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**ECONOMIC AND SUSTAINABILITY ASPECTS OF CHEMICAL PROCESS
INDUSTRIES BY THERMODYNAMICS ANALYSIS**

by

Mahdi H. Alhajji

A THESIS

Presented to the Faculty of

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Major: Chemical Engineering

Under the Supervision of Professor Yaşar Demirel

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ECONOMIC AND SUSTAINABILITY ASPECTS OF CHEMICAL PROCESS INDUSTRIES BY THERMODYNAMICS ANALYSIS

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Economics and sustainability improvements of some chemical processes are assessed after the retrofits suggested by thermodynamic analysis and energy analyzer. The main objective is to explore the scope of reducing the energy consumption and CO₂ emissions for a more sustainable operation in chemical process industries. Thermodynamic analysis is carried out by applying the thermal analysis capability of ‘Column Targeting Tool’ to address the ‘energy intensity,’ and/or the ‘Energy Analyzer’ to design and improve the performance of the heat exchanger network system for process heat integration. CTT is based on the ‘Practical Near-Minimum Thermodynamic Condition’ representing a close to practical reversible column operation. The environmental pollution impact metrics are estimated from the ‘Carbon Tracking’ options with a selected CO₂ emission data source of US-EPA-Rule-E9-5711 using the specified primary fuel. The results indicate that column targeting tool, energy analyzer, and carbon tracking can estimate some of the sustainability metrics of an existing design or a new design and determine the scope of improvements for reducing the costs of energy required and emissions of carbon dioxide in chemical processes industries.

DEDICATION

TO THE SAVIOR OF THE WORLD.

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CHAPTER 1. INTRODUCTION

Chemical processes industries produce a very broad range of commodity products such as, petrochemicals, hydrocarbon fuels, artificial fibers and films, paper products, concrete [1]. The most known examples of the chemical process industries are petrochemical plants where chemical intermediates such as ethylene, benzene, and methane are produced from petroleum or fossil fuels. On the other hand, refineries are the field where fuel products such as naphtha, kerosene, diesel, and fuel oil are produced from crude oil.

Chemical processes contain processing units such as distillation columns and heat exchangers that are energy intensive and hence greenhouse gas emitters. Since the energy is considered to be the main driver of the technological development, it strongly affects the economy, environment, and society and hence energy intensive processes need to be assessed in their economic feasibility as well as in their sustainability aspects.

A typical distillation column resembles a heat engine delivering separation work by using heat at a high temperature in the reboiler and discharging most of it to the environment at a lower temperature in the condenser [2,3,6,7]. One of the thermodynamic methodologies to assess the distillation column operation is the Column Targeting Tool (CTT), which is based on the Practical Near-Minimum Thermodynamic Condition (PNMTC) approximation representing a practical and close to reversible operation [8-13]. CTT exploits the capabilities for thermal and hydraulic analyses of distillation columns [5,14-17] to identify the targets for possible column retrofits for: 1) feed stage location, 2) reflux ratio, 3) feed conditioning, and 4) side condensing and/or reboiling to reduce the cost of utilities and improve the overall energy efficiency. These possible retrofits are performed using the column grand composite curves. The ‘Carbon Tracking’ options of

the Aspen Plus can help quantify the reduction in CO₂ emission in a simulation environment [8].

The other thermodynamic analysis tool is the pinch analysis based on a minimum temperature approach. Based on the pinch analysis a heat exchanger network system requiring minimum hot and cold utilities can be designed. The Energy Analyzer of the Aspen Plus package can help reduce the waste energy by a systematic process energy integration.

Sustainability has environmental, economic, and social dimensions and requires the responsible use of energy resources and reduction in CO₂ emission. The three intersecting dimensions illustrate the 3D-sustainability metrics that include nonrenewable material and energy intensities, toxic, and pollutant emissions per unit product [18-22]. If nonrenewable, energy usage affects environment adversely through the emission of pollutants such as CO₂. Therefore, a comparative assessment with the sustainability metrics may prove useful in identifying the scope for retrofits for possible reductions of the waste energy and emission of CO₂. The energy metrics are estimated from the CTT, while the carbon emission from the data source of US-EPA-Rule-E9-5711 using the fuel source of natural gas.

The main objective is to explore the scope of reducing the energy consumption and CO₂ emissions for a more sustainable operation in chemical process industries by applying the thermodynamic analysis. Thermodynamic analysis is carried out by applying the thermal analysis capability of 'Column Targeting Tool' to address the 'energy intensity,' and/or the 'Energy Analyzer' to design and improve the performance of the heat exchanger network system for process heat integration.

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CHAPTER 2. COLUMN TARGETING TOOL

Abstract

The Column Targeting Tool (CTT) is a retrofit tool for lowering cost of operation through modified operating conditions, and providing insight into understanding tray/packing capacity limitations. The CTT is based on the Practical Near-Minimum Thermodynamic Condition (PNMTC) representing a close to practical reversible column operation. The CTT has the capabilities of thermal and hydraulic analyses that can help identify the targets for appropriate column modifications in order to: (i) reduce energy costs, (ii) improve energy efficiency, (iii) reduce capital cost by improving thermodynamic driving forces, and (iv) facilitate column debottlenecking. These capabilities within the CTT are summarized in this Chapter.

2.1. Thermal Analysis

Thermal analysis capability distributes reboiling and condensing loads over the temperature range of operation to help identify design targets for improvements in energy consumption and efficiency [1,11-14]. In order to achieve this, the thermal analysis produces ‘Column Grand Composite Curves’ (CGCC) and ‘Exergy Loss Profiles.’ The user makes changes to column configurations and specifications until CGCCs and exergy profiles display actual and ideal operations that are closer to each other [2,4,15]. The CGCCs are displayed as the stage-enthalpy (Stage-H) or temperature-enthalpy (T-H) plots representing the theoretical minimum heating and cooling requirements in the temperature range of separation. This approximation takes into account the inefficiencies introduced

through column design and operation, such as mixing, pressure drops, multiple side-products, and side strippers. Using CGCC is significant because it is: (i) a graphical tool to assess the current energy use and flow conditions of distillation operations, (ii) based on the complex and rigorous stage-by-stage calculations, and (iii) capable of leading to the qualitative and quantitative assessment [2,4-7]. The CGCCs can help in identifying the targets for potential column modifications for:

- (1) Feed stage location (appropriate placement),
- (2) Reflux ratio modification (reflux ratio versus number of stages),
- (3) Feed conditioning (heating or cooling),
- (4) Side condensing or reboiling (adding side heater and/or cooler).

For estimation the enthalpy deficits, the equations for equilibrium and operating lines are solved simultaneously at each stage for specified light key and heavy key components. Using the equilibrium compositions of light L and heavy H key components, the enthalpies for the minimum vapor and liquid flows are obtained and used in the enthalpy balances at each stage to determine the net enthalpy deficits [3,5,6,9,10]

$$H_{\text{def}} = H_{\text{Lmin}} - H_{\text{Vmin}} + H_D \quad (\text{before the feed stage}) \quad (2.1)$$

$$H_{\text{def}} = H_{\text{Lmin}} - H_{\text{Vmin}} + H_D - H_{\text{feed}} \quad (\text{after the feed stage}) \quad (2.2)$$

After adding the individual stage enthalpy deficits to the condenser duty, the enthalpy values are cascaded, and plotted in the CGCC. This is called the top-down calculation procedure [6]. At the feed stage, mass and energy balances differ from an internal stage and the enthalpy deficit becomes

$$H_{\text{def},F} = Q_C + D[H_D + H_L(x_D - y_F^*) / (y_F^* - x_F^*) - H_V(x_D - x_F^*) / (y_F^* - x_F^*)] \quad (2.3)$$

The values of y_F^* and x_F^* may be obtained from an adiabatic flash for a single-phase feed, or from the constant relative volatility estimated with the converged compositions at the feed stage and feed quality. This procedure can be reformulated for multiple feeds and side products as well as different choices of the key components. In a CGCC, a pinch point near the feed stage occurs for nearly binary ideal mixtures. However, for nonideal multicomponent systems multiple pinches may exist in rectifying and stripping sections.

2.1.1. Feed location

In the analysis, the condenser and reboiler are defined to be the first and last stages respectively.

- If a feed is introduced too high up in the column, a sharp enthalpy change occurs on the condenser side on the stage-H CGCC plot; the feed stage should be moved down toward the reboiler.
- If a feed is introduced too low in the column, a sharp enthalpy change occurs on the reboiler side on the stage-H CGCC; the feed stage should be moved up toward the condenser [6 11].

When the feed locations are appropriate, these distortions are less sharp (Figure 2.1) and this may lead to reduced reboiler and condenser duties as well as stage exergy losses.

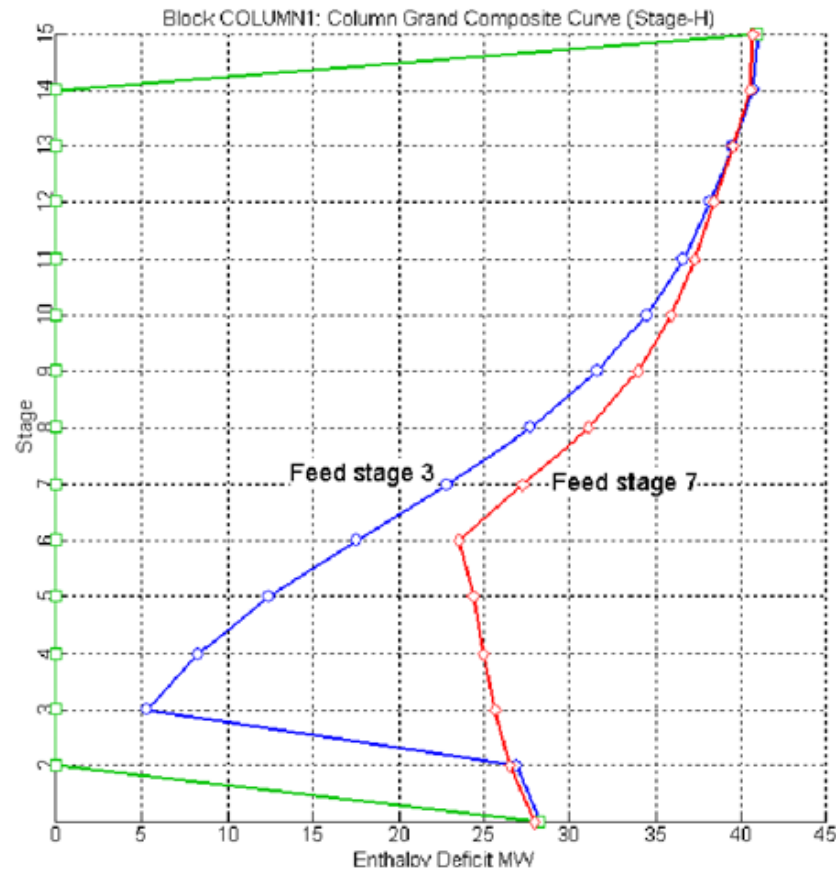


Figure 2.1 A CGCC where feed location modification is required [1] and the feed stage is moved down to 7 from 3.

2.1.2. Feed conditioning

Feed conditioning is necessary when sharp enthalpy change in reboiler side or condenser side is noticed on the stage-H CGCC plot (Figure 2.2):

- If a feed is excessively sub-cooled, the stage-H plots show a sharp enthalpy changes on the reboiler side, and extent of this change determines the approximate feed heating duty required.
- If a feed is excessively over heated, the stage-H plots show a sharp enthalpy changes on the condenser side, and extent of this change determines the approximate feed cooling duty required.

- Changes in the heat duty of pre-heaters or pre-coolers lead to similar duty changes in the column reboiler or condenser loads, respectively [11].

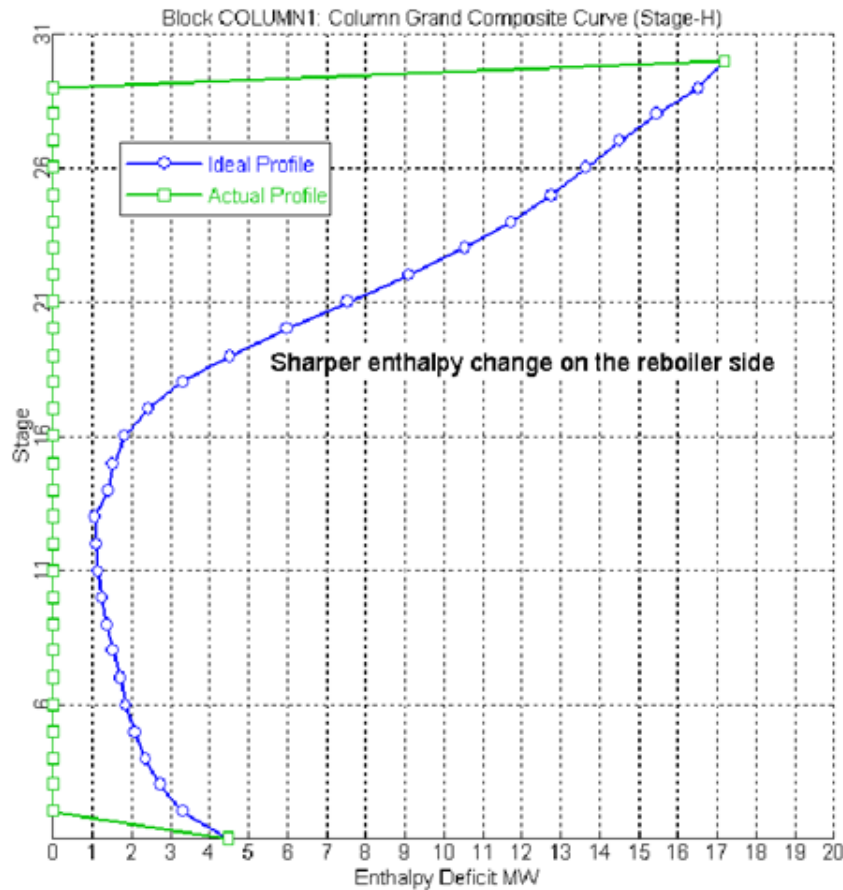
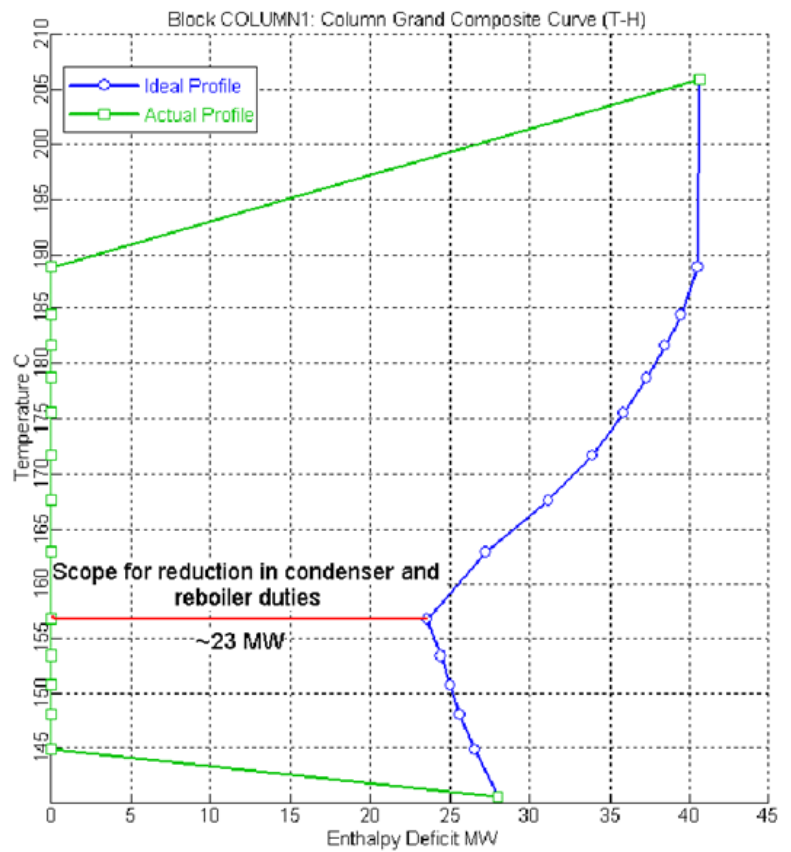


Figure 2.2 A CGCC where feed conditioning modification is required [1].

2.1.3. Reflux ratio

The gap between the pinch point and ordinate suggests that the duties in the reboiler and condenser can be further reduced by reducing reflux ratio [11] (Figure 2.3). However, to maintain the separation, the number of stages must increase. NQ curves analysis can be applied to find the optimum number of stages and the optimum feed stage based on an objective function, which may minimize total hot and cold duties or reflux ratio. The NQ curves are applied on columns with an objective function of minimizing the total duty

(reboiler + condenser). To generate NQ curves, several steps should be considered: (i) specify the total number of stages, (ii) activate design specifications such as purity, recovery, and/or stage temperature, (iii) specify upper and lower limits for the number of stages, (iv) select feed stage for the feed tray optimization, and (v) specify the objective function.



It must be noted that, as the reflux ratio is reduced, the number of stages required to achieve the desired separation increases. In order to make a judicious choice for the reflux ratio, the increase in the capital cost due to the increase

Figure 2.3 A CGCC where reflux ratio modification is required [1].

2.1.4. Side condensing or reboiling

Side condensing or side reboiling is external modification at a convenient temperature level. The area between the ideal and actual enthalpy (the CGCC pinch point) can be used to determine the scope for side condensing or side reboiling. This area could be reduced by

integrating side condensing or reboiling, (or both in some cases) on an appropriate stage [4,11,16]

- If a significant area exists above the pinch, a side reboiler can be placed at a convenient temperature level. This allows heat supply to the column using a low-cost hot utility, hence lowering the overall operating costs.
- If a significant area exists below the pinch, a side condenser can be placed at a convenient temperature level. This allows heat removal from the column more effectively and by a cheaper cold utility, hence lowering the overall operating costs.

However, the CGCC profile should be illustrated to determine the right stage of side condenser or reboiler, so the ideal heat duty is not exceeded as shown in Figure 2.4. In Chapters 5 and 6, the determination of scope of retrofits and possible modifications are discussed for different chemical process.

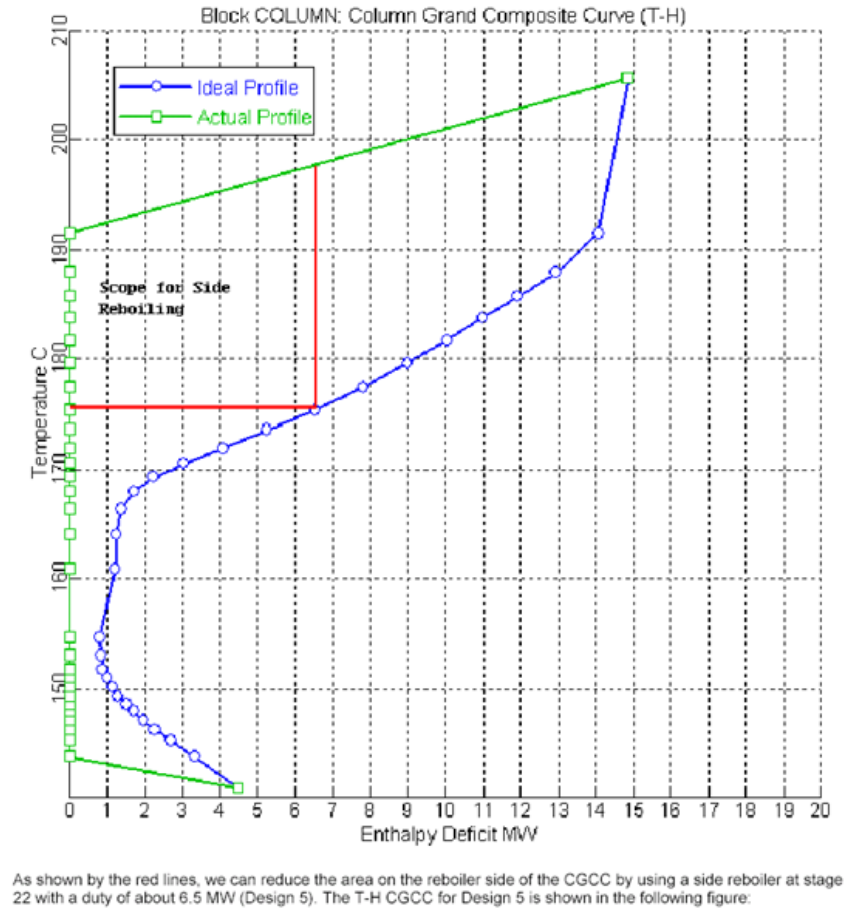


Figure 2.4 A CGCC that shows the stage and the reduced duty of side reboiling of a column [1].

2.2. Exergy Loss Profiles

Physical exergy (Ex) is the maximum amount of work that may be performed theoretically by bringing a resource into equilibrium with its surrounding through a reversible process

$$Ex = \Delta H - T_o \Delta S \quad (2.4)$$

where H and S are the enthalpy and entropy, respectively, and T_o is the reference temperature, which is usually assumed as the environmental temperature of 298.15 K.

Physical exergy balance for a steady state system is

$$\sum_{\text{into system}} \left[\dot{n}Ex + \dot{Q} \left(1 - \frac{T_o}{T_s} \right) + \dot{W}_s \right] - \sum_{\text{out of system}} \left[\dot{n}Ex + \dot{Q} \left(1 - \frac{T_o}{T_s} \right) + \dot{W}_s \right] = \dot{Ex}_{\text{loss}} \quad (2.5)$$

where \dot{W}_s is the shaft work. In general, the exergy loss profiles can be used to examine the degradation of accessible work due to: (i) momentum loss (pressure driving force), (ii) thermal loss (temperature driving force), and (iii) chemical potential loss (mass transfer driving force) (Figure 2.5) [3,17,18].

The exergy profiles are plotted as state-exergy loss or temperature-exergy loss. A part of accessible work potential is always lost in any real process. Exergy losses (destructions) represent inefficient use of available energy due to irreversibility, and should be reduced by suitable modifications [4,5,8]. As the exergy loss increases, the net heat duty has to increase to enable the column to achieve its required separation task. Consequently, smaller exergy loss means less waste energy.

Thermodynamic efficiency is estimated depending on the sign of the main goal; Eq. (2.6) for the negative main goal and Eq. (2.7) for the positive one

$$\eta_{(-)Ex_{\min}} = \frac{Ex_{\min}}{Ex_{\min} - Ex_{\text{loss}}} \quad (2.6)$$

$$\eta_{(+)Ex_{\min}} = \frac{Ex_{\min}}{Ex_{\min} + Ex_{\text{loss}}} \quad (2.7)$$

The main goal is the minimum exergy loss in accomplishing that goal [19]. Minimum exergy determined by calculating the difference between exergies of products and the feed streams

$$Ex_{\min} = \sum_{\text{out}} \dot{n}Ex - \sum_{\text{in}} \dot{n}Ex \quad (2.8)$$

where \dot{n} is the molar flow rate.

