is compressed to 100 bar by three stage compressor. At each stage, the calculated over all compression ratio is about X. Compressor block (Compr) of Aspen plus is used with model type isentropic. Afterwards, the compressed syngas is sent to methanol reactor at 230 °C. Following are the reactions which take place in synthesis section as shown by Eq. (17-19).



The reactions taking place in methanol synthesis reactor are exothermic in nature. Therefore, it is necessary to reduce the temperature continuously removing heat. Since high temperature effects the performance of catalyst. There are several types of methanol reactor which are being used in process industry [2.25]. In this study, the type of methanol synthesis reaction is adiabatic quench reactor containing five interlinked stages covered with Cu-based catalyst. A fraction of feed (syngas) enters from top and rest is added at each stage of reactor. The layout of used in Aspen Plus for five-stage methanol synthesis adiabatic quench reactor is shown in Figure 5. The kinetic model has been adapted in the

simulation which considers formation of methanol from both CO and CO₂ is proposed by Graaf et al. [44]. In the simulation for methanol synthesis reactor Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetic model is used to insert the kinetic equations represented by Eq. (20-22). All other numerical values and parameters used in simulation can be found in literature [27]. RPlug reactor block is used as plug flow reactor.

$$r_A = k_A \frac{K_{CO} \left[f_{CO} f_{H_2}^{\frac{3}{2}} - f_{CH_3OH} / (K_A \sqrt{f_{H_2}}) \right]}{(1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2}) [\sqrt{f_{H_2}} + \left(\frac{K_{H_2O}}{\sqrt{K_H}} \right) f_{H_2O}]} \quad (\text{Eq. 20})$$

$$r_B = k_B \frac{K_{CO_2} [f_{CO_2} f_{H_2} - f_{H_2O} f_{CO} / K_B]}{(1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2}) [\sqrt{f_{H_2}} + \left(\frac{K_{H_2O}}{\sqrt{K_H}} \right) f_{H_2O}]} \quad (\text{Eq. 21})$$

$$r_C = k_C \frac{K_{CO_2} \left[f_{CO_2} f_{H_2}^{\frac{3}{2}} - f_{H_2O} f_{CH_3OH} / (f_{H_2}^{\frac{3}{2}} K_C) \right]}{(1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2}) [\sqrt{f_{H_2}} + \left(\frac{K_{H_2O}}{\sqrt{K_H}} \right) f_{H_2O}]} \quad (\text{Eq. 22})$$

In order to cool down the effluent (syngas) from reactor, stream is mixed with crude methanol to separate the non-condensable vapor phase from the crude methanol. The vapor phase is compressed and recycled back to the reactor with small amount purged, to avoid the accumulation whereas crude methanol is sent to next section for purification. In Purification section, two distillation columns are employed which give 99.9 w. % methanol. The pure methanol from the top of second column is sent to methanol storage tank. 2 RadFrac column blocks are used as distillation columns in purification section with 6 and 25 number of stages respectively. Summary of whole process is given below.

The high purity oxygen with Vacuum residue is fed to the gasifier with the O₂/Feed mass ratio of unity. The outlet stream contains raw syngas with a H₂/CO ratio of unity, which

leaves the gasifier at 1300 °C. This raw syngas has thermal energy at high temperature which is recovered via a series of heat exchangers producing pressurized steam. The cooled syngas is sent to cleaning unit where the chilled methanol solvent removes the 99.9% of H₂S. Design spec has been employed in to achieve the required purity by manipulating the solvent flowrate. The sulfur free syngas is then split into two sections, one stream enters the WGS to increase hydrogen amount, while second stream is bypassed. At the inlet of methanol synthesis section, required SN is maintained by manipulating the split fraction by employing Design spec. The 99.5% CO conversion is achieved by manipulating air flow by installing calculator block in WGS section. The main syngas stream and bypassed stream is mixed and then sent to 3-stage compressor to increase its pressure to 100 bar. This compressed syngas is then added to methanol synthesis reactor to produce methanol. The key specifications used for the two processes in the Aspen Plus models are shown in **Table 6-1.**

Table 6-1. Simulation specifications for Aspen Plus models

Unit/ system	Aspen Model	Parameters
VRTM Process		
VR Gasification	Gasifier model: RGibbs	Gasifier type = Entrained flow Gasifier Temperature = 1301°C, Pressure = 64 bar VR/O ₂ (wt./wt.) = 1.0 VR/Steam (wt./wt.) = 2.05 VR conversion = 99 %
HRSG SECTION	Turbine: Compr Boiler:HeatX	Power Produced Turbine1 = -2672944 watt Heat Duty Obtained in Boiler = 6796398.69 watt