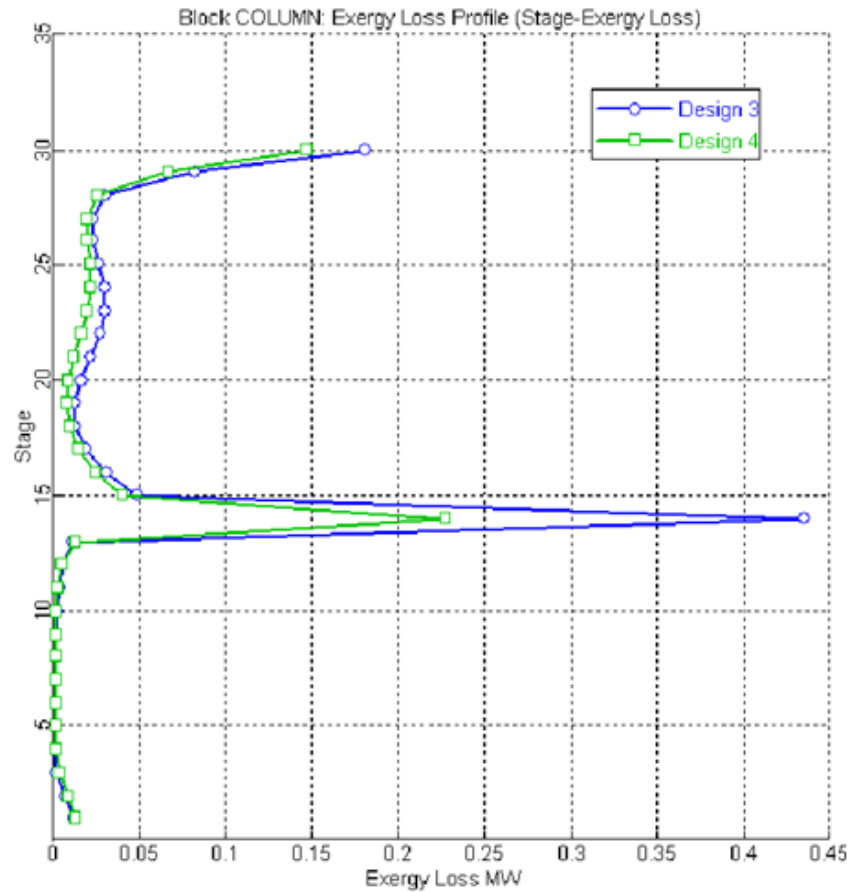


Figure 2.5 An exergy loss profile for two designs of a column [1]. Design 3 is the base and design 4 is the retrofitted design.

2.3. Hydraulic Analysis

The hydraulics analysis produces the stage profiles for (i) thermodynamic ideal minimum flow, (ii) hydraulic maximum flow, and (iii) actual flow (Figure 2.6). These flow profiles help understand how the vapor and liquid flow rates in a column compare with the minimum (corresponding to the PNMTTC) and maximum (corresponding to flooding) limits. Therefore, it can be used to identify and eliminate column bottlenecks [2,4]. Tray or packing rating for the entire column is necessary to activate the hydraulic analysis. In addition, allowable flooding factors (as fraction of total flooding) for flooding limit

calculations can be specified. Hydraulic analysis helps identify the allowable limit for vapor flooding on the Tray Rating|Design/Pdrop or Pack Rating|Design/Pdrop options. The assumed values are 85% for the vapor flooding limit and 50% for the liquid flooding limit. The liquid flooding limit specification is available only if the downcomer geometry is specified. The allowable limit for liquid flooding (due to downcomer backup) can be specified on the Tray Rating|Downcomers block. For packed and tray columns, jet flooding controls the calculation of vapor flooding limits. For tray columns, parameters such as downcomer backup control the liquid flooding limits.

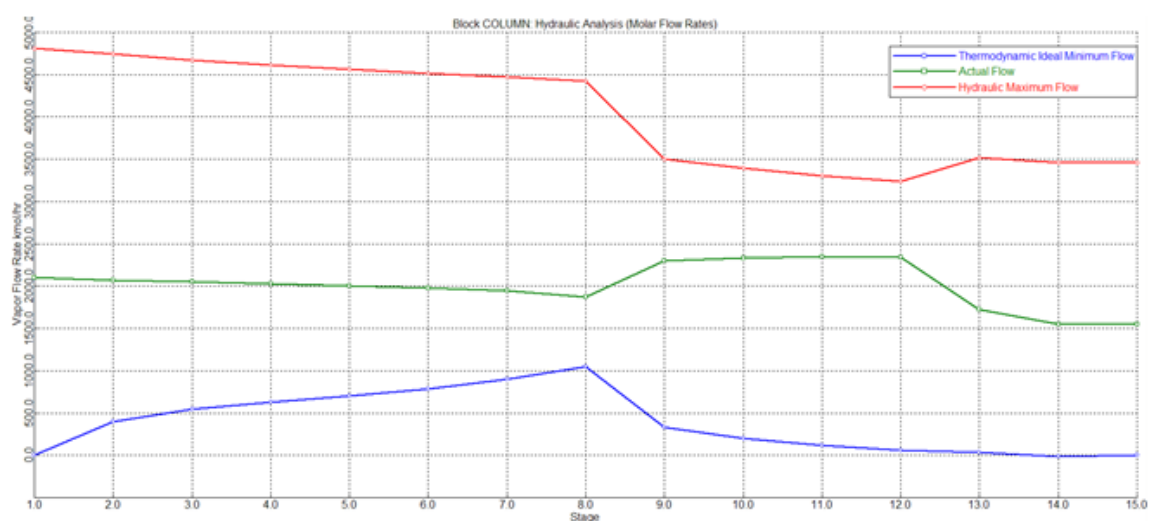


Figure 2.6 Hydraulic analysis stage profile [1].

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CHAPTER 3. ENERGY ANALYZER

Abstract

Energy analyzer (EA) is a tool for analyzing and improving the process heat integration through a heat exchanger network systems (HENS) based on the pinch analysis with a minimum temperature approach. Mainly, EA concentrates on operations and design analysis at the same time by suggesting adding or relocating heat exchangers and heat exchanger outlet temperature to recover process heat and minimize the waste energy. To clarify EA, pinch analysis and HENS will be discussed in this Chapter.

3.1. Pinch Analysis

Pinch analysis yields optimum process heat integration with a network of heat exchangers, where hot and cold streams can only exchange energy up to the pinch point which is a minimum allowable temperature difference ΔT_{\min} leading to the minimum driving force for heat transfer and then the minimum entropy production allowed in a network [1-3]. Using the hot and cold composite curves (see Figure 3.1) or grand composite curves available heat is matched with required heat at ΔT_{\min} .

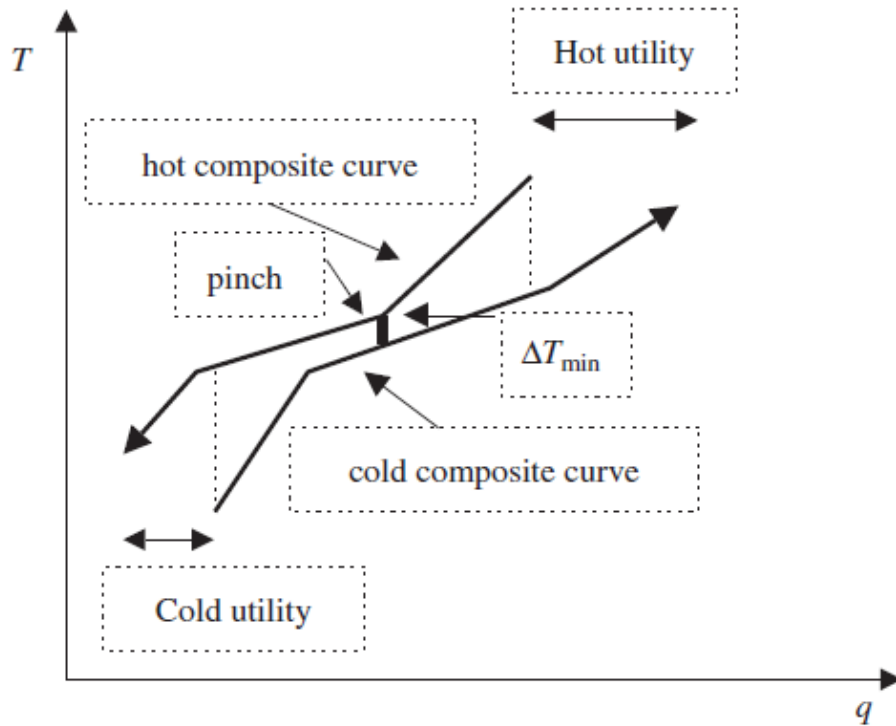
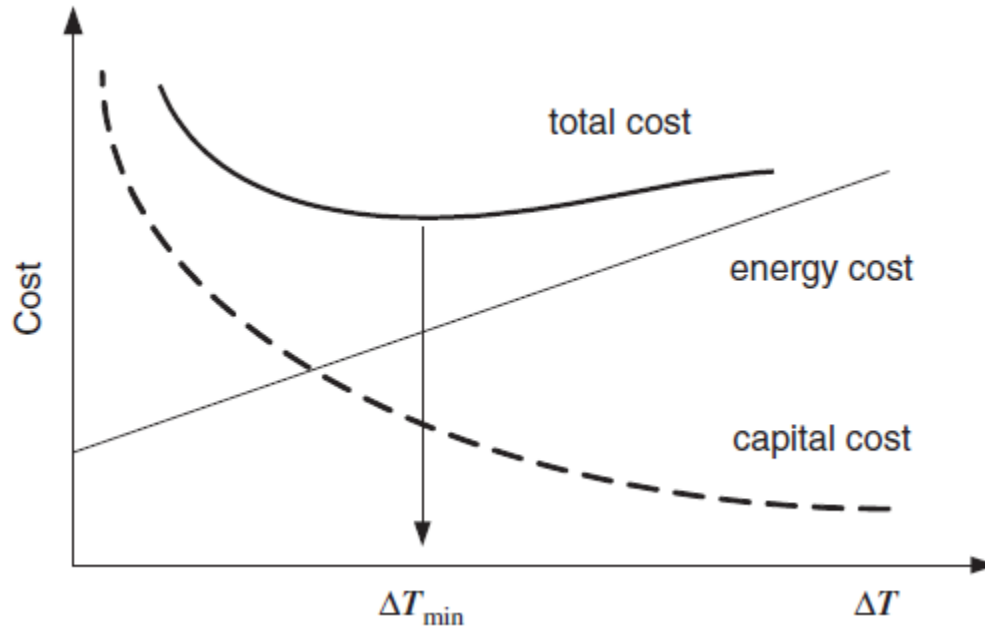


Figure 3.1 Hot and cold composite curves [2].

ΔT_{\min} is a key design variable for pinch analysis and hence for heat exchanger network, and it may be called approach temperature. Generally, the optimum value of ΔT_{\min} is in the range of 3–40 °C for heat exchanger network, as detailed in Table 3.1 [4]. To find ΔT_{\min} optimum, capital cost and energy cost should be considered; increasing ΔT will increase the heat exchanger energy cost and decrease the heat exchanger area which will lead to decreasing the capital cost as plotted in Figure 3.2. However, a whole plant operation can be optimized not only in a heat transfer side, but also in separation and reaction units as well.

Table 3.1 Optimum value of ΔT_{\min} for different industrial processes.

No	Processes	ΔT_{\min}
1	Oil Refinery	20–40 °C
2	Petrochemical	10–20 °C
3	Chemical	10–20 °C
4	Low Temperature Process	3–5 °C

Figure 3.2 Optimum ΔT_{\min} from energy cost and capital cost changes [2].

3.2. Heat Exchanger Network System (HENS)

A process may have available hot and cold streams that create the opportunity to match the available and required heats of these streams to reduce the hot and cold utility needed for a specified temperature approach at the pinch point. For instance, consider the crude oil refinery PFD shown in Figure 3.3, it has several product streams that is end with high temperature which is not suitable storage temperature; in the other hand, the feed stream temperature is started with high temperature as well which is not an ambient

temperature. In this case, the product stream is considered as available heat that could be used to optimize the process and the feed stream is considered to be the required heat, but one may ask some questions when look at similar PFD such as:

- Does the process in need of matching the available and required streams or it could work without?
- Does matching the available hot and required worth in energy and economy point view?
- What is the minimum number of heat exchanger the process required?

Such a questions will be answered in Chapter 6. A minimum number of heat exchanger $N_{Hx, \min}$ can be calculated using Eq. (3.1) [3].

$$N_{Hx, \min} = N_{Hs} + N_{Cs} + N_{HU} + N_{CU} - 1 \quad (3.1)$$

where N_{Hs} and N_{Cs} are the number of hot and cold streams respectively, and N_{HU} and N_{CU} are the number of hot and cold utilities, respectively. However, HENS analysis will be more useful if it includes the environmental protection such as CO₂ emission.

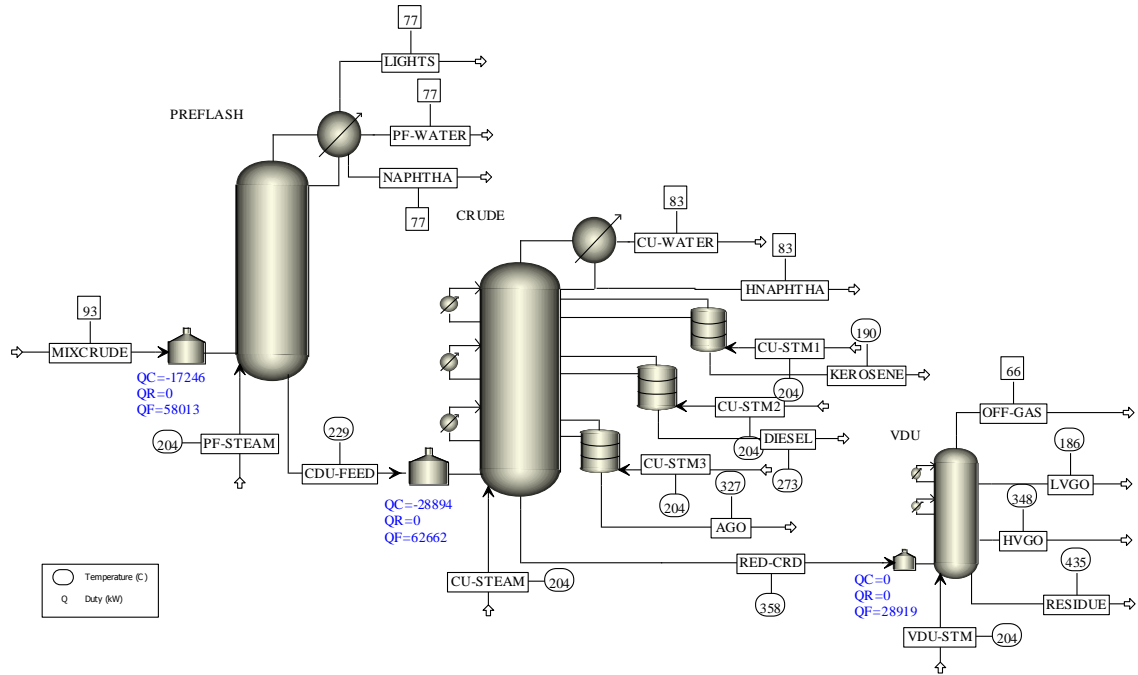


Figure 3.3 Process flow diagram. The temperature of the streams are in °C and the values of heats (Q) are in MW. PF-STEAM: pre-flash steam; CU-STEAM: crude unit steam; VDU-STM: vacuum distillation unit steam. These hot output streams can be used to heat the feed streams to reduce the hot utility necessary from outside.

The thermal characteristics of hot and cold streams and the amount of heat that can be exchanged between them can be represented by the composite curve (Figure 3.3) that show temperature-enthalpy relation where enthalpy change rate for each stream is calculated by Eq. (3.2) [2].

$$q = \Delta H = \dot{m}C_p\Delta T \quad (3.2)$$

where ΔH is the enthalpy change rate, \dot{m} the mass flow rate, C_p the heat capacity, ΔT the temperature change in a stream.

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CHAPTER 4. SUSTAINABILITY ECONOMIC IN CHEMICAL PROCESSES

Abstract

Sustainability is a development that has been defined and interpreted in numerous ways [1]. The most known and cited definition is that “development that meets the needs of the present without compromising the ability of future generations to meet their own needs”. Energy plays a significant role in the technological development and transition to modern chemical process industries; therefore, it is essential to account sustainability in process development and evaluation of the feasibility of chemical processes.

4.1. Sustainability in Chemical Process Industries

‘Sustainability’ is maintaining or improving the material and social conditions for human health and the environment over time without exceeding the ecological capabilities that support them [2-6].’ The dimensions of sustainability are economic, environmental, and societal as seen in Figure 4.1.

One- and two-dimensional metrics, while useful, cannot alone certify progress towards sustainability. Progress towards sustainability occurs only when all three aspects are improved. Economic and societal indicators may also be constrained with the environment, as seen in Figure 4.1b.

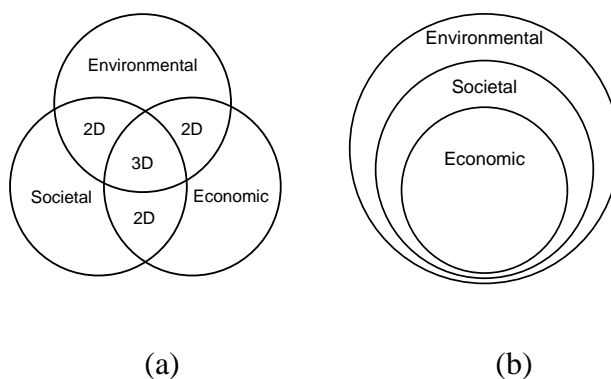


Figure 4.1 (a) Three dimensions of sustainability; (b) economic and societal dimensions are constrained with the environment.

Suitable environmental assessment tools are needed for the development of sustainable chemical products and processes [7-17]. Many multi-national chemical companies support the initiative of sustainable development and prepared programs for implementation of it. The formation of World Business Council for Sustainable Development [14], and the American Business Council for Sustainable Development [15,16] are examples of this world-wide effort. The U.S. Environmental Protection Agency's National Risk Management Laboratory joined the efforts of linking sustainability to ecological capabilities [17]. The collective environmental regulations and technical advances, such as pollution control, waste minimization, and pollution prevention has greatly diminished adverse environmental impacts of chemical process industries [18]. Tools for hazard characterization of chemicals, exposure assessment models, health effect models, and risk assessment models need to be incorporated in process and product designs for sustainable technologies [9-12].

Many industries acknowledge a need to measure, track, and compare their efforts in sustainability. The AIChE Sustainability Index may enable to assess a company's sustainability performance; sustainability innovation considers commitment to

development of products and processes with superior environmental, social and economic performance. Besides customer's safety, healthcare and clean water for the developing world, reducing greenhouse gases and improving energy efficiency are the main drivers [9,14]. Furthermore, several companies have integrated the use of sustainability approaches including sustainability decision checklists, life cycle assessment, total cost assessment, and others. These tools, however, are not yet widely used.

The Center for Waste Reduction Technologies (CWRT) of the American Institute of Chemical Engineers (AIChE) [5] and the Institution of Chemical Engineers (IChemE) [6] proposed a set of sustainability metrics that are applicable to a specific process:

- Material intensity (nonrenewable resources of raw materials, solvents/unit mass of products)
- Energy intensity (nonrenewable energy/unit mass of products)
- Potential environmental impact (pollutants and emissions/unit mass of products)
- Potential chemical risk (toxic emissions/unit mass of products)

This study considers the sustainability metrics of 'material and energy intensities.' 'Potential environmental impacts' is also considered by using the 'Carbon Tracking' and 'Global Warming Potential.' [19]

4.2. Carbon Tracking

'Carbon tracking' of Aspen Plus [19] allows the calculation of CO₂ emissions after specifying 'CO₂ emission factor data source' and 'ultimate fuel source.' The CO₂ emission factor data source can be from European Commission decision of '2007/589/EC' or United

States Environmental Protection Agency Rule of E9-5711. This study employs the CO₂ emission factor data source of US-EPA-Rule-E9-5711 and the fuel source of natural gas as seen in Table 4.1.

4.3. Global Warming Potential

The carbon equivalents of streams are based on data from three popular standards: (1) the IPCC's 2nd (SAR), (2) 4th (AR4) Assessment Reports, and (3) the U.S. EPA's (CO₂E-US) proposed rules from 2009 (Table 4.2) [19]. This study uses US-EPA with a predetermined cost for CO₂ fee/tax.

Table 4.1 Emission rates for various CO₂ emission factor data sources and fuel sources [19].

Fuel Source	US-EPA-Rule-E9-5711 lb/MMbtu	EU-2007/589/EC lb/MMbtu
Natural gas	130.00	130.49
Coal bituminous	229.02	219.81
Coal anthracite	253.88	228.41
Crude oil	182.66	170.49
Bio gas	127.67	0

Table 4.2 Standards used in global warming potential for reporting CO₂ emissions.

Standards for reporting CO ₂ emissions	Prop-Set properties corresponding to each standard
IPCC AR4 (2007)	CO ₂ E-AR4
USEPA (2009)	CO ₂ E-US

4.4. Life Cycle Analysis

LCA tracks all material, energy, and pollutant flows of a system—from raw material extraction, manufacturing, transport, and construction to operation and end-of-life disposal. LCA can help determine environmental burdens from "cradle to grave" and facilitate comparisons of energy technologies with a well-established and comprehensive framework [20-23] through the value chain, not just at the final manufacturing stage, with a product, process [23]. Large projects which have technical, ecological, economic and societal components must take sustainability into account since processes based on renewable sources may not necessarily be sustainable [11-13].

4.5. Economic Input-Output Life Cycle Assessment

EIO-LCA estimates the materials and energy resources required for, and the environmental emissions resulting from, activities in the economy of chemical process industries [21,23,25]. The results provide guidance on the relative impacts of different types of products or industries with respect to resource use and emissions throughout the supply chain. Thus, the effect of producing a product would include the impact from mining raw materials, transportation, storing, that are needed for production [7,21,23,24].

4.6. Gauging Reaction Effectiveness for Environmental Sustainability of Chemistries with A Multi-Objective Process Evaluator (GREENSCOPE)

GREENSCOPE measures the sustainability of a process in terms of environmental, efficiency, energy, and economic indicators, with each indicator being mathematically defined [26]. Efficiencies for chemical reactions are reflected in values such as conversion

and selectivity, which track yields, product distributions, and recycle flows needed to make a desired amount of product. Energy use depletes resources and creates potential environmental impacts, and a less efficient process can be expected to use more energy.

4.7. Economic Analysis in Chemical Industries

Economic analysis is an assessment method to determine the feasibility and profitability of chemical industry. Discounted cash flow diagram (DCFD) (Figure 4.2) is one way to analyze the chemical process economically where it shows the fixed capital investment, net present value, payback period, and the cash position. Another way to analyze the chemical industry, is converting the energy used or saved to \$/year based on any type of utility to determine if it is feasible or not, this method is used in Chapter 5 and 6.

A typical cash flow diagram, as shown in Figure 4.2, shows the years for construction where the cash flow has negative slope. Through years of operation, revenue exceeding the cost of manufacturing results a positive slope for the cash flow. This operation ends when the revenue cannot maintain the cost of manufacturing. Such cash flow diagrams indicate the three feasibility criteria that are net present value, payback period, and rate of return. At least two of these criteria should be favorable for the project to be economically feasible.

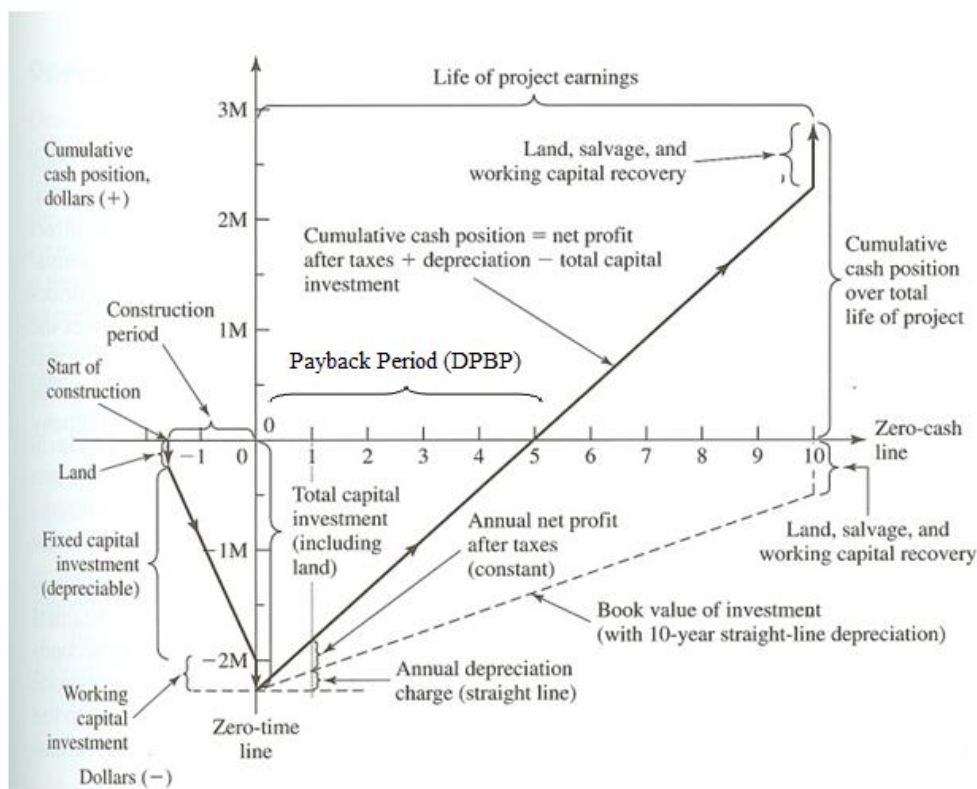


Figure 4.2 Discounted cash flow diagram (DCFD) [27,28].

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CHAPTER 5. ETHYLENE PLANT BACK END SEPARATION

Abstract

This Chapter presents metrics of energy intensity and environmental impact of the back end separation of ethylene plant consisting three interacting distillation columns by thermodynamic analysis. The objective is to explore the scope of reducing the energy for utilities and CO₂ emissions. Thermodynamic analysis is carried out by using the Column Targeting Tool (CTT) to address the sustainability metrics of ‘Energy Intensity.’ Environmental impact metrics are estimated from the Carbon Tracking options. CTT is based on the ‘Practical Near-Minimum Thermodynamic Condition’ representing a close to practical reversible column operation. The carbon tracking estimates are from the CO₂ emission data source of US-EPA-Rule-E9-5711 using natural gas as the primary fuel. The results show that the total reductions in exergy loss and the total hot and cold utility are around 44% and 10%, respectively; the total reductions in carbon dioxide are around 14%. Thermodynamic analysis with sustainability metrics may lead to more sustainable separation by distillation.

5.1 Introduction

Distillation based separations consume about 40% of the total energy used in petrochemical and chemical process industries in North America [1,2]. The relatively high purity recovery and low relative volatility require toll distillation columns with very high installation and operating costs in ethylene plants [3]. Therefore, the olefin/paraffin separation process of ethylene, propylene and other high volume olefin petrochemicals is

highly energy-intensive, and hence impacts environment. Cryogenic distillation is the commercially viable separation; however, it consumes over 20 Gigajoules of energy for every ton of ethylene produced. This energy consumption is associated with significant greenhouse gas emission and depletion of non-renewable energy resources. Consequently, there is a strong economic incentive to reduce the costs through improved process designs for the back end separation of ethylene by distillation [3,4].

A typical distillation column resembles a heat engine delivering separation work by using heat at a high temperature in the reboiler and discharging most of it to the environment at a lower temperature in the condenser [1,2,5,6]. One of the thermodynamic methodologies to assess the distillation column operation is the Column Targeting Tool (CTT), which is based on the Practical Near-Minimum Thermodynamic Condition (PNMTC) approximation representing a practical and close to reversible operation [7-12]. CTT exploits the capabilities for thermal and hydraulic analyses of distillation columns [4,13-16] to identify the targets for possible column retrofits for: 1) feed stage location, 2) reflux ratio, 3) feed conditioning, and 4) side condensing and/or reboiling to reduce the cost of utilities and improve the overall energy efficiency. The ‘Carbon Tracking’ options of the Aspen Plus can help quantify the reduction in CO₂ emission in a simulation environment [8].

Sustainability has environmental, economic, and social dimensions and requires the responsible use of energy resources and reduction in CO₂ emission. The three intersecting dimensions illustrate the 3D-sustainability metrics that include nonrenewable energy use, toxic, and pollutant emissions per unit product [17-21]. If nonrenewable, energy usage affects environment adversely through the emission of pollutants such as CO₂. Therefore, a comparative assessment with the sustainability metrics may prove useful in identifying

the scope for retrofits for possible reductions of the waste energy and emission of CO₂ for the three interacting distillation columns of a typical ethylene plant. The energy metrics are estimated from the CTT, while the carbon emission from the data source of US-EPA-Rule-E9-5711 using the fuel source of natural gas.

5.2. Ethylene Plant

Ethylene is produced by steam cracking in which light hydrocarbons are heated to 750–950 °C, inducing numerous reactions. Ethylene is separated from the resulting complex mixture by repeated compression and distillation processes. The separation of ethylene from ethane by distillation is normally the final step in the production of ethylene. The separation of ethylene is expensive because: (i) the required purity of ethylene usually exceeds 99.9% and (ii) the relative volatility of ethylene to ethane is moderately small ranging from about 1.13 for high pressure mixtures rich in ethylene to 2.34 for low pressure mixtures rich in ethane. Ethylene fractionation separates ethylene as a highly pure overhead product, 99.9wt%, free of olefins, acetylenes, dienes, and water. Ethylene production is close to the historic mid-range of 145 million lb/day in the U. S. States. Global production of ethylene was about 141 million mt in 2011 [3]. Approximately 90% of ethylene is used to produce ethylene oxide, ethylene dichloride, ethyl benzene and polyethylene.

As shown in Figure 5.1, stream 12 of 170.71 mt/hr, at 16 °C and 39 bar, consists of 56.63 mt/hr of ethane, 81.17 mt/hr of ethylene, 7.201 mt/hr of hydrogen, 4.86 mt/hr of methane, 0.02229 mt/hr of acetylene, 9.35 mt/hr of propylene, 3.75 mt/hr of propane, 1.53 mt/hr of butadiene, 0.77 mt/hr of butene, 0.82 mt/hr of butane, and 4.59 mt/hr of benzene. The feed enters a splitter S2. The separated streams pass through reactors and flash

separators till they reach the separation section containing the three RadFrac columns. The streams pass through the columns to produce ethylene as the distillate from column 3 and ethane as the bottom product which is recycled to C2REC reactor. Propylene is the bottom stream of column 2.

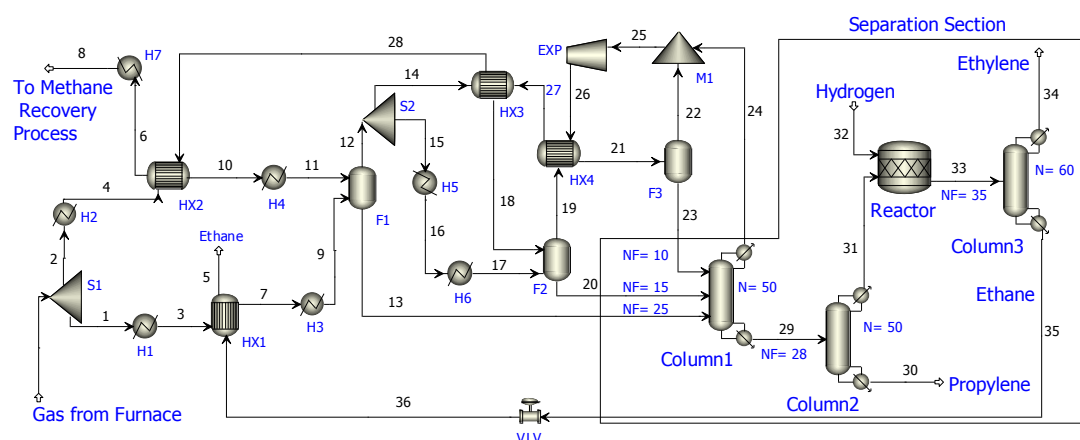


Figure 5.1 Process flow diagram of ethylene plant with back end separation.

This chapter focuses on the separation section having three distillation columns as shown in Figure 5.1. Column 1 has three feeds and the overhead contains the hydrogen and methane which are recycled, while the bottom flow contains the mixture of ethane, ethylene, propylene, butadiene, butane, butane, and benzene which are separated in column 2 to a bottom flow containing propylene, propane, butadiene, butane, and benzene. Ethane and ethylene in the presence of hydrogen goes to the overhead and finally becomes the feed to column 3 where the ethylene is the overhead product, while the ethane in the bottom is recycled. Table 5.1 shows the base configurations of the three columns. The Soave-Redlich-Kwong equation of state is used in the simulation of the plant.

Table 5.1 Columns base case configurations: N: number of total stages; NF1, NF2, NF3 are the feed stages; RR is the molar reflux ratio; F is the total mass flow rate; P is the column pressure; TF1, TF2, TF3 are the feed temperatures, and PF1, PF2, PF3 are the feed.

Configuration	Column 1	Column 2	Column 3
N	50	50	60
NF	NF1=25		
	NF2=15	28	35
	NF3=10		
Mole RR	0.65	0.53	4.75
F (mt/hr)	F1=97.3		
	F2=59.82	175.86	173.23
	F3=3.74		
P (bar)	35.15	23.90	16.87
TF (°C)	TF1= -37		
	TF2= -98	5.50	-24.60
	TF3= -129		
	PF1=37.3		
PF(bar)	PF2=37	35.15	17.60
	PF3=37		
Condenser duty (MW)	-0.29	-6.38	-37.81
Condenser temp.(°C)	-99.58	-13.68	-35.92
Reflux rate (mt/hr)	2.21	74.24	391.44
Distillate rate (mt/hr)	2.99	137.23	80.41
Reboiler duty (MW)	9.33	16.26	32.20
Reboiler temp. (°C)	5.53	74.41	-15.00
Boilup rate (mt/hr)	138.75	204.07	329.20
Bottoms rate (mt/hr)	157.86	20.63	56.820

5.3 Result and Discussion

Figure 5.1 displays the back end separation section of the ethylene plant considered in this study. Table 5.1 presents the base-case configurations for all the columns, which operate with large number of stages under high pressure, large reboiler duties, and large boilup rates. Column 3, especially, requires very large hot and cold utilities. The column targeting tool with activated carbon tracking is used to reduce the duties for condensing and reboiling, stage exergy losses, as well as the carbon dioxide emissions due to the

utilities for all the columns. The modified case operations with the determined scope of retrofits are compared with the base case operations to analyze and assess the impact of retrofits in the selected sustainability metrics.

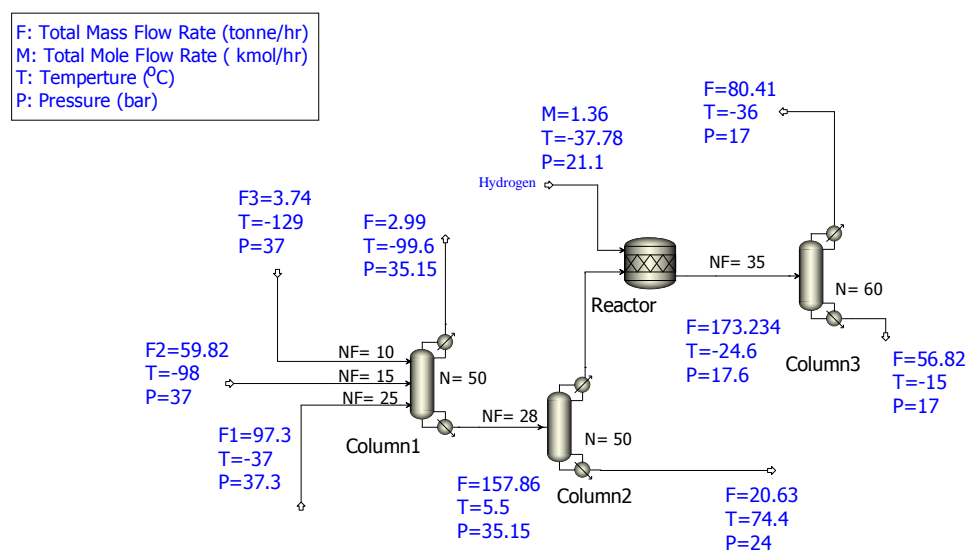
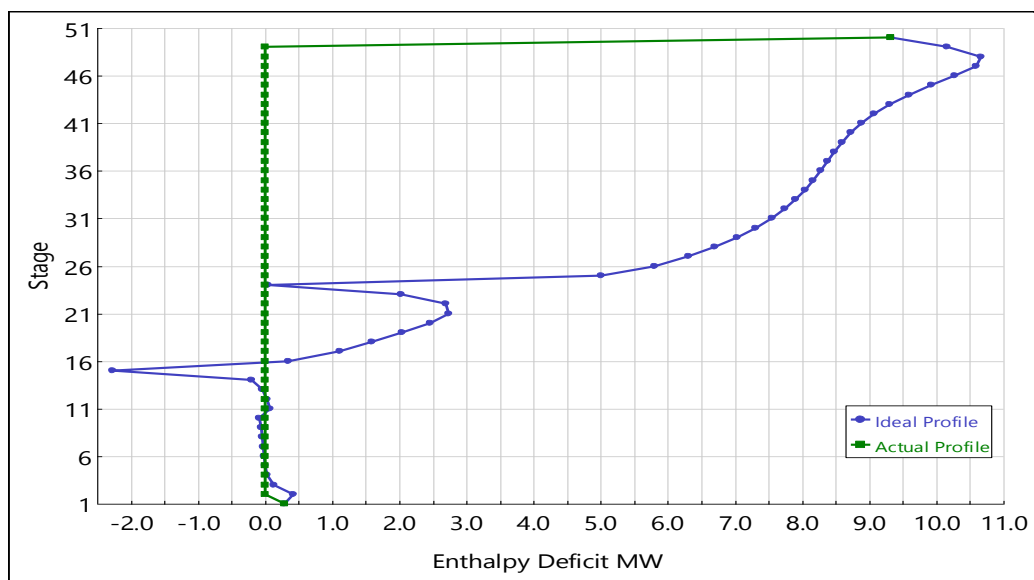


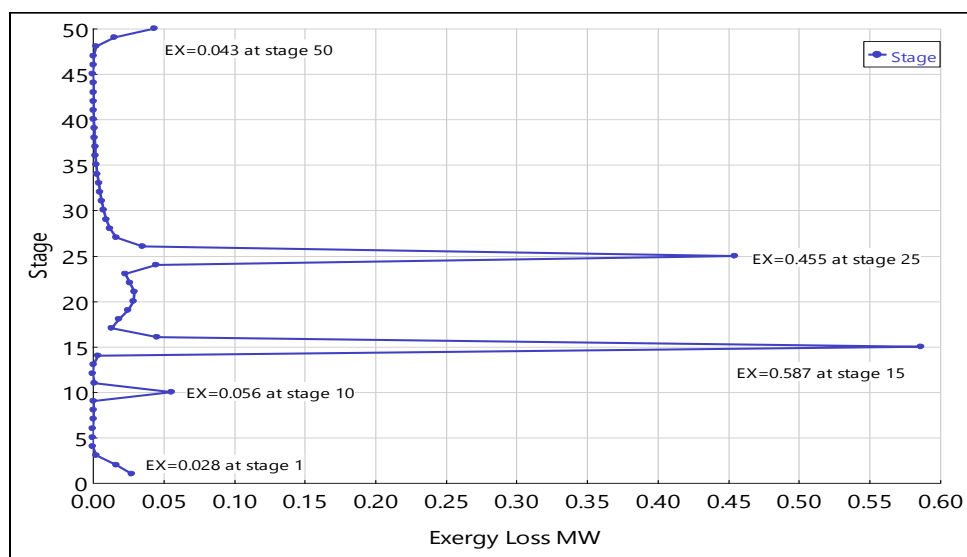
Figure 5.2 Section of ethylene plant back end separation; N: number of total stages; NF: feed plate location.

5.3.1. Column 1

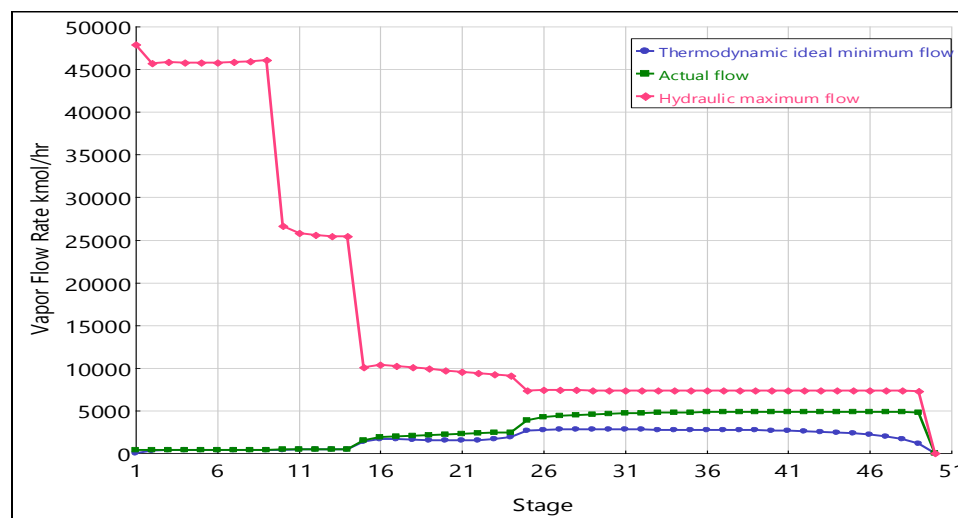
Table 5.1 shows that the first column operates with three feed streams under cryogenic conditions. Figure 5.3 shows the stage-H CGCC, exergy loss profiles, and hydraulic analysis for the base case operations.



(a)



(b)

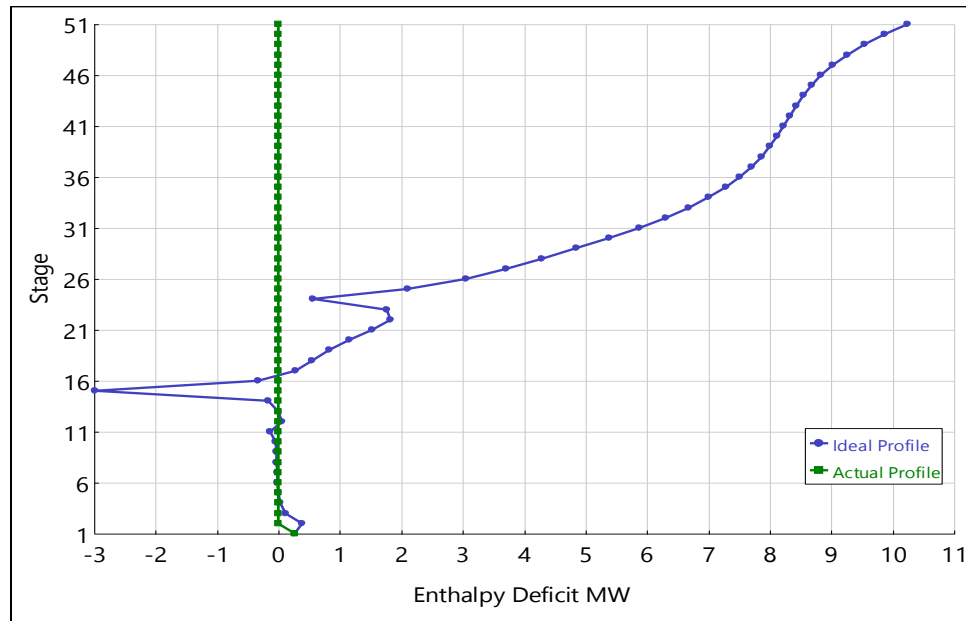


(c)

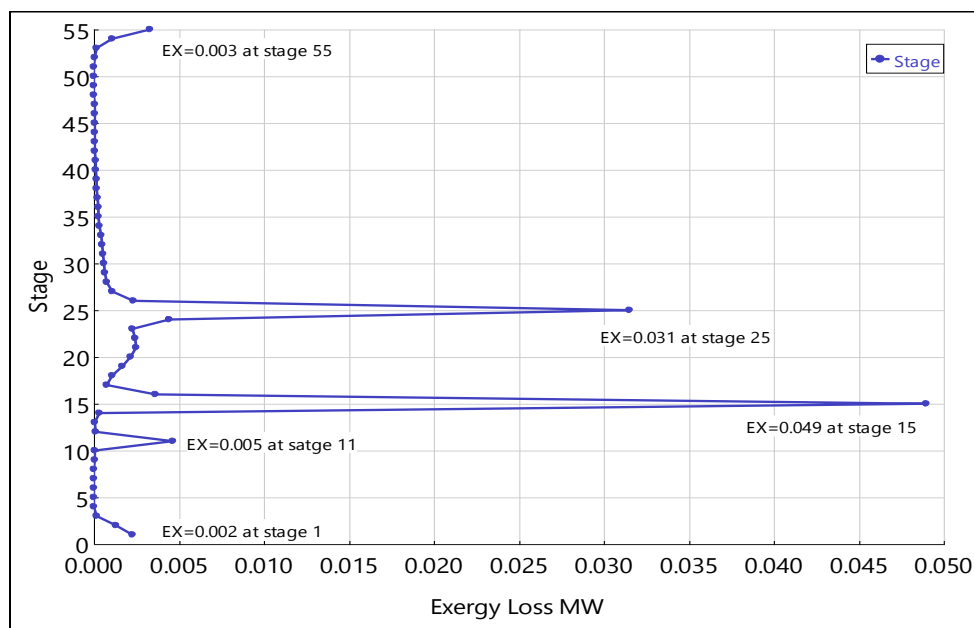
Figure 5.3 Base case operation for column 1 with: $N=50$; $NF1=25$, $NF2=15$, $NF3=10$; $RR=0.65$; N : number of total stages; $NF1$, $NF2$, $NF3$ are the feed stages, and RR is the reflux ratio. (a) CGCC (stage-H), (b) exergy loss profiles, and (c) hydraulic analysis.