Gas Cleaning(H ₂ S Removal)	Absorber: RadFrac Stripper: RadFrac	In Absorber H ₂ S removal efficiency from Syngas(99.9%) and CO ₂ partially removed Number of stages 20 In Stripper H ₂ S and CO ₂ removal: efficiency (98.0%) Number of stages 10 Solvent regeneration: Thermal
Water Gas Shift	Shift model: REquil	High temperature shift = 398 °C Low temperature shift = 141 °C Steam:CO Ratio~ 1:1.4 CO conversion ~99.5 % [47]
CO ₂ Removal	Absorber: RadFrac Stripper: RadFrac	In Absorber CO ₂ removal efficiency from Syngas~ (63%) Number of stages 15 In Stripper CO ₂ removal: efficiency (98.0%) Number of stages 10 Solvent regeneration: Thermal
DMR	Reformer : RGibbs Absorber: RadFrac	Reformer temperature 950 °C Above 99.5% CH ₄ Conversion In Absorber CO ₂ removal efficiency from Syngas~ (99.5%)
Methanol Section		
Gas Compression	Compressor: Compr (Isentropic)	Compression stages: 3 Inter-stage cooling (T = 45 °C) Isothermal flash drum: 3 Compressor efficiency: 72% No. of reactor stages = 5
Methanol synthesis	Reactor model: RPlug (Fixed bed adiabatic quench reactor)	Temperature = 230°C Pressure = 100 bar Cu-based catalyst Catalyst density = 1940 kg/m ³ Bed voidage = 0.33 No. of columns = 2
Methanol distillation	Distillation Column : Radfrac	Number of Stages Column 1 with partial condenser =6 Number of stages in Column 2 with Full condenser= 25 MeOH product purity ≥ 99.9 wt. %

6.4. Results and Discussions

The merits and competency of the two designs have been evaluated in terms of energy analysis, environmental performance, and economics.

6.4.1 Energy Analysis

A detailed energy analysis has been performed to ascertain the performance of the two methanol production technologies. Vacuum residue gasification is an exothermic process where significant amount of high-quality energy is available. The high temperature syngas stream leaving the gasifier is utilized to produce steam, a part of which is consumed back in the process while the remaining steam may be utilized to produce power. On the other hand, reforming is an endothermic process operating at more than 850 °C requiring substantial energy input. **Figure 6-13** shows the energy consumption in terms of utilities for the two designs. The results show that the methanol production through Case I scenario requires the highest energy which is 270 MW with roughly 25% of the energy demand attributed to dry methane reforming. The energy consumption for case II is 259 MW which is less than case I by almost 11 MW for the same feed rate of crude oil vacuum residue of 20,000 Kg/hr.. In addition to this advantage of case II design, Case II is also higher in energy efficiency by more than 7% (38.5% for Case II and 31.4 % for Case I). Moreover, if we look at electrical power produced, Case II of parallel integration with DMR can produce around 100 KW higher in comparison to case I which can produce up to 2079 KW knowing that both cases have the same feed rate basis of VR. It is worth noting that the

increase in energy consumption for case I was due to more energy demand from the dry reforming subsystem. Energy demand of DMR for Case II is 60% of energy demand of Case I. This is due to cooling utilities in the dry reforming where more cooling power is required. Electricity consumption for Case I is mainly by the pumps and compressors contribute to less than 4 % of the total energy demand. Heating power demand accounts for around 48% of the total energy for case I. Cooling power demand is more than 43% of the total energy where around 60% is consumed in the methanol synthesis and purification subsystem as the reaction conditions require more cooling. For Case II proposed design, where Gasification is in Parallel with Dry reforming subsystem, it appeared that more than 47 % of the total power demand is consumed by the cooling utilities, around 45% is consumed by heating equipment and remaining around 4% is electrical power consumed by Pumps and compressors. If we compare the cooling requirement of both designs, we see that Case II is less than Case I by around 6 MW which is 5% of Case I in terms of cooling power required and that is another advantage favoring Case II design.

When comparing the dry reforming of both designs, it is notable that Case I design is higher in energy demand than Case II by around 65% of DMR Case II consuming around 28 MW more in Case I Process design.

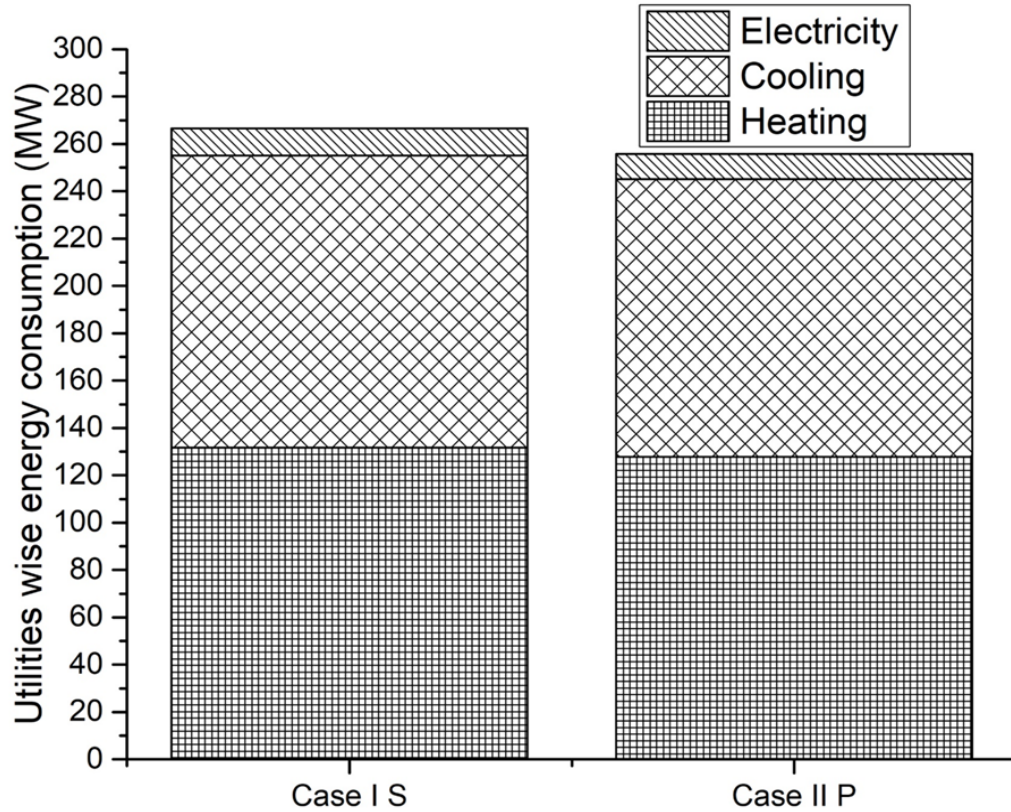


Figure 6-13. Total energy consumption in terms of the required utilities

Figure 6-14 shows the section-wise energy break down for the two methanol production technologies. The results also reveal that the heat energy extracted from the hot syngas can produce 2.7 MW for case I and 2.8 MW for Case II showing Case II is producing 100 kW more than Case I. One of the commonly employed indicators to gauge the performance of any process based on the first law of thermodynamics is energy efficiency as defined by equation (23).

$$\text{Energy Efficiency} = \frac{\text{Energy content in MeOH} + \text{Heat and Power}}{\text{Feed heating value} + \text{Energy Consumed}} \times 100 [\%] \quad \text{Eq. (23)}$$

Energy efficiency has been calculated for the two processes using the lower heating value (LHV) for the vacuum residue and natural gas 39.9 and 52.2 MJ/kg respectively.

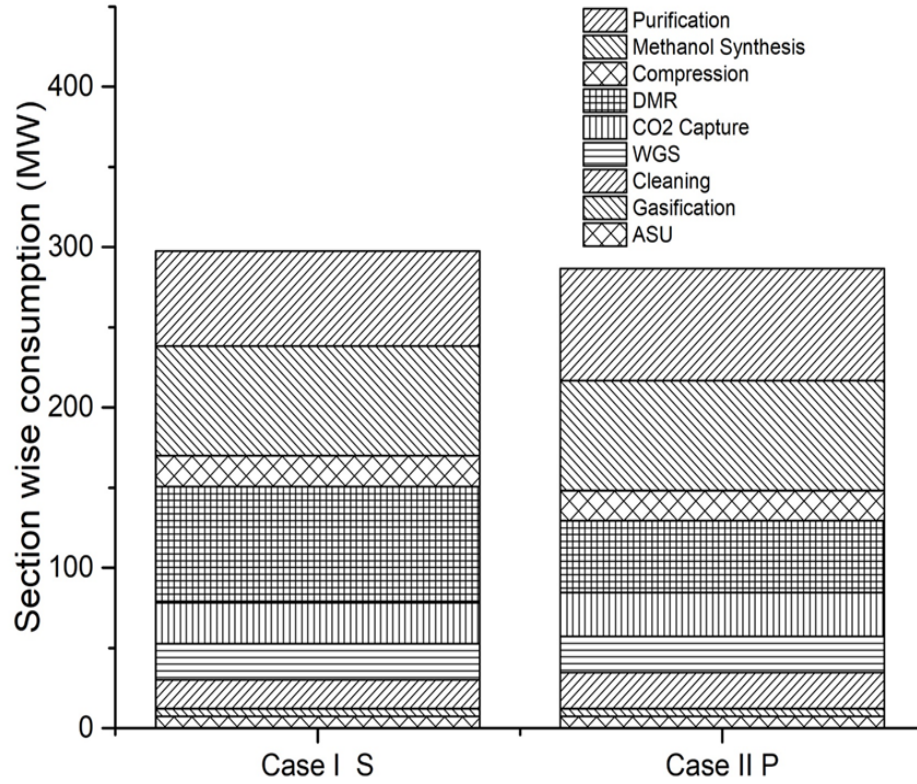


Figure 6-14. Section-wise total energy consumption for the Case I and Case II

6.4.2 Environmental Metrics

In order to assess the impact of the designs of fossil fuel-based methanol production on the environment, two key performance indicators namely carbon emissions and carbon efficiency are investigated for the Case I (Dry Reforming in sequence with Gasification Process) and Case II (DMR in parallel with Gasification Process). Carbon emission is defined as the amount of carbon emitted to the atmosphere per unit mass of methanol product produced from the process as shown in equation (24).

$$\text{Carbon emission} = \frac{\text{Total carbon released } (\frac{kg}{hr})}{\text{Methanol production } (\frac{kg}{hr})} \quad \text{Eq. (24)}$$

Carbon emissions for the two proposed design processes have been calculated as shown in **Table 6-2**. The results show that the emissions are a bit higher for Case I, with specific emissions of 0.97 and 0.95 Kg CO₂ per Kg of Methanol produced for Case I and II respectively. Most of the CO₂ emissions is coming from the WGS section with more than 16,000 Kg of CO₂ released per the given flow art of heavy residue processed. This is due to the stripper and condenser high demand of energy. The data shows that Case II more favored process due to its less CO₂ emissions.