Stage-H CGCC shown in Figure 5.3a displays sharp changes for the feeds 2 and 3 on the condenser side, which require moving the feeds up the column toward condenser. Also, it displays sharp enthalpy change on the reboiler side, which requires heating the first feed. Therefore, the first feed has been heated to -30°C instead of -37°C . The small gap to the ordinate requires a reflux ratio modification which leads to changing in the number of stages. Therefore; NQ curve analysis is used to get 55 stages with reflux ratio of 0.38, and the third feed is moved up the column for the $NF3$ to be 11. Exergy loss profile shown in Figure 5.3b displays the wasted available energy in the column and higher exergy losses on the feed stages, the reboiler and the condenser. Figure 5.3c displays the vapor flow rate profile, which is near minimum in the feed stages and the reboiler and near maximum in the condenser. The supporting data shows some of the data obtained from the NQ curve analysis.

NQ curves is applied for column 1 with: $N=55$; $NF1=25$, $NF2=15$, $NF3=11$, and $RR=0.32$, where N is the number of total stages, $NF1$, $NF2$, and $NF3$ are the feed stages, and RR is the reflux ratio. The results of NQ curve are presented in Table A5 within the appendix A. Figure 5.4a displays the modified CGCC (stage-H) with relatively less heat deficits around the feed stages. Figure 5.4b shows the exergy loss profiles of the column after the modifications. The total exergy losses on the feed stages are reduced from the base case of operation value of 1.098 MW to 0.085 MW after the modifications. Therefore the total reduction is around 92%. The hydraulic analysis shows that the changes in the internal vapor flow rates are negligible.



(a)



(b)

Figure 5.4 Modified case operation for Column 1 with: $N=55$; $NF1=25$, $NF2=15$, $NF3=10 \rightarrow 11$; $RR=0.38$; $TF1= -37^\circ\text{C} \rightarrow -30^\circ\text{C}$; N : number of total stages; $NF1$, $NF2$, $NF3$ are the feed stages, and RR is the reflux ratio. (a) CGCC (stage-H), and (b) exergy loss profiles.

Table 5.2 compares the sustainability metrics, which are normalized values with respect to unit mass of products for both the base case and modified case operations. The modifications applied are the reflux ratio, feed plate location, and heating feed 1 of column 1. As seen, the modification have resulted modest reductions in the duties, the cost of energy, and emissions of CO_2 , while reducing the exergy losses considerably. The emission calculations are based on CO_2 emission factor data source of US-EPA-Rule-E9-5711 and natural gas as the fuel source. Besides, the exergy loss is reduced by around 92 % after the modifications leading to efficiently usage of available energy and more thermodynamically optimum operation.

Table 5.2 Sustainability metrics for column 1 with the modification: N=50→55; NF1=25, NF2=15, NF3=11; RR=0.65→0.328; TF1= −37 °C →−30 °C.

Material intensity	Column 1		
	Base Case	Modified Case	Change %
Feed 1 rate (mt/day)	2335.22	2335.22	0
Feed 2 rate (mt/day)	1435.73	1435.73	0
Feed 3 rate (mt/day)	89.66	89.66	0
Distillate rate (mt/day)	71.96	71.96	0
Bottoms rate (mt/day)	3788.66	3788.66	0
Energy intensity metrics			
Condenser duty, kJ/day/(mt/day distillate), kJ/mt	−355,673.60	−344,387.33	−3.17
Reboiler duty, kJ/day/(mt/day bottoms), kJ/mt	212,712.22	199,987.21	−5.98
Feed conditioning, kJ/day/(mt/day feed 1), kJ/mt	0	20,285.62	—
Condenser duty cost, \$/day/(mt/day distillate), \$/mt	15.05	14.58	−3.12
Reboiler duty cost, \$/day/(mt/day bottoms), \$/mt	0.67	0.63	−5.97
Duty in feed 1 conditioning, kJ/day/(mt/day feed 1), \$/mt	0	0.04	—
Total exergy loss, kJ/day/(mt/day ethylene), kJ/mt	70,962.06	5,566.83	−92.15
Environmental impact metrics			
Condenser CO2 emission ¹ , mt/day/(mt/day distillate)	0.0198	0.0191	−3.53
Reboiler CO2 emission ¹ , mt/day/(mt/day bottoms)	0.012	0.011	−8.33
Feed conditioning CO2 emission ¹ , mt/day/(mt/day feed 1)	0	0.001	—

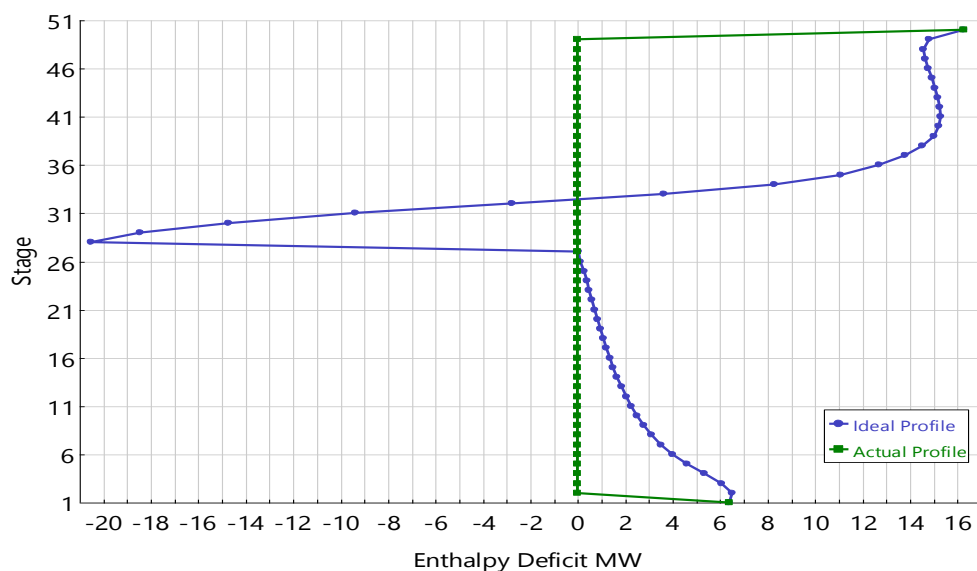
¹Emission based on US-EPA-Rule-E9-5711 and natural gas.

Reflux ratio and number of stages modifications have no impact on the bottoms flow rate and compositions of column 1. This means that there is no impact on column 2 after column 1 reflux ratio and number of stages modifications.

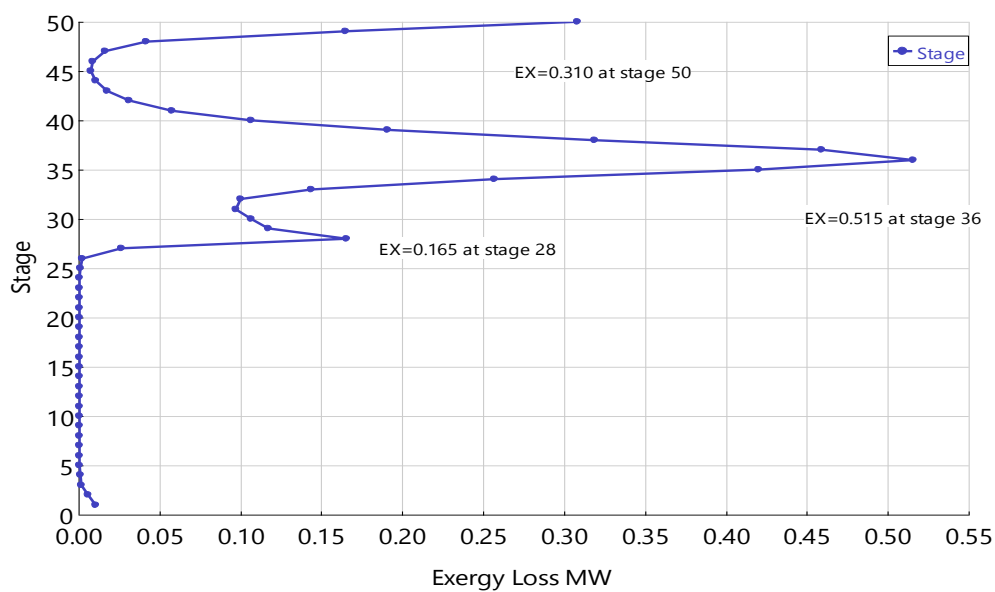
5.3.2 Column 2

For the base case operation of column 2, which is summarized in Table 5.1, Figure 5.5 shows CGCC (stage-H), exergy loss profiles, and hydraulic analysis. Figure 5.5a displays a sharp enthalpy change close to the reboiler side, which means that the feed heating may improve the operation. Also, reflux ratio modification may be required to further reduce

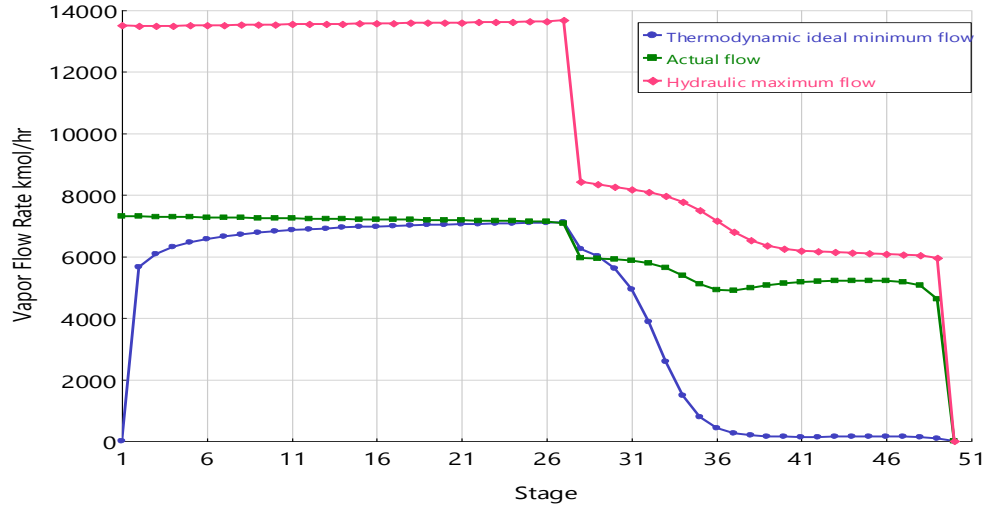
the small gap to the ordinate. Figure 5.5b shows that the exergy loss is higher in the feed stage, stage 36, and stage 55. As Figure 5.5c shows that the vapor flow rate is near minimum on the feed stage.



(a)



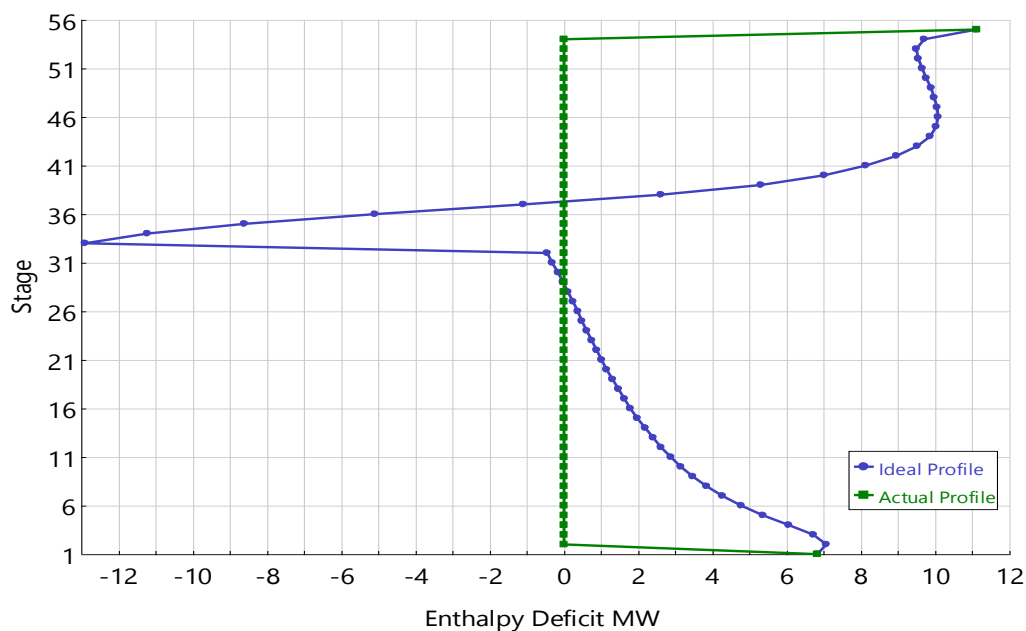
(b)



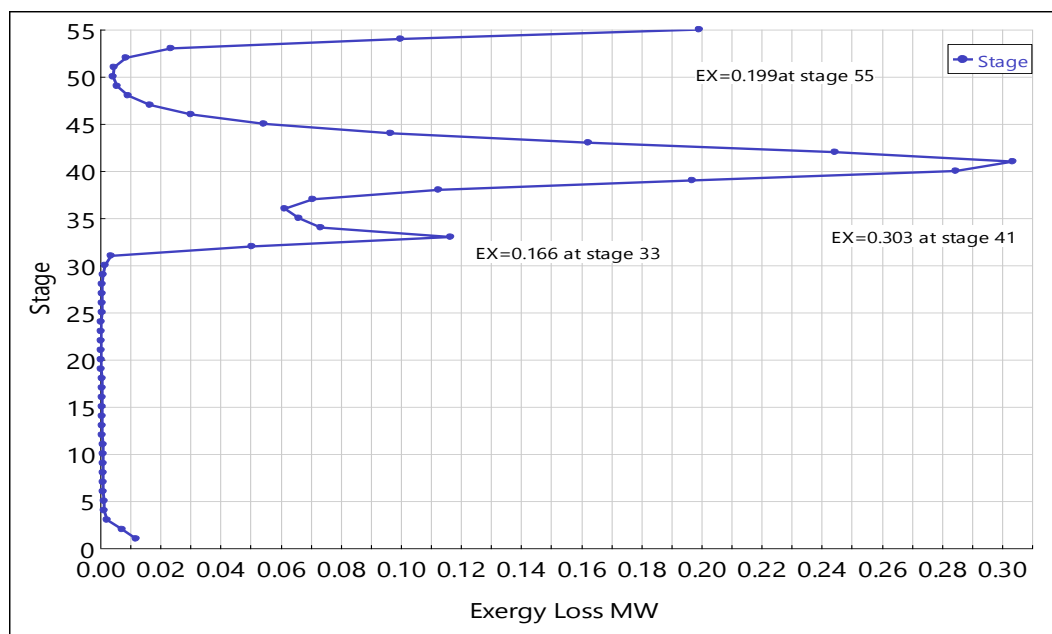
(c)

Figure 5.5 Column 2 base case operation with: $N=50$; $NF=28$; $RR=0.53$; N : number of total stages; $NF1$, $NF2$, $NF3$ are the feed stages, and RR is the reflux ratio. (a) CGCC (stage-H), (b) exergy loss profile, and (c) hydraulic analysis.

Using the NQ curves approach which is presented in Table A6 within the appendix A, column 2 has been modified with: $N=55$; $NF=33$; $RR=0.53$, where N is the number of total stages, NF is the feed stages, and the RR is the reflux ratio. Figure 5.6a shows that the deficit at the feed stage has been reduced considerably on the CGCC (stage-H) after changing the number of stages, and heating the feed up to 9 °C. Figure 5.6b shows considerable reduction of around 37% in the exergy losses with the modified operations. The hydraulic analysis the vapor flow rate profiles are negligible after the modification.



(a)



(b)

Figure 5.6 Modified case operation for column 2 with: $N=55$; $NF=33$; $RR=0.53$; N : number of total stages; NF is the feed stage, and RR is the reflux ratio. (a) CGCC (stage-H), and (b) exergy loss profiles.

Table 5.3 compares the sustainability metrics for the base case and modified case operations for column 2. As seen, the duties and cost of energy are decreased in the reboiler side, while the condenser duty is increased due to heating the feed. In a similar trend, the emissions of CO₂ decreased around 31.6% in the reboiler, while increased around 6.6% in the condenser. This indicates the tradeoff taking place during the modifications. The reduced exergy losses lead to a more thermodynamically optimum operation.

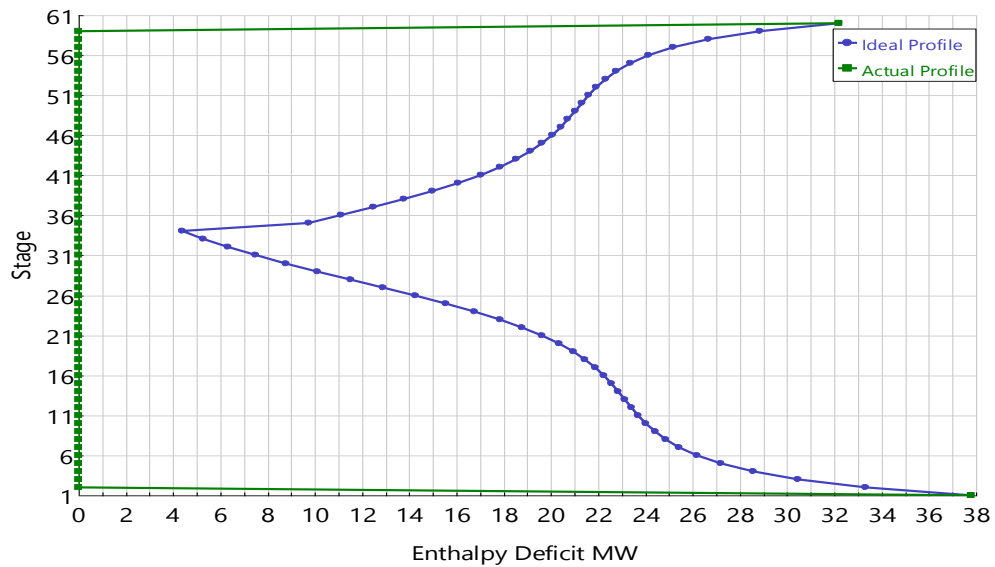
Table 5.3 Sustainability metrics for column2 with the modifications: N=50→55; NF=33; RR=0.65→0.53; TF= 5 °C → 9 °C.

Material intensity	Column 2		
	Base Case	Modified Case	Change %
Feed rate (mt/day)	3,788.66	3,788.66	0
Distillate rate (mt/day)	3,293.55	3293.55	0
Bottoms rate(mt/day)	495.10	495.10	0
Energy intensity metrics			
Condenser duty, kJ/day/(mt/day distillate), kJ/mt	-167,491.73	-179,413.10	+6.63
Reboiler duty, kJ/day/(mt/day bottoms), kJ/mt	2,837,588.200	1,941,146.76	-31.60
Feed conditioning, kJ/day/(mt/day feed), kJ/mt	0	127,508.33	—
Condenser duty cost, \$/day/(mt/day of distillate), \$/mt	1.97	2.11	+6.63
Reboiler duty cost, \$/day/(mt/day bottoms), \$/mt	5.38	3.68	-31.60
Duty in feed 1conditioning, kJ/day/(mt/day feed), \$/mt	0	0.24	—
Total exergy loss, kJ/day/(mt/day ethylene), kJ/mt	166,822.62	104,941.02	-37.10
Environmental impact metrics			
Condenser CO ₂ emission ¹ , mt/day/(mt/day distillate)	0.009	0.01	+10.00
Reboiler CO ₂ emission ¹ , mt/day/(mt/day bottoms)	0.16	0.01	-93.75
Feed conditioning CO ₂ emission ¹ , mt/day/(mt/day feed)	0	0.007	—

¹Emission based on US-EPA-Rule-E9-5711 and natural gas.

5.3.3. Column 3

Column 3 uses the distillate rate of column 2 as the feed. Table 5.3 shows that distillate rate of column 2 remains the same after the modifications; therefore, column 3 base case does not change after the modifications on column 2. For the base case operation of column 3, Figure 5.7 shows the stage-H CGCC, exergy loss profiles, and hydraulic analysis. Figure 5.7a shows that the gap between the ordinate and the composite curve should to be reduced by modifying the reflux ratio. Figure 5.7b displays large exergy losses on stages 23 and 41. The vapor flow rate (shown in Figure 5.7c) reaches hydraulic maximum flow in stage 61.