Table 6-2 Results summary in terms of energy, environment and economic parameters

	Series	Parallel
Total energy requirement (MW)	270	259
Energy efficiency (%)	31.4	38.5
Specific emission (kg CO ₂ /kg MeOH)	0.97	0.95
Carbon efficiency (%)	50	50
Direct CAPEX (M\$)	31.5	26.8
Indirect CAPEX (M\$)	25.8	24.06
OPEX (M\$/y)	108.14	103.97
Annualized CAPEX (M\$/y)	2.03	1.8
TAC (M\$/y)	110.16	105.77
MeOH cost (\$/t)	363.1	342.2

6.4.3 Economic Analysis

The energy analysis performed in the previous section showed that Case II process consumes around 12 MW less compared to the Case I process for the same rate of methanol production (38.00 t/h). However, the findings reported in energy analysis alone are not sufficient to conclude the comparative performance of the two processes. Therefore, a detailed economic analysis has been performed to investigate the economic feasibility of the methanol production processes. The economic analysis includes the estimation of capital expenditure (CAPEX) and annual operating expenditure (OPEX). The CAPEX includes the direct and indirect cost. The costs associated with the direct CAPEX includes equipment cost, materials required for installation (piping, instrumentation and electrical, insulation, painting, fireproofing, foundation and structures) and the labor cost to install the equipment and materials. The indirect CAPEX contains freight, insurance, taxes and permits costs, construction overhead, contractor engineering expenses and contingencies. **Table 6-2** shows the CAPEX breakdown in terms of direct and indirect costs. The results show that the direct CAPEX contributes around 60%, while the indirect costs add approximately 40% of the total CAPEX. An insight into the CAPEX estimation reveals that equipment cost is 35 % and 38 % of the total CAPEX for the Case I and Case II processes, respectively.

The OPEX calculation include the feed cost, utilities, labor and supervisory costs, maintenance, plant overhead and general and administrative costs. The cost of vacuum residue and natural gas is taken as 47.6 \$/bbl and 10 \$/1000 ft³ respectively, while the price X shows the OPEX for the two hydrogen production processes. The results show that the price of raw material is the largest factor contributing to the OPEX followed by the utilities

cost. Raw materials and utility costs range between 45 – 47 % and 4 – 7 % of the total OPEX respectively for the two processes. The results show that Case I Process requires an extra 5 M\$ per year than the Case II process for the utilities cost. This is due to the high electricity consumption in the DMR process is attributed to the compressor power, where the syngas is compressed from X bar to X bar. Compressors in the Case I process consumes 31 MW more power compared to the Case II. In addition, the heating load in the case of Case I process is also a bit higher because of the endothermic reactions taking place in the reformer. The results show that the Case I process requires an additional 26 M\$ per year of OPEX compared to the VRTM process.

CAPEX has been converted to the annualized capital charge (ACC) assuming a project life of 30 years and an interest rate of 10% using the relation shown in equation (25).

$$ACC = \frac{[i (1+i)^n]}{[(1+i)^n - 1]} \times CAPEX \quad \text{Eq. (25)}$$

Table 6-2 shows the TAC in terms of annualized CAPEX and OPEX for the two processes. The results show that the TAC for the Parallel Case Design RTM is 5 % less compared to the Series Case Design Process Model. Since the methanol production rate is fixed for both the design, the TAC translates into the product cost of 368 \$ and 316 \$ per ton of methanol for the SRTM and VRTM process, respectively.

6.5 Conclusions

In view of limiting the increase of global carbon emissions and to enable fossil fuels utilization in a sustainable manner, this study investigated the vacuum residue to methanol (VRTM) production process integrated with Dry Methane Reforming Process into different ways or routes in terms of energy, environmental and economic aspects. The proposed

VRTM process integrated with Dry Methane Reforming is compared with the way the DMR process is integrated with Gasification process, where one time (Case I) both processes are working in sequence to produce syn-gas and another time (Case II) in parallel to produce the same product but the two main processes, gasification and DMR are arranged to work in parallel. A comprehensive simulation model with methanol production rate of 38 t/h and 99.9 wt. % purity was developed in Aspen Plus to analyze the process performance of the two cases. The major findings of this study are summarized here:

- The proposed VRTM is a potential process to produce clean fuel like methanol. This process can enable the utilization of bottom of the oil barrel to convert it to a petrochemical useful in many downstream applications.
- The developed Case II for VRTM with DMR in parallel is competitive and feasible in comparison to Case I, VRTM with DMR in series. The overall energy requirement of the Case II is 5% lower in comparison to Case I process. The heating load and electricity for the VRTM with DMR process in parallel arrangement is 6% and 10% less, respectively compared to Case I process. The results for Case II process show lower cost of methanol production per ton of methanol by \$ 21/ton accounting for millions of dollars over the year. Also know that the price of methanol in the market is around \$430 per ton give another advantage of the process overall which clearly demonstrates the process viability.
- The carbon emissions for Case II and Case I Are almost very close to each other which leave both equally favored in this sense.

- This study performed a detailed economic analysis, and the results show that the Case II process requires a TAC of \$ M110 in comparison to \$ M105 for Case I process, offering an annual cost saving of roughly \$ M 5. For a production rate of 38 t/h, this translates to the methanol product cost of \$ 342/t methanol for Case II process in contrast to \$ 363/ t methanol of Case I process. However, the product cost is a strong function of raw materials cost which contributes around 45% to the TAC.
- The profitability of the VRTM process can be further enhanced by integrating it with the renewable energy source. For example, the energy requirements in ASU and WGS sections of the VRTM process can be omitted with the integration of VRTM process with solar-powered water electrolysis process.

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CHAPTER 7

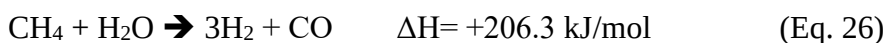
Eco-Technical study for Methanol Production through the Gasification of Vacuum Residue Integrated with steam Reforming

7.1 Summary

In this study, another different route to produce high purity methanol from vacuum residue are proposed while minimizing the carbon emissions. The route studied the gasification of heavy vacuum residue (VR) in parallel with steam methane reforming (STMR). After investigating the process, a brief analysis is presented that looked into methanol production in terms of CO₂ emissions, energy efficiency, energy consumption, and environmental impacts. In this study, the vacuum residue to methanol (VRTM) processes are simulated using Aspen Plus for a methanol production capacity of 100 t/h with 99.9 wt. % purity. The results showed that the proposed design offers a process energy efficiency of 24% . The unit cost of methanol product for is 342.2 \$/t of methanol. In terms of environmental analysis, both cases have comparably low carbon emissions of around 0.95 kg of CO₂/kg of methanol produced with high purity that can be used for further downstream production of other products or application of industrial use

7.2 Introduction

To build on the success achieved in gasification of vacuum residue integrated with DMR in sequence and parallel in the previous chapter (**Chapter 6**) to produce clean methanol. We extended the study by gasifying vacuum residue integrated with steam reforming (STMR) in parallel. In spite of the traditional processes this research employs progressing approach for production of methanol by using heavy oil residues. In which gasification of heavy residues from oil refinery integrated with steam reforming is being studied. The conventional processes cannot be continued in future, due to their higher carbon dioxide emissions. This research is focusing on the integration of steam reforming (STMR) accompanying gasification and water gas shift processes. The literature shows that the syngas (Carbon monoxide and hydrogen) is produced by the reaction of methane and carbon dioxide in STMR as shown in equation (26) [66].



Though, Gasification is an industrial process with many operational plants yet insufficient information has been reported about the gasification of vacuum residue in literature. Therefore, the aim of this study is to provide substantial information about the production of methanol by heavy residues integrated with steam reforming.

7.3. Process description

7.3.1 Vacuum Residue to Methanol (VRTM)

There is only one proposed route for the STMR process to take place. Similarly, the process description of STMR in parallel to produce methanol is analogous to the DRM to the parallel configuration studied in **Chapter 6**. The process of gasification of heavy residue

in parallel with steam as illustrated in **Figure 7-1**. In this parallel configuration, gasification of heavy residue is achieved first and followed by CO₂ capturing and H₂S removal in the gas cleaning unit afterward. And unlike in the DMR (**Figure 6-2.**), here the stream goes in parallel to the STMR and WGS section. Overall, in the parallel process route, two CO₂ capturing units are installed. The first which is bridged between gasifier and STMR and the second installed right after WGS unit as shown in **Figure 7-1**.

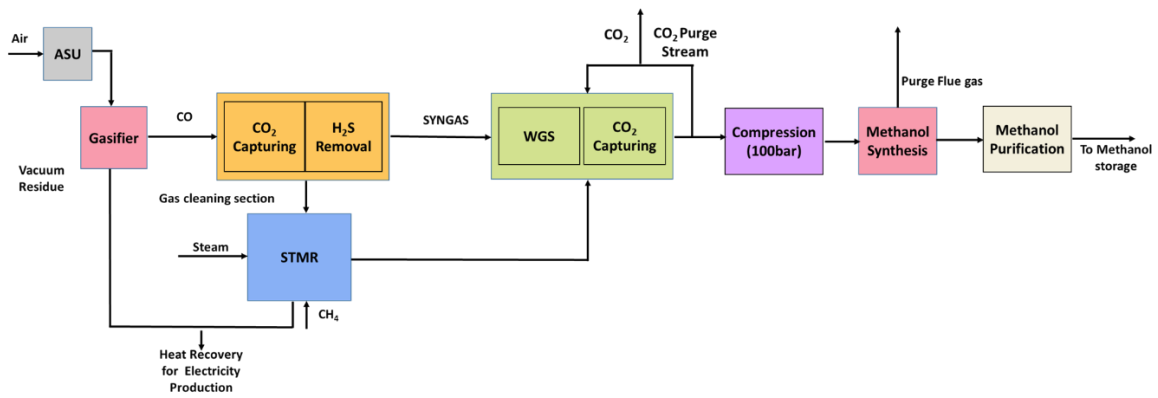


Figure 7-1. Process flow diagram for Methanol production with steam reforming in parallel

7.3.2 Simulation methodology

The two technologies namely steam reforming and gasification are simulated and evaluated to produce methanol from natural gas and vacuum residue feedstock, respectively. The methanol production rate and purity has been set as 90 tons/h and 99.9 wt. % respectively for both processes. The selection of components that correctly represent the actual compounds in the system is the foremost step before the simulation model development. The simulation has been performed using a commercial process simulator, Aspen Plus that contains a large database of the conventional components. All the components involved in

the SRTM process exist as conventional components. The feed specification and composition for the reforming SRTM process are similar to STMR in chapter 5. The thermodynamic package used to estimate the physical properties of components is Peng-Robinson (PR) equation of state.

Pre-heated natural gas stream and high pressure super-heated steam is fed to the reformer operating at 870 °C and 20 bar to produce the raw syngas. Calculator block tool in the Aspen Plus has been used to calculate the required steam molar flowrate which is three times that of the methane flowrate. The reformer effluent is initially cooled down by exchanging heat with the incoming feed stream. The raw syngas is then sent to the heat recovery section, where the syngas passes through a series of heat exchangers to generate steam and finally leaves at 50 °C.