(a)

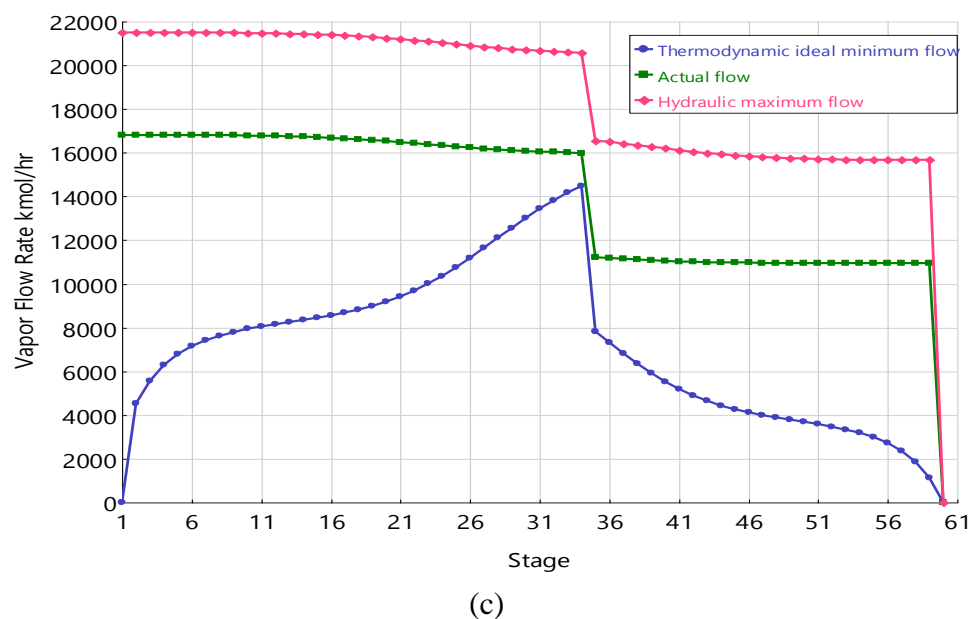
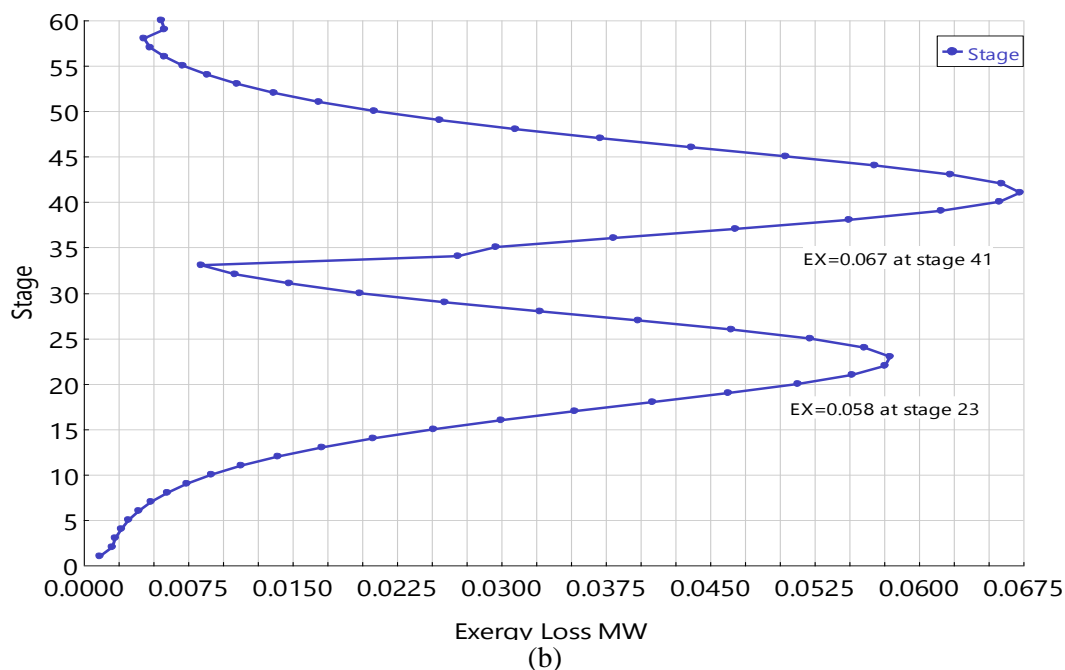
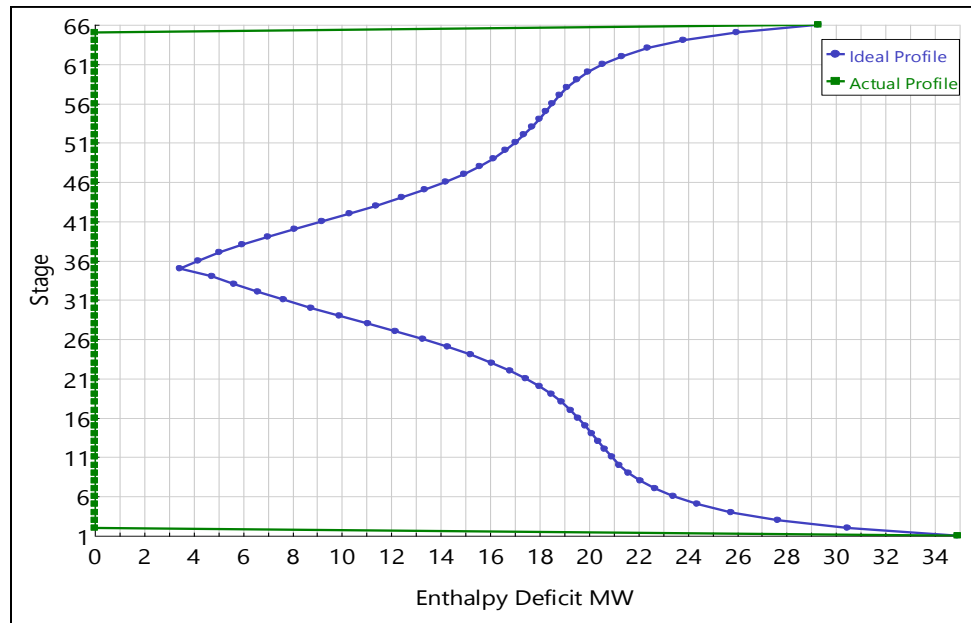


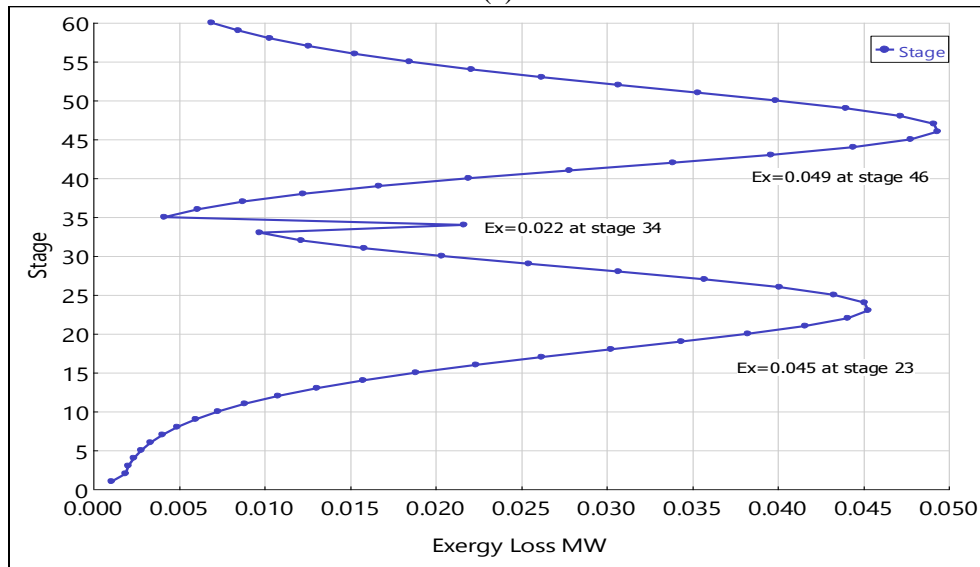
Figure 5.7 Column 3 base case operation with: $N=60$; $NF=35$; $RR=4.75$; N : number of total stages; NF is the feed stages, and RR is the reflux ratio. (a) CGCC (stage-H), (b) exergy loss profile, and (c) hydraulic analysis.

Using the NQ curve approach which is presented in Table A7 within the appendix A, column 3 has been modified with: $N=66$; $NF=35$; $RR=4.49$. Figure 5.8 shows the CGCC (stage-H) and exergy profiles after these modifications. The change in hydraulic analysis

is negligible. Table 5.4 compares the sustainability metrics for the base case and modified case operations. The reduction in energy usage, energy cost, and exergy losses are achieved after the modifications. The sustainability metrics indicate that the total exergy losses and total CO₂ emissions are reduced around 17.4% and 20%, respectively.



(a)



(b)

Figure 5.8. Modified case operation for column 3 with: $N=66$; $NF=35$; $RR=4.49$; N : number of total stages; NF is the feed stage, and RR is the reflux ratio. (a) CGCC (stage-H), and (b) exergy loss profiles.

Table 5.4 Sustainability metrics for column 3 with modifications: N=66; NF=35; RR=4.49.

Material intensity	Column 3		
	Base Case	Modified Case	Change %
Feed rate (mt/day)	3,293.62	3,293.62	0
Distillate rate (mt/day)	1,929.82	1,929.82	0
Bottoms rate (mt/day)	1,363.80	1,363.80	0
Energy intensity metrics			
Condenser duty, kJ/day/(mt/day distillate), kJ/mt	-1,692,980.11	-1,570,571.68	-7.23
Reboiler duty, kJ/day/(mt/day of bottoms), kJ/mt	2,039,871.18	1,845,170.26	-9.54
Condenser duty cost, \$/day/(mt/day of distillate), \$/mt	28.66	26.59	-7.22
Reboiler duty cost, \$/day/(mt/day of bottoms), \$/mt	6.47	5.85	-9.58
Total exergy loss, kJ/day/(mt/day ethylene), kJ/mt	75,290.97	62,187.83	-17.40
Environmental impact metrics			
Condenser CO ₂ emission ¹ , mt/day/(mt/day distillate)	0.09	0.08	-11.11
Reboiler CO ₂ emission ¹ , mt/day/(mt/day bottoms)	0.11	0.10	-9.09

¹Emission based on US-EPA-Rule-E9-5711, natural gas.

The side reboiling or condensing is the modification which is not applied in this study because it does not show the desired results.

5.4 Economic Analysis

Table 5.5 shows the estimated thermodynamic efficiency and the energy savings based on electricity, which is around \$2 million against the fixed capital cost of around \$624,600 (U.S. \$- 2014). This considerable energy saving, especially from reduction in exergy losses, also leads to the considerable CO₂ reductions as shown in Tables 5.6 and 5.7; the total reductions in the cold utility is around is 5.1%; the total reductions in the hot utility is

around 4.5%. Table 8 shows that the total reductions in the emission of CO₂ is around 19.0%. Table 5.8 shows the approximate total capital costs of \$666,800 for the retrofits. The hot utility for the feed conditioning of columns 1 and 2 has been counted in Table 5.8.

Table 5.5 Estimated efficiencies and energy savings for the three columns.

Base Case				Modified Case						
System	Ex_{\min} (MW)	Ex_{loss} (MW)	η %	Ex_{\min} (MW)	Ex_{loss} (MW)	η %	Saved Ex_{loss} (MW)	Change Ex_{loss} %	FCC ¹ of Retrofits \$	Electricity Saving ² (\$/year)
Col.1	-2.63	1.85	62.4	-2.48	0.12	95.2	1.46	92.2	100,600	964,038
Col.2	-1.72	3.73	31.5	-1.69	2.34	41.9	1.38	37.1	186,000	911,214
Col.3	0.77	1.68	31.4	0.97	1.39	41.0	0.29	17.1	338,000	191,487
Total									624,600	2,066,739

Ex_{loss} : Total column exergy loss from the converged simulation by Aspen Plus with the SRK method.

¹FCC: Fixed capital cost.

²Electricity equivalent of energy saving is based on a unit cost of electricity of \$0.0775/kW-hr.

Table 5.6 Estimated total reductions in hot and cold duties, and exergies for the three columns.

Base Case				Modified Case			
System	Condenser (kW)	Reboiler (kW)	Exergy (kW)	Condenser (kW)	Reboiler (kW)	Feed conditioning (kW)	Exergy (kW)
Col.1	-296.23	9327.48	1585.00	-286.83	8769.74	548.28	124.34
Col.2	-6384.75	16260.30	3726.13	-6839.19	11123.40	5591.27	2343.95
Col.3	-37814.20	32198.80	1681.69	-35080.10	29125.50	—	1389.02
Total	-44495.18	57786.58	6992.82	-42206.12	49018.64	6139.55	3857.31

Table 5.7 Estimated total reductions in CO₂ emissions for the three columns.

Base Case		Modified Case
System	CO ₂ emissions (mt/day)	CO ₂ emissions (mt/day)
Col.1	46.47	46.37
Col.2	109.35	113.61
Col.3	388.08	310.03
Total	543.90	470.01

Table 5.8 Approximate total costs of the retrofits and duty.

Retrofits	Type	Duty (kW)	P (bar)	Material	Area (m ²)	Total cost (\$)
Col. 1 heater	S/T ¹ fixed	550.0	36.88	Carbon steel	4.40	9,900
Col. 1 retrofit						110,500
Col. 2 heater	S/T ¹ fixed	5,590.0	34.47	Carbon steel	60.17	11,200
Col. 2 retrofit						197,200
Col. 3 retrofit						338,000
Total						666,800

¹S/T: Fixed shell and tube.

5.5. Conclusions

As distillation columns are highly energy intensive processes, tools for reducing the energy consumptions, and hence the carbon emissions through reasonable retrofits are highly valuable for petrochemical industry. One such tool, based on the thermodynamic analysis, is the Column Targeting Tool with capabilities of thermal and hydraulic analyses, which are applied to the back end separation of an ethylene plant. By using the CTT, it is possible to assess the operations with the current and modified configurations. Best possible column retrofits may be obtained by using the modifications on feed conditioning, feed stage, and reflux ratio. This analysis also includes the carbon tracking using an appropriate standard and a primary fuel. Using thermodynamic analysis, higher thermodynamic efficiencies are obtained for all the three columns, and the energy savings due to these modifications are about \$2 millions/year (2014 U.S. \$) after a one time fixed capital cost of \$664,000. The reduction in total hot and cold utilities is around 10%. Besides, the reduction in carbon emission is around 14%. The results illustrate that it may be possible to achieve a sustainable distillation operation by simple retrofits determined by thermodynamic analysis. However, care has to be exercised as the thermodynamic analysis

is a methodology based of tradeoffs among the complex competing factors and mainly leads to thermodynamic optimum, which may not always lead to monetary optimum.

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CHAPTER 6. CRUDE OIL REFINERY

Abstract

This Chapter presents assessments for some of the sustainability metrics for a crude oil refinery consisting three distillation columns after the retrofits suggested by thermodynamic analysis and energy analyzer. The main objective is to explore the scope of reducing the energy consumption and CO₂ emissions for a more sustainable operation. Thermodynamic analysis is carried out by using the thermal analysis capability of ‘Column Targeting Tool’ to address the ‘energy intensity,’ and the ‘Energy Analyzer’ to design and improve the performance of the heat exchanger network system for process heat integration. Environmental pollution impact metrics are estimated from the ‘Carbon Tracking’ options with a selected CO₂ emission data source of US-EPA-Rule-E9-5711 using crude oil as the primary fuel. The results indicate that column targeting tool, energy analyzer, and carbon tracking can estimate some of the sustainability metrics of an existing design and determine the scope of improvements for reducing the costs of energy required and emissions of carbon dioxide in a crude oil refinery operation.

6.1. Introduction

A typical distillation column resembles a heat engine delivering separation work by using heat at a high temperature in the reboiler and discharging most of it to the environment at a lower temperature in the condenser [1-4]. One of the thermodynamic methodologies to assess the distillation column operation is the Column Targeting Tool (CTT), which is based on the Practical Near-Minimum Thermodynamic Condition (PNMTC) approximation representing a practical and close to reversible operation [5-10].

CTT exploits the capabilities for thermal and hydraulic analyses of distillation columns [11-15] to identify the targets for possible retrofits by the following modifications: 1) feed stage location, 2) reflux ratio, 3) feed conditioning, and 4) side condensing and/or reboiling. Some of these retrofits may improve the overall energy efficiency of the refinery and reduce the carbon emissions and the cost of energy consumption. The ‘Carbon Tracking’ options of the Aspen Plus can help estimate the reduction in CO₂ equivalent (CO_{2e}) emissions [1].

Sustainability has environmental, economic, and social dimensions and requires the responsible use of energy resources and reduction in CO_{2e} emission. The three intersecting dimensions illustrate the 3D-sustainability metrics that include material and energy intensities related to nonrenewable material and energy usage, toxic, and pollutant emissions per unit mass of the product [16-20]. Therefore, a comparative assessment of the sustainability metrics for the base and modified cases obtained from thermodynamic analysis may prove useful in assessing the extent of reductions in the energy consumptions and emission of CO₂ for the three interacting columns of a typical crude oil refinery operation. The energy metrics are estimated from the CTT, while the carbon emission from the data source of US-EPA-Rule-E9-5711 using crude oil as the fuel source. A heat exchanger network system for the process heat integration is suggested by using the energy analyzer.

6.2. Crude Oil Refinery

Crude oil refinery mainly consist of three PetroFrac columns as shown in Figure 3. An 80% of Arabian light from Ras Tanura with an API gravity of 33.4, and 20% of Arabian

medium from Khurasaniya oil field with an API gravity of 28.5 are blended to form a mixed oil feed with an API gravity of 32.63. A 5228.42 bbl/hr of mixed crude enters the preflash column to produce 12670.9 bbl/hr lights, 13.20 bbl/hr water, and 756.14 bbl/hr naphtha in the distillate. Preflash bottom produces a mixture of 4102.35 bbl/hr that fed to main crude column at 229 °C. The crude column produces 387.44 bbl/hr of heavy naphtha, 584.38 bbl/hr of kerosene, 716.06 bbl/hr of diesel, and 470.59 bbl/hr of automotive gas oil (AGO); the bottom produces 2070.34 bbl/hr mixture that enters the vacuum distillation unit (VDU) column at 358 °C, The VDU produces 475.334 bbl/hr of light vacuum gas oil (LVGO), 905.39 bbl/hr of heavy vacuum gas oil (HVGO), and 629.509 bbl/hr of residue.

However, as discussed in Chapter 4, the available and required hot streams were matched to get the PFD as shown in Figure 6.1. Figure 6.1 shows the refinery operation with process heat integration where the hot streams provide heat for the cold streams through the flow arrangements in newly installed shell and tube heat exchangers. Figure 6.2 shows the pinch temperatures of 350.7 °C for hot (solid line) composite curve, and 341.7 °C for cold (dashed line) composite curve to get $\Delta T_{\min} = 9$ °C. As a result, furnace duty and CO₂ emissions were reduced for all three columns, more details will be provided in Section 6.1.

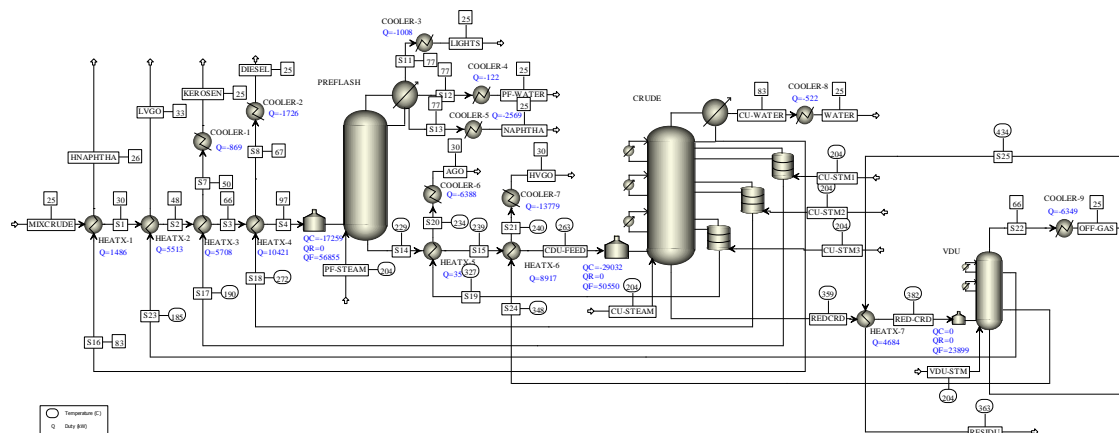


Figure 6.1 Process flow diagram after using newly installed heat exchangers in order to match the available and required heats. All the heat duties required by the heat exchangers are in kW and inlet and outlet temperatures are in °C.

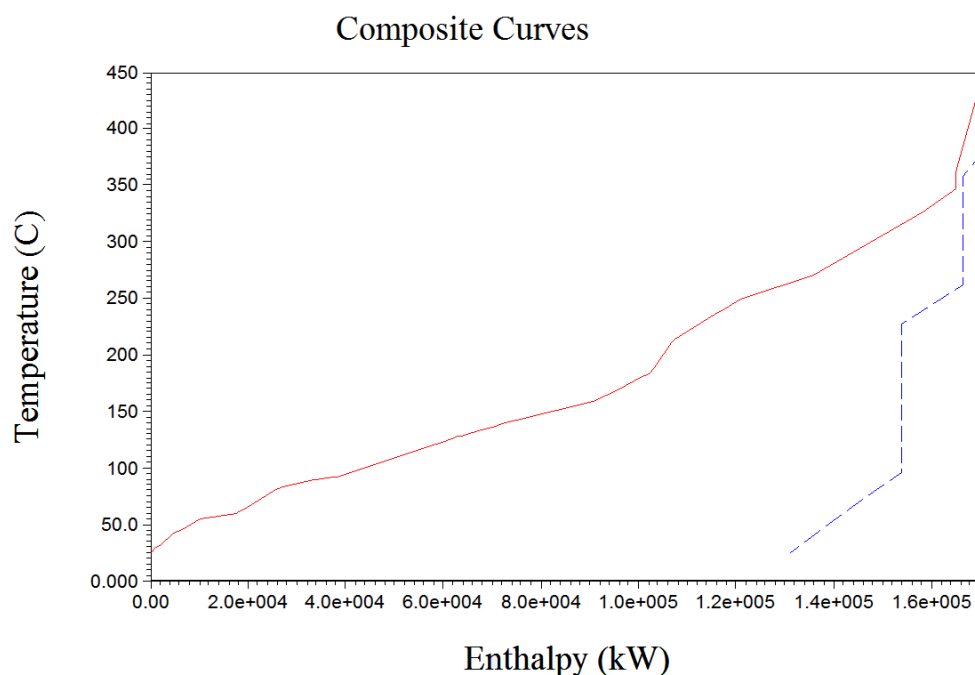


Figure 6.2 Composite curve diagram for the process with the hot composite curve and the cold composite curve.

6.3. Result and Discussion

The thermal analysis capability of the column targeting tool is used to estimate and reduce the column reboiler and condenser duties and stage exergy losses. The carbon

tracking with a selected fuel source is used to estimate the carbon dioxide equivalent emissions due to the utilities for all the columns. The modified case operations with the determined scope of retrofits are compared with the base case operations to analyze and assess the impacts of retrofits in the selected sustainability metrics. In this section each column will be assessed using the thermodynamic analysis and energy analyzer to determine which type of modifications may be applied to reach a more sustainable operation.