The key specifications used for the SRTM process in the Aspen Plus models are shown in **Table 6-1**. However, to account for SRTM in Aspen Plus models, the DRM Process was replaced with Steam Reforming process, while the Aspen Model: RGibbs was maintained. Equally, the DMR parameters were replaced in which the temperature, pressure and feed ration (steam/NG) were set at 870 °C, 20 bar and 2.90 respectively

7.4. Results and Discussions

The merits and capability of the designs has been evaluated in terms to energy analysis, environmental performance, and economics.

7.4.1. Energy Analysis

A detailed energy analysis has been performed to ascertain the performance of the methanol production technologies. Vacuum residue gasification is an exothermic process

where significant amount of high-quality energy is available. The high temperature syngas stream leaving the gasifier is utilized to produce steam, a part of which is consumed back in the process while the remaining steam may be utilized to produce power. On the other hand, reforming is an endothermic process operating at more than 850 °C requiring substantial energy input. **Figure 7-2** shows the energy consumption in terms of utilities for the suggested design. The results show that the methanol production requires 628 MW with roughly 10% of the energy demand attributed to steam methane reforming. . Moreover, if we look at electrical power produced, the design created 43 MW. Most of energy demand in STMR is due to cooling utilities in the reforming where more cooling power is required. Electricity consumption is mainly by the pumps and compressors contribute to less than 5 % of the total energy demand. Heating power demand accounts for around 46% of the total energy. Cooling power demand is more than 44% of the total energy where around 60% is consumed in the methanol synthesis and purification subsystem as the reaction conditions require more cooling.

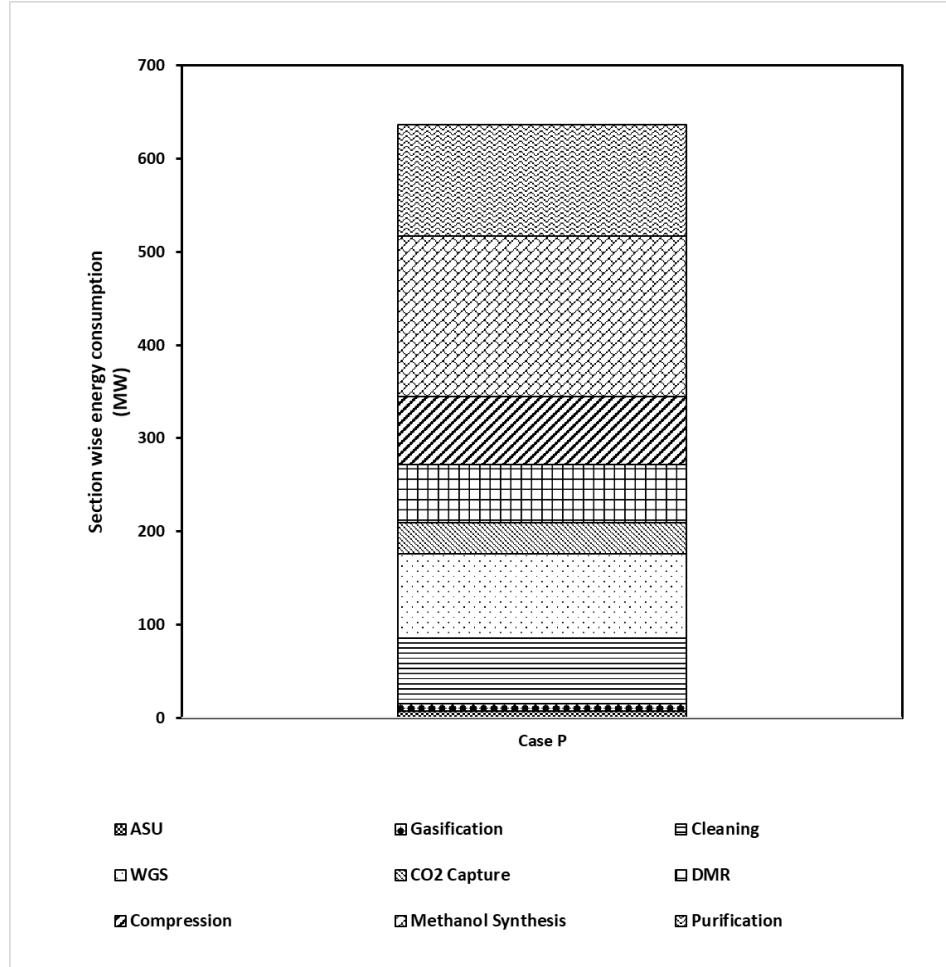


Figure 7-2 Section-wise total energy consumption

Figure 7-3 shows the section-wise energy break down for the methanol production technologies. The results also reveal that the heat energy extracted from the hot syngas can produce 43 MW. One of the commonly employed indicators to gauge the performance of any process based on the first law of thermodynamics is energy efficiency as defined by equation (28).

$$\text{Energy Efficiency} = \frac{\text{Energy content in MeOH} + \text{Heat and Power}}{\text{Feed heating value} + \text{Energy Consumed}} \times 100 [\%] \quad \text{Eq. (28)}$$

Energy efficiency has been calculated for the whole processes using the lower heating value (LHV) for the vacuum residue and natural gas 39.9 and 52.2 MJ/kg respectively.