6.3.1. Preflash column

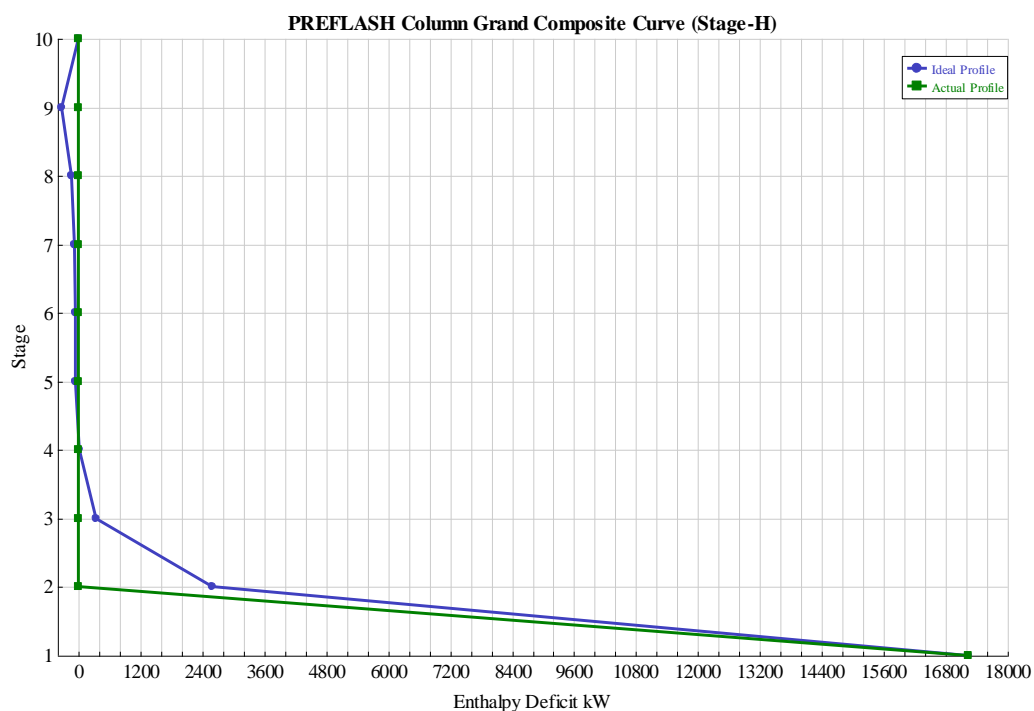
Figure 6.3 shows the (stage-H) CGCC, and exergy loss profiles for the preflash column performance. The stage-H CGCC in Figure 6.3a shows that operation is close to optimum for most of the stages, except the sharp enthalpy change in stage 1 (the condenser side). This requires normally either lowering the feed temperature or moving the feed stage toward reboiler. However, changing the furnace temperature has caused reduction in the naphtha production rate. Moreover, because of petrofrac configuration with the built-in furnace, feed location modification is not recommended. Figure 6.3a shows that there is no distance between the pinch point and ordinate and hence there is no need for the reflux ratio modification. Similarly, the closeness of the actual and ideal operations in most of the column height, the side heating or cooling modifications are not needed. Figure 6.3b shows higher exergy losses in stage 1 (condenser stage) and at the bottom where steam is injected. These losses result from the high temperature differences between the internal and external streams at the top and bottom of the column.

Using the process heat integration (Figure 6.4), the available hot streams from the crude and vacuum distillation units are used to gradually increase the feed temperature from 25 °C to 97 °C by using heat exchangers network system (HENS) which is summarized in Table 6.1. The major effects of this modification are the reduction in furnace duty of 1.16 MW as well as heating the feed (MIXCRUDE) without any external heat duty. Newly installed four heat exchangers have recovered 23.12 MW from the product streams in order to heat the feed stream. Tables 6.2 compares the sustainability indicators for material, energy, and environmental impact for the base case and modified case; there is no change in the material intensity, while the indicators for energy and environmental impact are reduced because of modifications. Table 6.3 shows how the preflash modifications affect material, energy, and environmental impacts metrics, which are obtained by normalizing the indicators per unit mass of product. The energy metrics show a reduction in the furnace duty by about 2%, and a total reduction in heating duty for the feed of mixed crude oil of about 146 MJ/mt. The environmental metrics shows a total reduction of 0.031kg of CO₂e/kg feed.

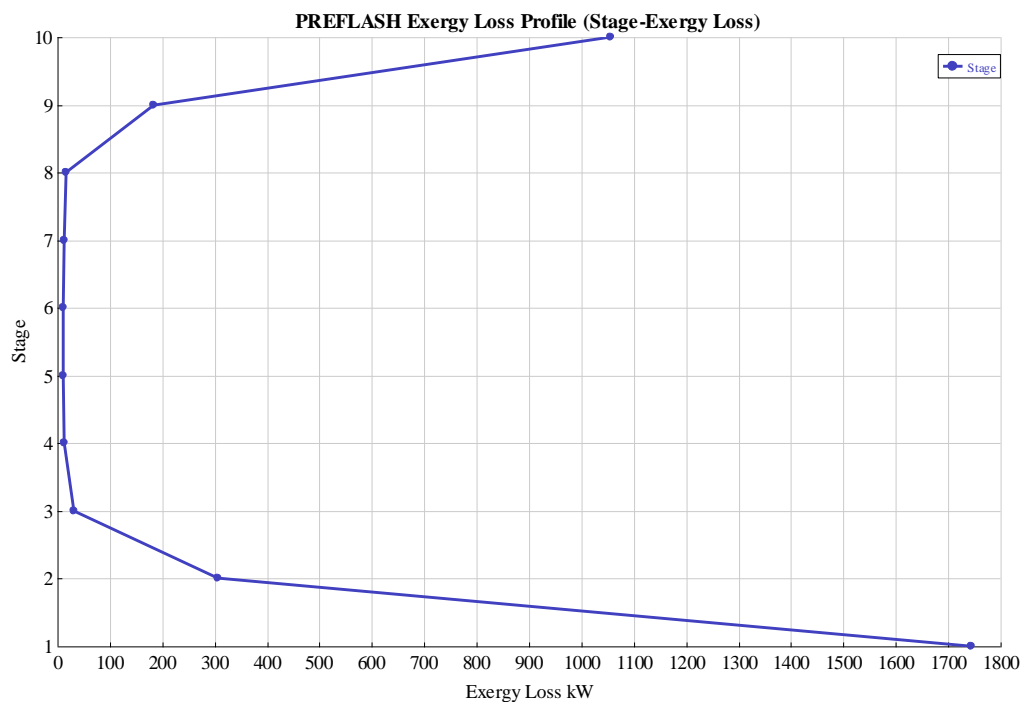
Table 6.1 Heat exchanger network system around preflash column.

Heat Exchanger	Duty (MW)	Hot		Cold		Area (m ²)	Hot Side Fluid	Cold Side Fluid	U* (W/m ² K)
		T _{in} (°C)	T _{out} (°C)	T _{in} (°C)	T _{out} (°C)				
Heatx-1	1.486	184.7	33.4	29.9	47.9	812.1	HNAPHTHA	MIXCRUDE	147.6
Heatx-2	5.513	190.0	49.1	47.9	65.7	551.8	LVGO	MIXCRUDE	275.8
Heatx-3	5.708	272.4	66.3	65.7	96.6	577.6	KEROSEN	MIXCRUDE	374.8
Heatx-4	10.411	49.1	25.0	18.0	23.0	858.0	DIESEL	MIXCRUDE	379.7
Cooler-1	0.869	66.3	25.0	18.0	23.0	90.3	KEROSEN	CW	747.4
Cooler-2	1.725	183.5	76.7	18.0	23.0	147.5	DIESEL	CW	635.1
Cooler-3	0.996	76.7	25.0	18.0	23.0	93.0	LIGHTS	CW	479.2
Cooler-4	0.122	76.7	25.0	18.0	23.0	2.7	WATER	CW	2118.3
Cooler-5	2.569	76.7	25.0	18.0	23.0	136.6	NAPHTHA	CW	876.0

*Overall heat transfer coefficient used in the Aspen Plus [1].



(a)



(b)

Figure 6.3 Preflash operation. (a) stage-H CGCC, (b) exergy loss profiles.

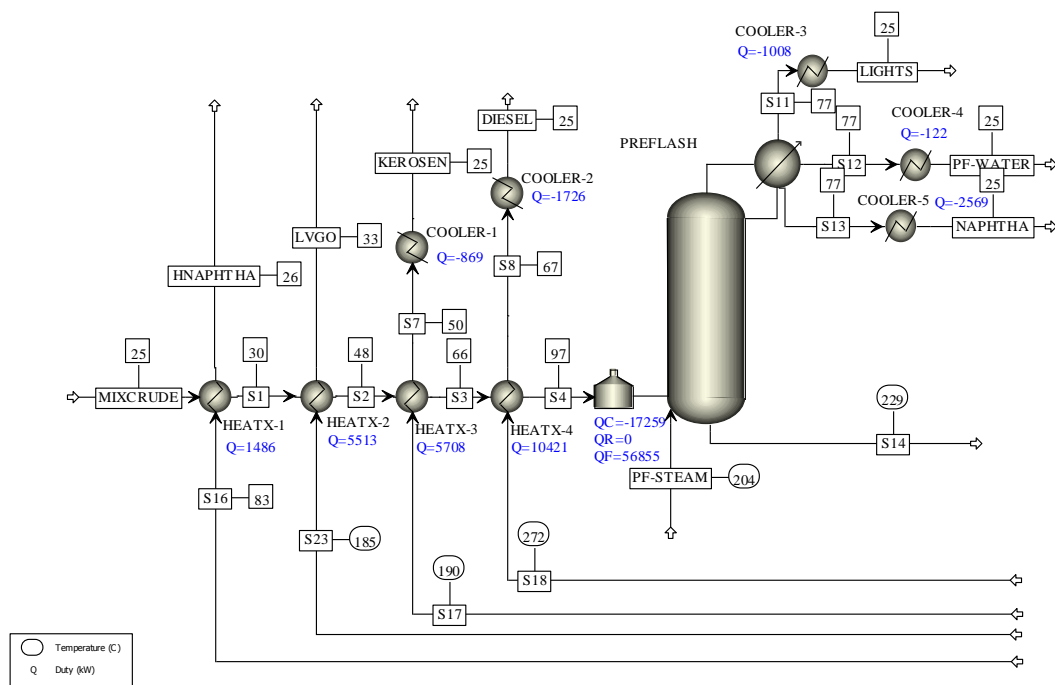


Figure 6.4 Process heat integration around preflash column.

Table 6.2 Sustainability indicators for the preflash with the process heat integration and feed conditioning: $T_F = 25\text{ }^{\circ}\text{C} \rightarrow 97\text{ }^{\circ}\text{C}$; T_F : feed temperature.

Indicators	Preflash column		
	Base case	Modified case	Change %
Material intensity (mt/hr)			
Feed rate	569.98	569.98	–
Distillate rate (Lights+Water+Naphtha)	89.73	89.73	–
Bottoms rate	480.47	480.47	–
Energy intensity^a (MW)			
Cold utility	17.24	17.24	–
Hot utility (furnace + PF-STEAM)	59.75	58.60	–1.92
Total process heat integration (heat-x: 1-4)	–	–23.11	–100.0
Total exergy loss	1.05	1.05	–
Cost (\$/hr)			
Cold utility	148.66	148.66	–
Hot utility (furnace + PF-STEAM)	903.25	885.63	–1.92
CO ₂ e fee ^b (hot utility)	198.73	194.90	–1.92
Environmental impact: CO₂e emissions^c (mt/hr)			
Hot utility (furnace + PF-STEAM)	19.87	19.49	–1.98
Reduced CO ₂ e due to process heat integration	–	–7.21	–100.0

^aReduced amount of feed duty; ^bcarbon fee is assumed to be \$10/mt; ^creduced emission based on US-EPA-Rule-E9-5711 and crude oil as ultimate fuel.

Table 6.3 Sustainability metrics for preflash with the process heat integration and feed conditioning: $T_F = 25\text{ }^{\circ}\text{C} \rightarrow 97\text{ }^{\circ}\text{C}$; T_F : feed temperature.

Sustainability metrics	Preflash column		
	Base Case	Modified Case	Change %
Material intensity (mt/hr)/(mt/hr)			
Feed/Distillate	6.35	6.35	–
Feed/Bottoms rate	1.18	1.18	–
Energy intensity (MJ/mt)			
Cold utility/Distillate	691.86	691.86	–
Hot utility/Feed	377.41	370.14	–1.95
Total process heat integration (heatx1-4)/feed	–	–146.01	–100.0
Total exergy loss/product	18.26	18.26	–
Cost, (\$/mt)			
Cold utility cost/Distillate	1.65	1.65	–
Hot utility cost/Feed	1.58	1.55	–1.95
CO ₂ e fee (hot utility)/Feed	0.35	0.34	–1.95
Environmental impact: CO₂e emission/product (mt/hr)/(mt/hr)			
Hot utility (furnace + PF-STEAM)/Feed	0.0348	0.0342	–1.95
Total process heat integration (heatx1-4)/Feed	–	–0.0310	–100.0

6.3.2. Crude column

Figure 6.5 shows the stage-H CGCC, and exergy loss profiles for the base case operations of the crude column. The stage-H CGCC shown in Figure 6.5a displays sharp enthalpy changes toward the condenser side through the stages between 1 and 13. This requires normally either lowering the feed temperature or moving the feed stage toward reboiler in a conventional column. Moving the feed stage to toward the reboiler is more convenient because reducing the furnace temperature will reduce the heavy naphtha production; therefore, feed stage is moved to be at stage 23 instead of stage 22. Furthermore, the stage-H CGCC displays sharp enthalpy changes on stages 6, 8, 13, and 14 where the pumparounds are installed. Therefore, pumparound stages should be moved down the column toward bottom stage. Figure 6.5b shows the exergy loss is higher in the condenser and bottoms side mainly due to steam injection at the bottom and the working configurations of the crude unit, which should be preserved for the required outputs. The moderated exergy losses around the pumparounds stages suggest modifying the pumparounds draw and return stages.

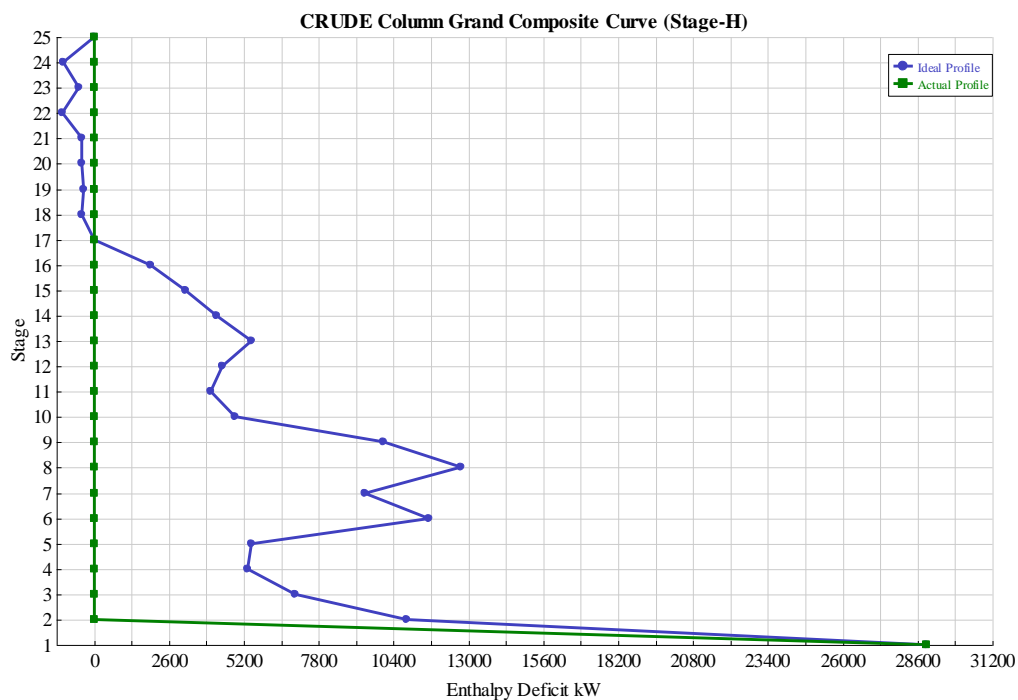
Besides applying the process heat integration (Figure 6.6), the available hot streams from the crude and vacuum distillation units are used to gradually increase the feed temperature from 228 °C to 263 °C by using the HENS that is summarized in Table 6.4. The major effects of this modification are the reduction in the duty used in furnace by 12.11 MW as well as heating the feed (CDU-FEED) without any external heat duty. Newly installed two heat exchangers have recovered 12.49 MW from the product streams in order to heat the feed stream. Table 6.5 compares the sustainability indicators and metrics for material, energy, and environmental impact for the base case and modified case; there is

negligible change in the material intensity due to the change of operation conditions, while the indicators for energy and environmental impact are reduced because of modifications. Table 6.6 shows how the crude modifications affect material, energy, and environmental impacts metrics, which are obtained by normalizing the indicators per unit mass of product. The energy metrics show a reduction in the furnace duty by about 19%, and a total reduction in heating duty for the feed of mixed crude oil of about 93.62 MJ/mt. The environmental metrics shows a total reduction of 0.0064 kg of CO₂e/kg feed.

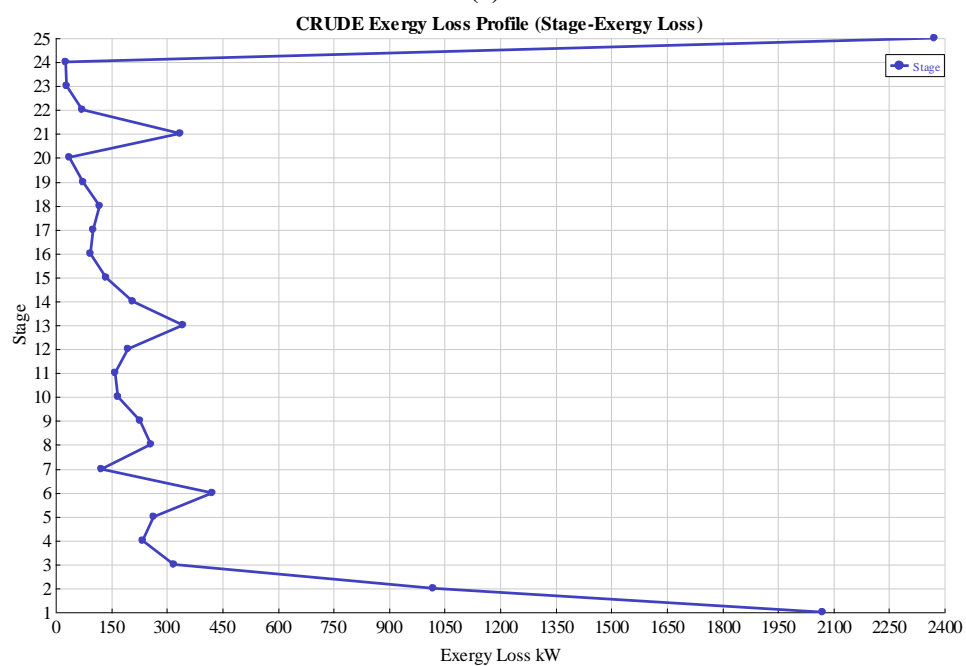
Table 6.4 Heat exchanger network system around the crude column.

Heat exchanger	Duty (MW)	Hot		Cold		Area (m ²)	Hot side fluid	Cold side fluid	U^* (W/m ² K)
		T_{in} (°C)	T_{out} (°C)	T_{in} (°C)	T_{out} (°C)				
Heatx-5	3.579	327.2	232.7	228.7	238.5	297.4	AGO	FEED	472.3
Heatx-6	8.916	347.9	239.9	238.5	262.8	1122.2	HVGO	FEED	439.2
Cooler-6	6.386	232.7	30.0	18.0	23.0	159.1	AGO	CW	556.6
Cooler-7	13.770	239.9	30.0	18.0	23.0	814.5	HVGO	CW	228.0
Cooler-8	0.522	83.1	25.0	18.0	23.0	10.6	CU-WATER	CW	2124.4

*Overall heat transfer coefficient used in Aspen Plus [1].



(a)



(b)

Figure 6.5 Base case operation for crude unit with $T_F=129\text{ }^{\circ}\text{C}$; $N_F=22$; PA-1 Draw at stage 8 return to stage 6, PA-2 Draw at stage 14 return to stage 13; T_F : feed temperature, N_F : feed stage, and PA: pumparound. (a) CGCC (stage-H), (b) exergy loss profiles.

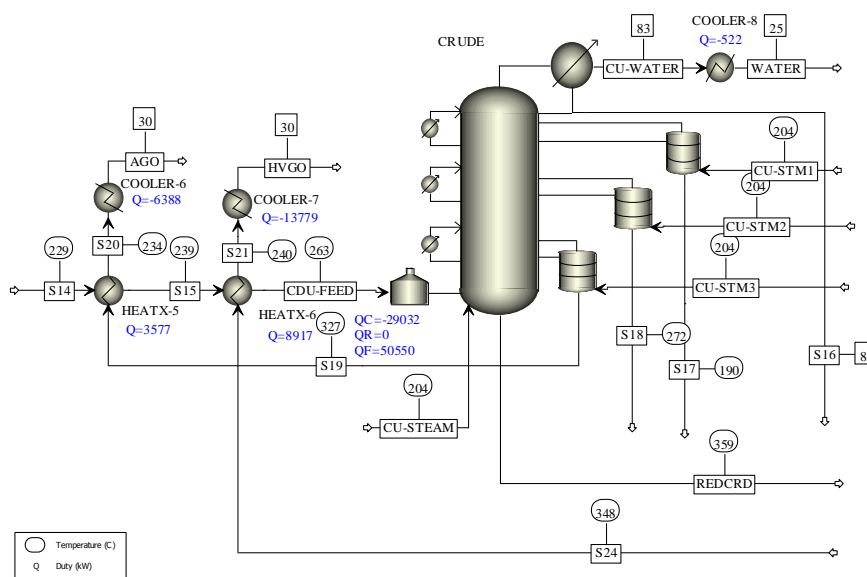


Figure 6.6 Process heat integration around crude column.

Table 6.5 Sustainability indicators for crude with the process heat integration and feed conditioning: $T_F=228\text{ }^{\circ}\text{C} \rightarrow 263\text{ }^{\circ}\text{C}$; $N_F=22 \rightarrow 23$; PA-1 Draw at stage 8 return to stage 6 \rightarrow Draw at stage 12 return to stage 10, PA-2 Draw at stage 14 return to stage 13 \rightarrow Draw at stage 17 return to stage 16.