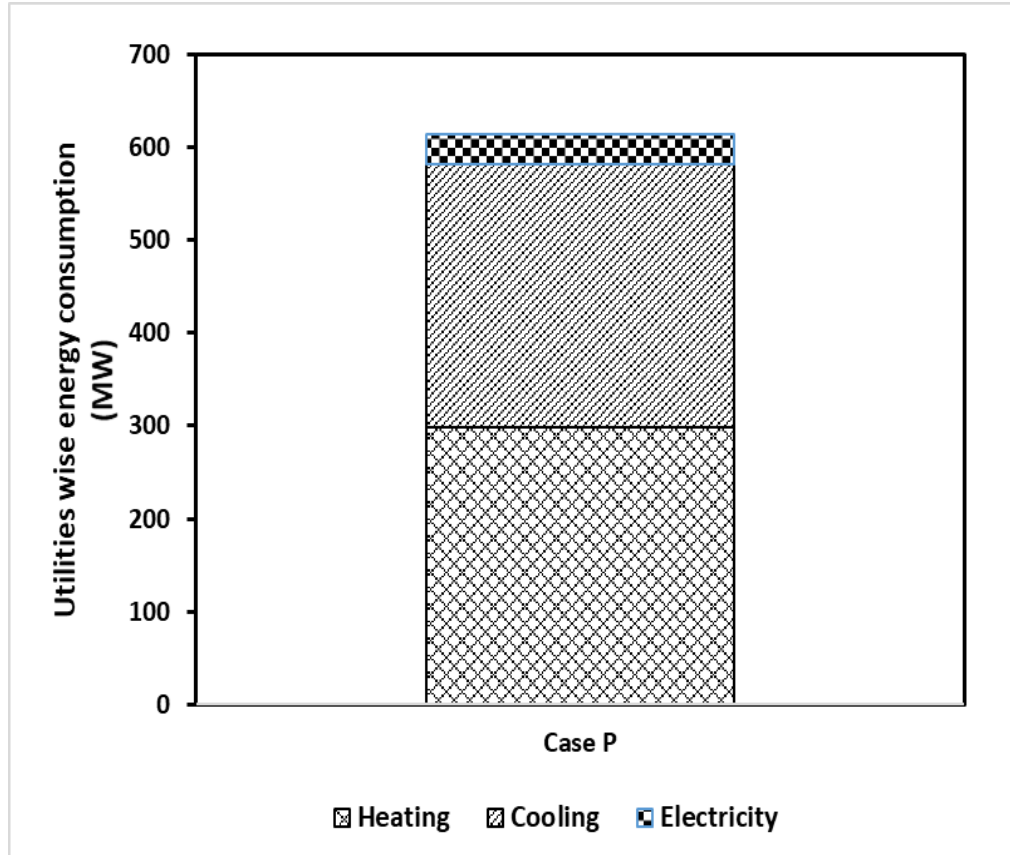


Figure 7-3. Total energy consumption in terms of the required utilities

7.4.2. Environmental Metrics

In order to assess the impact of fossil fuel based methanol production on the environment, two key performance indicators namely carbon emissions and carbon efficiency are investigated for the SRTM and VRTM processes. Carbon emission is defined as the amount of carbon emitted to the atmosphere per unit mass of methanol product produced from the process as shown in Eq. (27).

$$\text{Carbon emission} = \frac{\text{Total carbon released } (\frac{\text{kg}}{\text{hr}})}{\text{Methanol production } (\frac{\text{kg}}{\text{hr}})} \quad \text{Eq. (27)}$$

Carbon emissions for the two processes have been calculated as shown in **Table 2**. The results show that subsystem of SRTM process emits relatively small amount of emissions compared to the main VRTM process. The carbon emissions from the VRTM process are approximately 15.5 times higher compared to the SRTM process on a mass basis. This is because the carbon captured in the VRTM process is considered as emissions in this study. However, it should be noted that the carbon captured in the VRTM process is 99.2 mol. % CO₂ and may be considered as a by-product useful for another application such as enhanced oil recovery (EOR) or chemical manufacturing. In the case of high purity CO₂ captured stream considered as a by-product and not as emissions, the carbon emissions for the VRTM process can be reduced by 80 %.

Table 7-1 Results summary in terms of energy, environment and economic parameters

	Parallel
Total energy requirement (MW)	686.3
Energy efficiency (%)	24%
Specific emission (kg CO ₂ /kg MeOH)	0.95
Carbon efficiency (%)	50

7.5 Conclusions

In view of limiting the increase of global carbon emissions and to enable fossil fuels utilization in a sustainable manner, this study investigated the vacuum residue to methanol (VRTM) production process integrated in parallel with Steam Methane Reforming Process, environmental and economic aspects. The proposed VRTM process integrated with Steam has been analyzed in different ways. A comprehensive simulation model with methanol production rate of 38 t/h and 99.9 wt. % purity was developed in Aspen Plus to analyze the process performance of the two cases. The major findings of this study are summarized here:

- The proposed VRTM is a potential process to produce clean fuel like methanol. This process can enable the utilization of bottom of the oil barrel to convert it to a petrochemical useful in many downstream applications.
- The developed VRTM with STMR in parallel is competitive and feasible. The overall energy requirement is 628 MW. Most energy is consumed by cooling and heating utility are comparable with previous reported findings. Also know that the price of methanol in the market is around \$430 per ton give another advantage of the process overall which clearly demonstrates the process viability.
- The carbon emissions for the design can be reduced by considering the CO₂ emissions as a byproduct and captured for further processing to produce another product

CHAPTER 8

Conclusions and Recommendation

8.1 Conclusions

In conclusion, to mitigate the rise in global CO₂ emission we studied the gasification of vacuum residue to robust sustainable clean fuels. In this work we evaluated the production of methanol through the gasification of vacuum residue process and compared with conventional reforming process. Additionally, we integrated DMR in sequence and parallel and STMR to the system to evaluate the production of methanol. The systems were studied in terms of economic analysis which include CAPEX and OPEX, CO₂ emissions, carbon efficiency (%), total energy and cost/t MeOH.