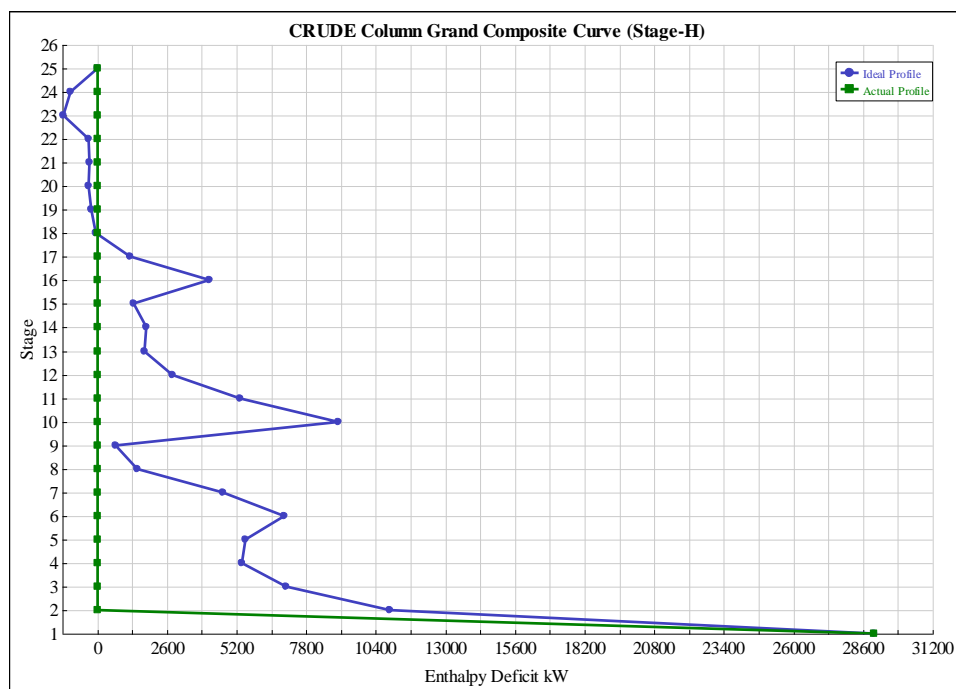
Indicators	Crude column		
	Base case	Modified case	Change %
Material intensity, (mt/hr)			
Feed rate	480.47	480.47	–
Distillate rate (Heavy Naphtha)	42.80	42.81	+0.03
Kerosene	62.68	62.68	+0.01
Diesel	75.11	74.56	–0.72
Ago	49.90	49.90	–
Bottoms rate	249.99	250.51	+0.21
Energy intensity^a, (MW)			
Cold utility	28.89	29.00	+0.37
Hot utility (furnace + CU-STEAM) 4.177	66.838	54.74	–19.29
Total process heat integration (heat-x: 5-6)	–	–12.49	–100
Total exergy loss	9.41	8.76	–6.87
Cost, (\$/hr)			
Cold utility	249.06	499.96	+0.36
Hot utility (furnace + PF-STEAM)	972.31	787.35	–19.29
CO ₂ e fee ^b (hot utility)	218.02	168.20	–19.29
Environmental impact: CO₂e emission^c, (mt/hr)			
Hot utility (furnace + CU-STEAM)	22.23	18.20	–19.29
Total reduced CO ₂ e due to process heat integration	–	3.11	–100

^aReduced amount of feed duty; ^bcarbon fee is assumed to be \$10/mt; ^creduced emission based on US-EPA-Rule- E9-5711 and crude oil as ultimate fuel.

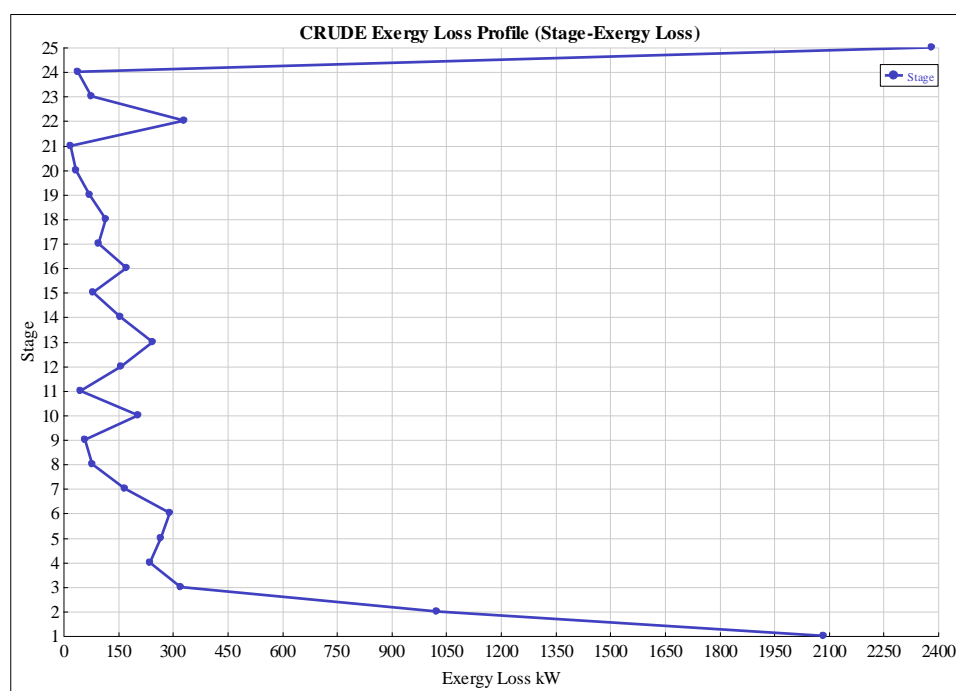
Table 6.6 Sustainability metrics for crude with the process heat integration and feed conditioning: $T_F=228\text{ }^{\circ}\text{C} \rightarrow 263\text{ }^{\circ}\text{C}$; $N_F=22 \rightarrow 23$; PA-1 Draw at stage 8 return to stage 6 \rightarrow Draw at stage 12 return to stage 10, PA-2 Draw at stage 14 return to stage 13 \rightarrow Draw at stage 17 return to stage 16.

Sustainability metrics	Crude column		
	Base case	Modified case	Change %
Material intensity (mt/hr)/(mt/hr)			
Feed/Distillate rate (Heavy Naphtha)	11.22	11.22	–
Feed/Kerosene	7.66	7.66	–
Feed/Diesel	6.39	6.44	–
Feed/Ago	9.62	9.62	–
Feed/Bottoms	1.92	1.92	–
Energy intensity (MJ/mt)			
Cold utility/Distillate	2430.06	2439.06	+0.37
Hot utility/Feed	469.51	378.92	–19.29
Total process heat integration (heat-x: 5-6)Feed	–	–93.62	–100
Total exergy loss/product	70.54	65.69	–6.87
Cost, (\$/mt)			
Cold utility cost/Distillate	5.84	5.84	–
Hot utility cost/Feed	2.02	1.63	–19.03
CO _{2e} fee (hot utility)/Feed	0.45	0.38	–19.35
Environmental impact (kg/hr)/(kg/hr)			
Hot utility (furnace + CU-STEAM)/Feed	0.046	0.037	–18.10
Total reduced CO _{2e} due to process heat integration/Feed	–	0.0064	–100

Figure 6.7a displays the modified CGCC (stage-H) with a negligible increase of heat deficits around the condenser stage, while it displays relatively less heat deficits around the pumparounds stages. Figure 6.7b shows the exergy loss profiles of the crude unit after the modifications.



(a)



(b)

Figure 6.7 Modified case operation for crude unit with $T_F=263\text{ }^{\circ}\text{C}$; $N_F=23$; PA-1 Draw at stage 12 return to stage 10, PA-2 Draw at stage 17 return to stage 16; T_F : feed temperature, N_F : feed stage, and PA: pumparound. (a) CGCC (stage-H), (b) exergy loss profiles.

6.3.3. Vacuum distillation column (VDU)

Figure 6.8 shows the (stage-H) CGCC, and exergy loss profiles for the VDU Performance. The stage-H CGCC shown in Figure 6.8a displays sharp enthalpy change in stages where the pumparound is installed. This requires either moving the pumparound up or down, but due to the small number of stages this modification is not recommended. Figure 6.8b shows that the exergy loss is higher at the bottom mainly due to direct steam injection. As there is no reflux in the preflash column, a possible modification based on reflux ratio is not recommended. As there is no reflux in the preflash column, a possible modification based on reflux ratio is not recommended.

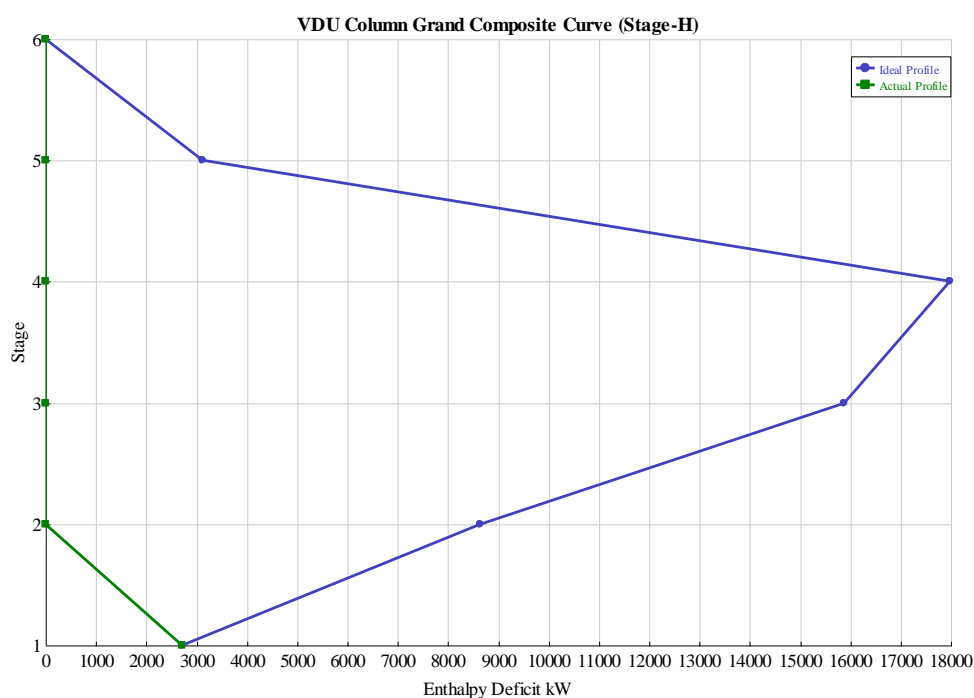
For the process heat integration (Figure 6.9) there is only one available hot stream from the vacuum distillation unit which is used to increase the feed (RED-CRD) temperature from 358 °C → 382 °C by using HENS summarized in Table 6.7. The major effects of this modification is the reduction in furnace duty of 5.02 MW as well as for heating the feed (RED-CRD) without any external heat duty. Newly installed heat exchanger have recovered 4.69 MW from the product streams in order to heat the feed stream. Table 6.8 compares the sustainability indicators for material, energy, and environmental impact for the base case and modified case; there is negligible change in the material intensity due to the new operation conditions, while the indicators for energy and environmental impact are reduced because of modifications. Tables 6.8 and 6.9 shows how the VDU modifications affect material, energy, and environmental impacts metrics, which are obtained by normalizing the indicators per unit mass of product. The energy metrics show a reduction in the furnace duty by about 14%, and a total reduction in heating duty for the feed of

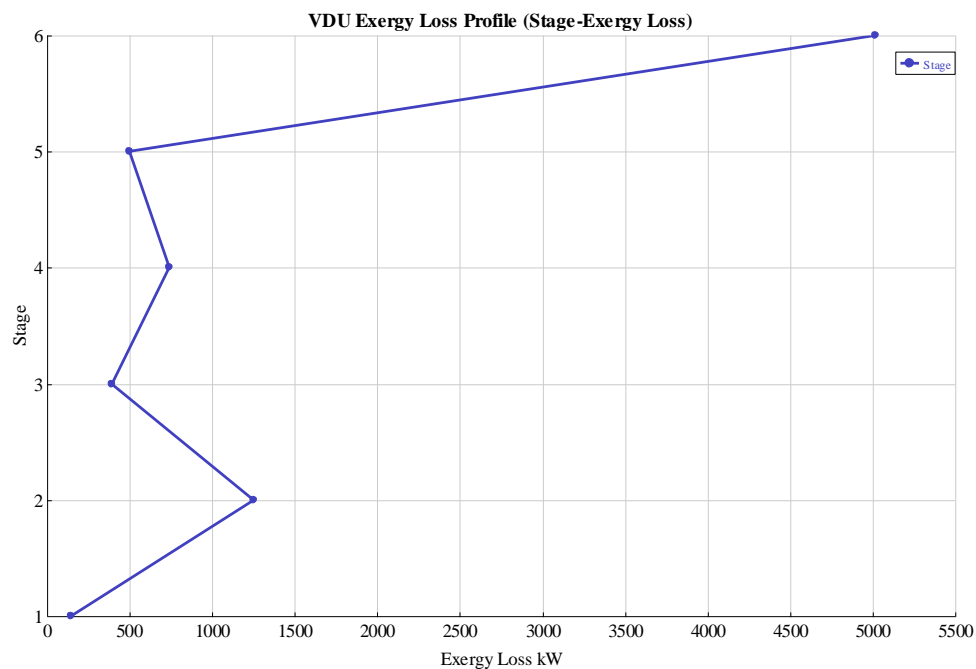
mixed crude oil of about 0.067 MJ/mt. The environmental metrics shows a total reduction of 0.0571kg of CO₂e/kg feed.

Table 6.7 Heat exchanger network system for the vacuum distillation column.

Heat Exchanger	Duty (MW)	Hot		Cold		Area (m ²)	Hot Side Fluid	Cold Side Fluid	U^* (W/m ² -K)
		T_{in} (°C)	T_{out} (°C)	T_{in} (°C)	T_{out} (°C)				
Heatx-7	4.688	434.4	363.6	359.4	382.3	871.8	RESIDU	REDCRD	330.7
Cooler-9	6.349	65.6	25	18	23	908.4	OFF-GAS	CW	209.4

*Overall heat transfer coefficient used in Aspen Plus [8].





(b)

Figure 6.8 VDU operation with $T_F=342\text{ }^{\circ}\text{C}$, $T_{Fr}=451\text{ }^{\circ}\text{C}$; T_F : feed temperature, and T_{Fr} : furnace temperature. (a) CGCC (stage-H), (b) exergy loss profiles.

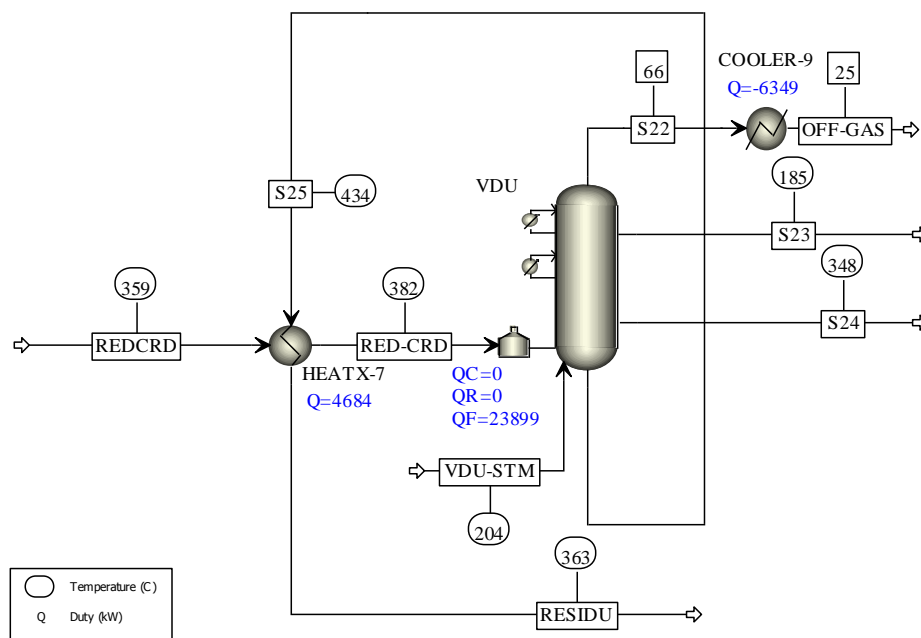


Figure 6.9 VDU column process heat integration.

Table 6.8 Sustainability indicators for the vacuum distillation column with the process heat integration and feed conditioning: $T_F=358\text{ }^{\circ}\text{C} \rightarrow 382\text{ }^{\circ}\text{C}$.

Indicators	Vacuum distillation unit		
	Base Case	Modified Case	Change %
Material intensity, (mt/hr)			
Feed rate	249.99	250.51	+0.21
Off gas rate	9.08	9.10	+0.21
LVGO rate	60.90	61.21	+0.50
HVGO rate	108.92	108.90	-0.01
RESIDU rate	80.15	80.35	+0.25
Energy intensity^a, (MW)			
Hot utility (furnace + PF-STEAM)	35.83	30.81	-14.01
Total process heat integration (heat-x: 7)	–	-4.69	-100.0
Total exergy loss	8.05	8.08	+0.21
Cost, (\$/hr)			
Hot utility (furnace + VDU-STEAM)	505.10	428.31	-15.20
CO ₂ e fee ^b (hot utility)	119.33	102.63	-13.99
Environmental impact CO₂e emission^c, mt/hr)			
Hot utility (furnace + VDU-STEAM)	11.93	10.26	-13.99
Reduced CO ₂ e due to process heat integration	–	1.44	-100.0

^aReduced amount of feed duty; ^b carbon fee is assumed to be \$10/mt; ^creduced emission based on US-EPA-Rule-E9-5711 and crude oil as ultimate fuel.

Table 6.9 Sustainability metrics for VDU with the process heat integration and feed conditioning: $T_F=358\text{ }^{\circ}\text{C} \rightarrow 382\text{ }^{\circ}\text{C}$.

Sustainability metrics	Vacuum distillation column		
	Base Case	Modified Case	Change %
Material intensity (kg/hr)/(kg/hr)			
Feed/Off gas	27.52	27.52	–
Feed/LVGO	4.10	4.10	–
Feed/HVGO	2.29	2.29	–
Feed/RESIDU	3.12	3.12	–
Energy intensity (MJ/mt)			
Hot utility (furnace + PF-STEAM)/Feed	0.51	0.44	-13.9
Total process heat integration (heat-x: 7)/Feed	–	-0.067	-100.0
Total exergy loss/Product	0.11	0.11	+0.21
Cost, (\$/mt)			
Hot utility cost/Feed	2.02	1.70	-15.4
CO ₂ e fee (hot utility)/Feed	0.47	0.41	-14.1
Environmental impact (mt/hr)/(mt/hr)			
Hot utility (furnace + CU-STEAM)/product	0.047	0.040	-14.1
Reduced CO ₂ e due to process heat integration /product	–	0.057	-100.0

6.4. Economic Analysis

Tables 6.10 and 6.11 show the estimated thermodynamic efficiency and the energy savings based on electricity and operation hour of 8520 hr/yr. Saved energy is estimated to be around \$37,000,000/yr against the fixed capital cost of around \$5,293,900/yr; this is considerable energy saving, especially from the reductions of heat duty. On Pre-flash and VDU columns exergy loss is not saved and it cost around \$554.65/yr and \$22,740.73/yr respectively, and that is because of increasing the feed temperature of columns; however, increasing the feed temperature reduced the furnace duty as shown in Table 6.11. Table 6.12 shows the estimation of the annual utility cost that come from the additional coolers in the process.

Table 6.10 Estimated efficiencies and exergy savings for the three columns.

Base case				Modified case					
Unit	Ex_{\min} (kW)	Ex_{loss}^1 (kW)	η %	Ex_{\min} (kW)	Ex_{loss} (kW)	η %	Saved Ex_{loss} (kW)	Change Ex_{loss} %	Electricity Saving ² (\$/year)
Preflash	14836.6	3385.4	81.4	18229.5	3385.5	84.3	-0.8	0.005	-554.6
Crude	9749.9	9414.7	50.8	41015.9	8768.0	82.4	646.7	6.8	427,009.4
VDU	-3813.3	8051.7	31.1	-6210.5	8085.9	43.4	-34.4	0.3	-22,740.7
Total									403,714.0

¹ Ex_{loss} : Total column exergy loss from the converged simulation by Aspen Plus with the BK-10 method.

²Electricity equivalent of energy saving is based on a unit cost of electricity of \$0.0775/kW hr.

Table 6.11 Estimated duty savings for the three columns and heat exchangers.

Unit	Base case duty (kW)	Modified case duty (kW)	Saved duty (kW)	Change duty %	FCC ¹ of retrofits \$	Electricity saving ² (\$/year)
Pre-flash furnace	58012.6	56861.1	1151.6	1.9	–	760,388.2
Crude furnace	62661.6	50572.6	12089.0	19.3	–	7,982,386.5
VDU furnace	28918.5	23899.4	5019.2	17.3	–	3,314,171.1
Heatx-1	–	1486.2	1486.2	100	517,000	981,331.2
Heatx-2	–	5513.2	5513.2	100	432,000	3,640,379.1
Heatx-3	–	5707.8	5707.8	100	520,000	3,768,853.7
Heatx-4	–	10411.3	10411.3	100	617,000	6,874,581.4
Heatx-5	–	3578.8	3578.8	100	263,000	2,363,127.8
Heatx-6	–	8916.2	8916.2	100	512,000	5,887,386.6
Heatx-7	–	4692.8	4692.8	100	535,000	3,098,655.8
Total					3,396,000	38,671,261.8

¹FCC: Fixed capital cost with a CEPCI of 580.2 for September 2014 [21].

²Electricity equivalent of energy saving is based on a unit cost of electricity of \$0.0775/kW hr.

Table 6.12 Estimated utility cost for the coolers.

Unit	Base case duty (kW)	Modified case duty (kW)	Utility	FCC ¹ of retrofits \$	Utility cost (\$/year) ²
Cooler-1	–	869.2	CW	152,000	469,036.2
Cooler-2	–	1724.5	CW	189,000	1,011,501.2
Cooler-3	–	996.4	CW	154,000	38,355.3
Cooler-4	–	122.4	CW	65,000	63,837.6
Cooler-5	–	2569.4	CW	182,000	126,653.8
Cooler-6	–	6386.3	CW	195,000	73,183.3
Cooler-7	–	13772.5	CW	67,000	8,994.2
Cooler-8	–	522.2	CW	434,000	188,709.4
Cooler-9	–	6348.5	CW	459,000	466,245.0
Total				1,745,900	2,446,516.5

¹FCC: Fixed capital cost with a CEPCI of 580.2 for September 2014 [21].

²Cooling water indexed price is \$0.05/mt.

6.5. Conclusions

As an oil refinery is a highly energy intensive process, a methodology for reducing the energy consumptions, and hence the carbon emissions through reasonable retrofits can make the refinery industry more sustainable. One such methodology is based on the thermodynamic analysis and energy analyzer, which employ the ‘Column Targeting Tool’ with the capabilities of thermal and hydraulic analyses as well as the capabilities of pinch analysis and heat exchanger network system. This study also incorporates the ‘Carbon Tracking’ to assess and compare some of the sustainability metrics of the base and retrofitted (modified) refinery operations for the mixture of two Saudi Arabia crude oils. Some of the possible column retrofits may be obtained by using the modifications on feed conditioning, feed stage, and draw and return stages of pumparounds. Higher thermodynamic efficiencies are obtained for all the three columns; the energy savings due to these modifications are about \$37 millions/year (with Chemical Engineering Plant Cost Index (CEPCI–Sept. 2014 =580.2) after a one time fixed capital cost of about \$5.3 million. The results illustrate that it may be possible to achieve a more sustainable refinery process by simple retrofits determined by thermodynamic analysis and energy analyzer. However, thermodynamic analysis mainly leads to thermodynamic optimum, which may not always lead to monetary advantage and is a methodology based of tradeoffs among the complex competing factors.