The finding concludes that VRTM integrated with DMR and STMR process discloses less cost, total energy, CO₂ emissions in comparison with VRTM. Similarly, DRM integrated process reveals less CO₂ emissions compared to STMR integrated route

8.2 Recommendation and future work

In order to scale up the research findings accomplished in the gasification of vacuum residue to produce clean and environment friendly fuels in an economical manner. The followings are recommended opportunities for further research in this area.

1. Economic analysis: It is imperative to study the economic benefits of the proposed STMR process and compare with other process of methanol production. Because the energy and environmental analysis single-handedly are not sufficient to conclude performance of the processes. Therefore, a comprehensive economic analysis may be performed to investigate the economic practicability of the

methanol production processes. The economic analysis might include the estimation of the capital expenditure (CAPEX) and annual operating expenditure (OPEX). The CAPEX should encompass the direct and indirect cost. In order to be comprehensive, the costs associated with the direct CAPEX might include equipment cost, materials required for installation (piping, instrumentation and electrical, insulation, painting, fireproofing, foundation and structures) and the labor cost to install the equipment and materials. The indirect CAPEX might contain freight, insurance, taxes and permits costs, construction overhead, contractor engineering expenses and contingencies. On the other hand, the OPEX studies should include the feed cost, utilities, labor and supervisory costs, maintenance, plant overhead and general and administrative costs.

The CAPEX should be converted to the annualized capital charge (ACC) assuming a project life of 30 years and an interest rate of 10% using the relation shown in equation below.

$$ACC = \frac{[i(1+i)^n]}{[(1+i)^n - 1]} \times CAPEX \quad \text{Eq. (28)}$$

To harness the full benefits of these models optimization of the following are essential;

2. Energy integration and optimization: The energy of the system is not fully utilized yet, there is need to lower the energy of the system through exchange of heat from and within the whole system and the process. Furthermore, there is also an opportunity to produce electrical power from the system.
3. Carbon efficiency: Carbon efficiency is another essential parameter that reflects the conversion of carbon present in the feed to the product. It is defined as the ratio of

carbon content in the methanol product to the carbon present in all the components of the feed stream as shown in the equation below.

$$\eta_c = \frac{Carbon_{MeOH}}{Carbon_{feed}} [\%] \quad \text{Eq. (29)}$$

Consequently, the carbon efficiency of the proposed models can be further investigated to achieve higher percent of carbon conversion (>90%).

4. Carbon dioxide emission factor: Carbon emission defined as the amount of carbon emitted to the atmosphere per unit mass of methanol product produced from the process as shown in the equation below.

$$Carbon\ emission = \frac{Total\ carbon\ released\ (\frac{kg}{hr})}{Methanol\ production\ (\frac{kg}{hr})} \quad \text{Eq. (30)}$$

The impact of fossil fuel-based methanol production on the environment for these process need to be further investigated.

5. Data validation: The simulation model reliability is an important factor, therefore, in order to ascertain the robustness of the developed models, validation of the models should be investigated with real plant in terms of feed and syn-gas and the data compare.

Also, this studies should be extended to other products such as ethanol and dimethyl ether (DME) production through the gasification of vacuum residue process integrated with methane dry reforming in both parallel and sequence or integrated with steam reforming

LIST OF PUBLICATIONS

❖ Published/Accepted

- **F.N. Al-Rowaili**, S.S. Khalafalla, A. Jamal, D.S. Al-Yami, U. Zahid, E.M. Al-Mutairi, F.N.; Al-Rowaili, S.S.; Khalafalla, A.; Jamal, D.S.; Al-Yami, U.; Zahid, E.M. Al-Mutairi, A. Meneghetti, P. Simeoni, Techno-Economic Evaluation of Hydrogen Production via Gasification of Vacuum Residue Integrated with Dry Methane Reforming, (2021). <https://doi.org/10.3390/su132413588>. **IF: 3.251**
- **F.N. Al-Rowaili**, S.S. Khalafalla, D.S. Al-Yami, A. Jamal, U. Ahmed, U. Zahid, E.M. Al-Mutairi, Techno-economic evaluation of methanol production via gasification of vacuum residue and conventional reforming routes, *Chem. Eng. Res. Des.* 177 (2022) 365–375. <https://doi.org/https://doi.org/10.1016/j.cherd.2021.11.004>. **IF: 3.739**

❖ Submitted manuscript.

- **Fayez Nasir Al-Rowaili**, Siddig S. Khalafalla, Aqil Jamal, Umer Zahid, and Eid M. Al-Mutairi, Eco-Technical study for Methanol Production through the gasification of vacuum residue process integrated with Methane Dry Reforming, *Journal of Fuel Processing Technology*

❖ Manuscript under preparation

- **Fayez Nasir Al-Rowaili**, Umer Zahid, and Eid M. Al-Mutairi, Eco-Technical study for Methanol Production through the Gasification of Vacuum Residue Integrated with steam Reforming

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Work Experience

I am working at Saudi Aramco as research scientist in carbon management at Research and Development center. My research which is in line with my department strategy is mostly related to carbon dioxide reduction through conversion to valuable fuel using different techniques like electrochemical conversion, chemical conversion, etc. In addition, I am working on the hydrogen production and CO₂ sequestration and utilization plus other related topics to carbon management |