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CHAPTER 7. METHANOL AND AMMONIA PRODUCTIONS

Abstract

This Chapter analyzes and compares the economics and sustainability aspects of two hydrogenation processes for producing methanol and ammonia by using wind-power based electrolytic hydrogen. The carbon dioxide comes from an ethanol plant for producing methanol, while the nitrogen is supplied by an air separation unit (ASU) for producing ammonia. The integral facilities of both the methanol and ammonia are evaluated by introducing a multi-criteria decision matrix to assess the impact of the usage of renewable and nonrenewable hydrogen. The capacities are 99.96 mt/day methanol and 1202.55 mt/day anhydrous ammonia. The methanol plant requires 138.37 mt CO₂/day and 19.08 mt H₂/day. The ammonia is synthesized by using 217.72 mt H₂/day and 1009.15 mt N₂/day. The production costs and the carbon equivalent emissions (CO₂e) associated with the methanol and ammonia processes, electrolytic hydrogen production, carbon capture and compression, and ASU are considered for economic and sustainability aspects of the two plants. The methanol is treated as a fuel, cycling the CO₂, and also as a chemical feedstock, fixing the CO₂. Discounted cash flow diagrams are established for both the methanol and ammonia plants to estimate the economic constraints, unit product costs, and unit costs of hydrogen. The hydrogen cost is the largest contributor to the economics of the plants. For the methanol, the values of emissions are -0.85 kg CO₂e/kg methanol as a chemical feedstock and +0.53 kg CO₂e/kg methanol as a fuel with complete combustion. For the ammonia, the value of emission is around 0.97 kg CO₂e/kg ammonia. The electrolytic hydrogen from wind power helps reduce the emissions; however, the cost of hydrogen at the current level adversely affects the feasibility of the plants. A process evaluation matrix

is proposed to balance the effects of economics and sustainability, providing a better evaluation of plant feasibility.

7.1. Introduction

Renewable hydrogen produced from electrolysis of water, using wind power, may serve as a feedstock for hydrogenation processes and hence chemical storage for renewable electricity [1-5]. This study compares economics and sustainability aspects of the hydrogenation processes for methanol and ammonia using renewable hydrogen. Hydrogen is a clean fuel, its burning causes no harmful emissions; however the cost to produce, store, compress, and transport of hydrogen is still high [6-12]. Hydrogenation of carbon dioxide and nitrogen can produce methanol and ammonia, respectively, and may store renewable energy (wind, solar, hydro) used in electrolytic hydrogen production [13-16]. Methanol may be used as a fuel and also a valuable feedstock for producing methyl t-butyl ether, dimethyl ether, dimethyl carbonate, formaldehyde, acetic acid and other chemical secondary intermediates which are used in producing plywood, particleboard, foams, resins and plastics [14,17-21].

Methanol production using fossil fuels, mainly natural gas and coal, is a mature technology [13]. Renewable hydrogen-based methanol as an alternative fuel is widely investigated by researchers worldwide [1,2,13,23-24]. CO₂ may come from flue gas, gasification of biomass, or ethanol plants [1,13,25]. Energy analysis of recycling CO₂ and reaction mechanisms of hydrogenation of CO₂ are some of the efforts toward non-fossil fuel-based methanol as a renewable energy storage and carrier [26-32]. Rihko-Struckmann et al. [33] carried out an energetic evaluation in order to assess the overall efficiency of methanol and hydrogen-based storage systems for renewable electric energy; the efficiency

of the system using hydrogen is higher compared with that of using methanol as storage medium; however, storage and handling of methanol as chemical storage is favorable when compared with H_2 [18-20,33-36].

The utilization of CO_2 as carbon source for chemical synthesis could have a positive but only marginal impact on the global carbon balance [1,14,15,17]. Because, we add 3500 million mt CO_2 /year worldwide, while we use only 110 million mt CO_2 /year to produce other chemicals (mainly urea); this is only around 3% usage of the CO_2 as feedstock [1,2,14,20,30]. On the other hand, the utilization of CO_2 in the fuel production or as a chemical storage of energy, such as methanol, could make a significantly larger impact, as only 16.8% of the world oil consumption was used in 2007 for non-energy purposes [14,17,36].

Like methanol, ammonia is another chemical from hydrogenation, a feedstock for manufacturing fertilizers such as urea, and may be considered as a chemical storage medium of renewable electricity [37-42]. Pure nitrogen for ammonia synthesis is produced using an air separation unit. In the U. S., about 98% of ammonia is produced by catalytic steam reforming of natural gas, while about 77% of world ammonia capacity is based on natural gas. The total energy consumption for the production of ammonia in a modern steam reforming plant is 40-50% above the thermodynamic minimum [40-42].

Since the synthesis of both ammonia and methanol requires hydrogen, this study is for the analyses and comparison of economics and sustainability aspects of renewable hydrogen-based methanol and ammonia productions. The analyses also include the processes wind-based electrolytic hydrogen production, carbon capture and compression from an ethanol plant, and an air separation process to produce nitrogen. Therefore, the integral facilities of both the methanol and ammonia are evaluated by introducing a multi-

criteria decision matrix to assess the impact of the usage of renewable and nonrenewable hydrogen.

7.2. Hydrogen Production

Currently, 96% of H_2 is produced directly from fossil fuels and about 4% is produced indirectly by using electricity generated through fossil fuels [53]. The conventional technologies are steam reforming of natural gas, coal gasification, and partial oxidation of hydrocarbons such as biomass. Renewable hydrogen comes from the electrolysis of water using hydropower, wind power, and solar photovoltaic power [54-56].

7.2.1. Hydrogen production from syngas

Commercial processes for H_2 production are based on syngas feedstock produced from natural gas steam reforming (Figure 7.1) and coal (or biomass) gasification (Figure 7.2) with carbon capture and storage. These processes are complex, sensitive to the feedstock quality, and require large investments for larger units. The generated CO can also be used in the water-gas shift reaction to yield more hydrogen. In these processes, however, at least 20% of the energy of the fossil fuel is lost as waste heat.

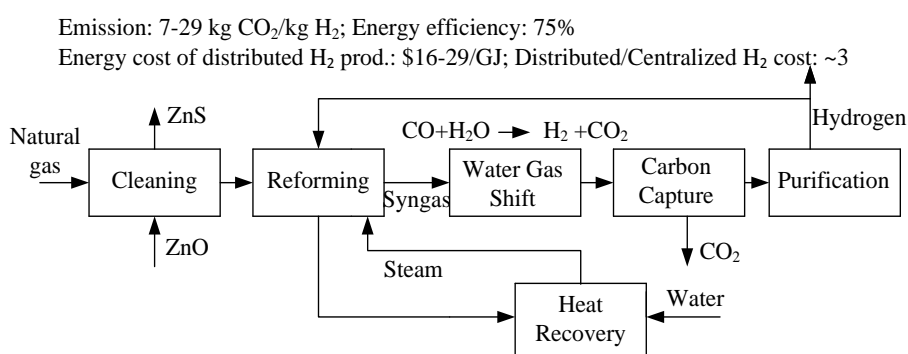


Figure 7.1 Hydrogen production by steam reforming of natural gas [53-58].

Energy efficiency for biomass-based H_2 production is around 60% and likely become competitive in the future [55]. A representative gasification reaction of biomass is $C_aH_b + O_2 \rightarrow H_2 + CO + CO_2 + H_2O$. Here the biomass reacts with oxygen supplied by an air separation unit (ASU) at 1150 °C-1400 °C and 400-1200 psig. Most modern plants purify the crude H_2 to 99.99-wt% by removing methane, CO_2 , N_2 , and CO using multi-bed pressure swing adsorption [53-59].

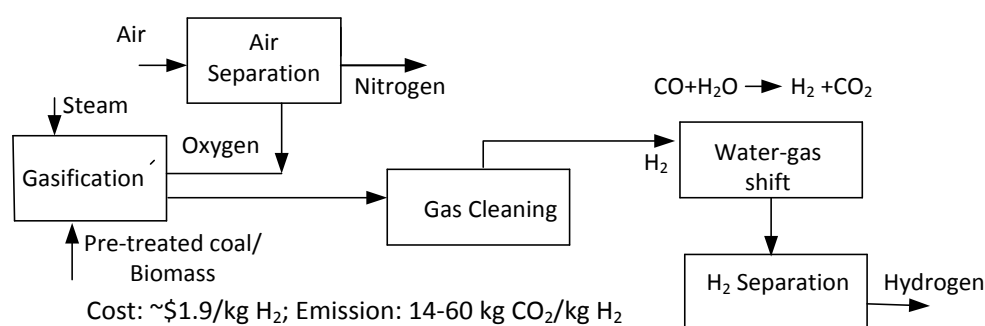


Figure 7.2 Hydrogen production by gasification of coal [53-58].

Current production of H_2 from natural gas and coal accounts for 48% and 18% of the total production, respectively. The emission of CO_2 varies between 7.33 kg CO_2 /kg H_2 and 29.33 kg CO_2 /kg H_2 using conventional fuels at about 75% energy efficiency. CO_2 emission (beside SO_x and NO_x) associated with producing H_2 from coal is about two-three times higher than that of the H_2 produced from natural gas [2,5-8,11,12].

7.2.2. Hydrogen production from water electrolysis

Renewable option is electro-chemical conversion by water electrolysis using electricity from renewable sources or nuclear power [48-50,53-58]. Figure 7.3 shows the schematic of wind power-based hydrogen production. Alkaline electrolysis technologies are the most mature commercial systems. The electrolyzer units use process water for electrolysis, and

cooling water for cooling. KOH is needed for the electrolyte in the system. The system includes the following equipment: transformer, thyristor, electrolyzer unit, feed water demineralizer, hydrogen scrubber, gas holder, two compressor units to 30 bar, deoxidizer, twin tower dryer (Figure 7.3) [5,48]. These electrolyzers have the energy efficiencies (57%-75%) based on higher heating value- HHV and 50–60% based on the lower heating value-LHV. The typical current density is 100–300 mA/cm² [12,48].

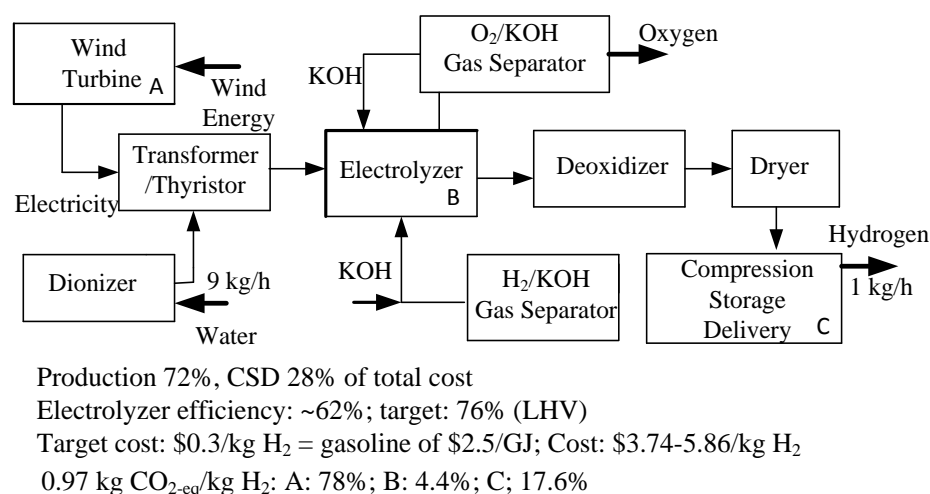


Figure 7.3. Schematic for alkaline electrolysis of water for hydrogen production with compression, storage and delivery [5-10,12,48,49,59].

The amount of total water used is 26.7 kg/kg H₂; electrolysis uses approximately 45%, while the manufacturing the wind turbines and the hydrogen storage consume around 38% and 17% of the total water used, respectively. The total greenhouse gas emission is 0.97 kg CO_{2e}/kg H₂, which is distributed as 0.757 kg CO_{2e}/kg H₂ (78%) for the wind turbine production and operation (because of steel and concrete used in its construction), 0.043 kg CO_{2e}/kg H₂ (4.4%) for the electrolyzer construction and operation, and 0.17 kg CO_{2e}/kg H₂ (17.6%) for the hydrogen compression and storage (mainly due to the production of steel used in the storage tanks) [59].

M-Langer et al. [54] evaluated hydrogen production processes based on natural gas steam reforming, coal and biomass gasification, and water electrolysis. H₂ production cost is around \$65/GJ using wind electricity, \$30/GJ using nuclear power, and \$600/GJ using photovoltaic electricity based on 2007 \$. Large-scale processes, using natural gas and coal, are the most economical processes while biomass gasification still needs technological improvements. The operating cost of an electrolyzer is driven by the energy efficiency and the cost of electricity. Energy efficiency needs to be increased to 76% from the current average of about 62%. The capital costs of wind-based H₂ are \$2086/kW (2011) and \$2067/kW (2012) for 50000 kg H₂/day for a centralized production plant. New classes of materials could be designed at the nanoscale to produce catalysts that are more selective, less prone to poisoning, and able to operate at lower temperatures [5-9]. High-temperature solid oxide electrolysis can use lower cost energy (in the form of steam) for water-splitting to decrease electricity consumption [12,48].

Wind power-based electrolysis production cost estimates are limited geographically and the base costs of H₂ range from \$3.74/kg H₂ to \$5.86/kg H₂. Capacities of H₂ productions range from 1,000 to 50,000 kg H₂/day [2-5]. Other factors such as large-scale storage, compression, pipeline transport, and dispensing economics need separate analyses [47-49]. Currently, the production of H₂ by electrolysis using renewable electricity is not competitive with chemical production methods based on fossil fuels. However, using the off-peak power could increase plant load factor and improve the economics [48,49,53]. Electrolytic H₂ may be more attractive for regions without access to natural gas or if H₂ is used as an energy storage medium [33,49].

The cost of electrolytic hydrogen depends on the cost of electricity as well as the capital cost of the electrolyzer systems and their operating efficiency. The current capital equipment cost for advanced electrolysis is between \$600/kW and \$700/kW. This cost needs to be reduced to \$200/kW to achieve \$2.75/GGE (untaxed gasoline gallon equivalent) by 2015 [48-50]. This shows around 60% improvement needed. Table 7.1 shows some electrolyzer types with their efficiencies. Higher efficiencies are possible with polymer electrolyte membrane (PEM) and solid oxide electrolytic cell (SOEC) electrolyzers, which are still under development. The primary research challenge is to reduce the capital and operating costs of electrolysis systems as the wind turbines are not designed to produce hydrogen from electrolyzers, which typically operate using constant direct current supply. Power control and conditioning may help optimize the efficient integration of electrolyzers with wind sources [1-5]. Declining of coal-fired and nuclear electricity generation capacity may lead to gain in electricity generation by natural gas and renewables. Table 7.2 shows a typical sensitivity analysis to determine how the availability of wind farm and the capacity of electrolyzer affect the electricity needed for the production of H₂ [53-56]. Capital cost of electrolyzer increases considerably as the wind farm availability and electrolyzer capacity decrease.

Table 7.1 Electrolyzer types [9-11]¹.

Electrolyzer	Capacity (kW)	Efficiency % (HHV)	Efficiency % (LHV)
Alkaline	1-2,300	72	61
PEM	1-130	60	51
Solid Oxide	Pilot scale only	82	69

¹Norsk Hydro's 30,000 Nm³/hr (~ 150 MW) connected to a hydroelectric power plant, generating about 70,000 kg H₂/day. The higher heating values for hydrogen: HHV= 39.42 kWhr/kg and the lower heating value LHV= 33.31 kWhr/kg. 100% HHV efficiency translates into 84.5 % efficiency based on LHV.

Table 7.2. Sensitivity analysis changing the unit cost of H₂ with the production efficiency and electricity cost [9,10,55-57].

Wind turbine capital cost (\$/kW)	1654	2067	2481
Electrolyzer energy use (kWh/kg H ₂)	47.5	50	60
Electrolyzer capital cost (\$/kW)	326	408	489
Wind farm availability (%)	90	88	86
Electrolyzer capacity factor (%)	99.5	98	96

Integration with low-cost renewables and the flexibility to produce H₂ from the grid electricity during off-peak periods may help lower the production cost of H₂. A large alkaline (bipolar design) electrolyzer unit is the Norsk Hydro Atmospheric Type No. 5040, which can produce 1046 kg H₂/day (381,790 kg H₂/year) by using approximately 2.3 MW of electricity. Small systems however, are often built around polymer electrode membrane (PEM) electrolyzer cell technology. Table 7.3 shows the streams of the Norsk hydro atmospheric type electrolyzer unit [10]. The levelized cost is \$6.63/kg H₂ (2007\$) and the purchased electrolyzer system cost: \$489/kW (2014\$) [5-10]. Economic analysis shows that final production cost is around \$4.97/kg H₂, which is much higher compared with the cost of \$1.91/kg H₂ from coal gasification [9,10].

Table 7.3 Stream table of the norsk hydro atmospheric type electrolyzer unit [9,10].

Water		Hydrogen		Oxygen		Water	
kg/hr	kmole/hr	kg/hr	kmole/hr	kg/hr	kmole/hr	kg/hr	kmole/hr
485	26.9	43.59	21.6	346.51	10.8	94.82	5.3

The gas output streams from the electrolyzer are assumed to be 100% pure (typical real outputs are 99.9 to 99.9998% for H₂ and 99.2 to 99.9993% for O₂). Electricity cost is typically 70 to 80% of the total cost of H₂ production. Table 7.4 shows the typical energy usage by the Norsk electrolyzer. The system energy requirement includes compression to

bring the gas output to 33 bar (480 psi) [7,8]. The minimum power conversion system would require rectification of the variable ac output from the wind turbines to dc output for the electrolyzer cells. Future energy requirements are targeted at 50 kWh/kg H₂ [9,10,57-59].

Table 7.4 Energy usage for the norsk electrolyzer [9,10].

System energy required (includes compression)		Hydrogen production		Electrolyzer energy required	System power required
kWh/(Nm ³)	kWh/kg H ₂	kg/h	kmole/hr	kWh/(Nm ³)	kW
4.8	53.5	43.59	21.6	4.3	2330

Hydrogen production costs change approximately from \$1.75/kg H₂ to \$4.6/kg H₂ as the electricity prices change from \$0.02/kWh to \$0.08/kWh, for an advanced electrolyzer technology at 76% efficiency, and capital cost of \$250/kW (current state of technology is 56%-75% efficiency and \$700/kW) [12,48]. These costs represent distributed hydrogen production and include compression, storage, and delivery. The electrolyzer has a capacity factor of 70% to adjust for seasonal and weekend/weekday fluctuations in demand and a 97% availability of the equipment.

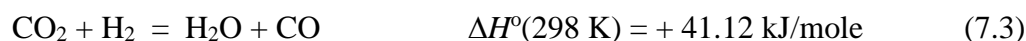
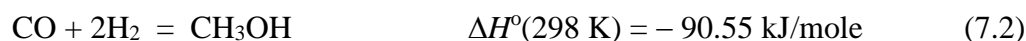
7.2.3. Hydrogen economy

Production of H₂ is an energy-consuming process, and may not be environmentally friendly [18,56]. In addition, the low density and extremely low boiling point of H₂ increase the energy cost of compression or liquefaction and the investment costs of storage and delivery. Distributed electrolysis case may play a role in the transition to the hydrogen economy when there is little delivery infrastructure for hydrogen [12]. Underground gas storage of hydrogen and oxygen in connection with the electrolysis may enable the

electrolyzer to accommodate the variations in the power produced by renewable resources. The output-input efficiency cannot be much above 30%, while the advanced batteries have a cycle efficiency of above 80%. Even the most efficient fuel cells may not recover these losses [56,58].

7.3. Methanol Production

Methanol synthesis needs carbon-rich feedstock (natural gas, coal or biomass), hydrogen, and a catalyst, mainly Cu/ZnO/Al₂O₃ [26-34]. Methanol is produced almost exclusively by the ICI, the Lurgi, and the Mitsubishi processes. These processes differ mainly in their reactor designs and the way in which the produced heat is removed from the reactor. To improve their catalytic performance, the CuO/ZnO catalysts have been modified with various metals, such as chromium, zirconium, vanadium, cerium, titanium, and palladium [30-33,62]. The long-term stability of the catalysts may be improved by adding a small amount of silica to the catalysts at reaction conditions of 5 MPa, 523 K [63]. A high catalyst activity is related to a high copper surface area or small crystallite size combined with intimate contact with the zinc promoter. Table 7.5 shows some of the experimental reactor operating temperatures and pressures with the catalyst Cu/ZnO/Al₂O₃. During the synthesis these following reactions occur [63-69].



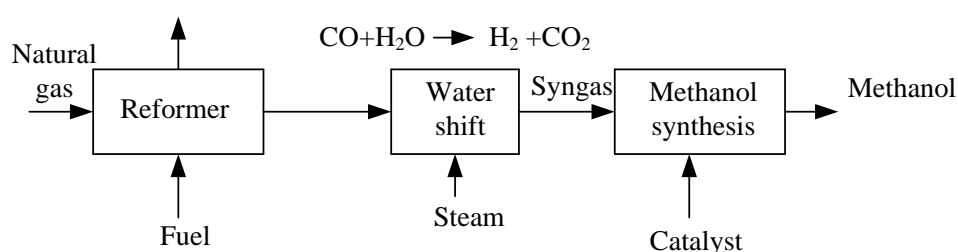
Only two of these reactions are linearly independent and two reaction rate equations can describe the kinetics of the all reactions.

Table 7.5 Experimental conditions of methanol synthesis with the catalyst Cu/ZnO/Al₂O₃.

Reactions	<i>T</i> , °C	<i>P</i> , bar
Based on all three reactions (1-3) [63]	250	50
Based on all three reactions (1-3) [65]	200-244	15-50
Based on reaction (1) and (2) [66]	215-270	50
Based on reaction (1) and (3) [67]	187-277	30-90
Based on reaction (1) and (3) [68]	180-280	51
Based on reaction (1) and (3) [69]	220-300	50-100

7.3.1. Methanol from natural gas

Figure 7.4 shows the main blocks of natural gas-based methanol production. Three fundamental steps are: (i) natural gas reforming to produce syngas with an optimal ratio of $[(H_2 - CO_2)/(CO + CO_2)] = 2$, (ii) conversion of syngas into crude methanol, and (iii) distillation of crude methanol. Methanol synthesis from natural gas emits around 1.6 kg CO₂/kg methanol [13]. Commercial process of methanol production from natural gas is the most efficient process with a typical energy efficiency of 75% [13]. Specific energy consumption for natural gas-based methanol is around 8.0 GJ/mt methanol [22]. Captured CO₂ is commonly reused internally in ammonia and some methanol plants.



Energy required: 8 GJ/mt methanol from natural gas; 23.7 GJ/mt methanol from coal
 Emissions: 1.6 kg CO₂/kg methanol from natural gas; 3.8 kg CO₂/kg methanol from coal
 Production cost ratio of natural gas base/ coal base = ~2.5

Figure 7.4 Main blocks in Lurgi's methanol production from natural gas [13,20-23].

Table 7.6 compares the cost of methanol production and emissions from fossil fuel resources. Coal-based syngas process has the highest emission of GHGs, which is around

2.8-3.8 kg CO₂/kg methanol. Typical energy efficiency for the coal-based methanol is in the range of 48 % to 61% [13, 22]. Technical and economic analyses of methanol production from biomass-based syngas show that overall energy efficiency is around 55% based on HHV. The level of emission is around 0.2 kg CO₂/kg methanol, which is mainly from biomass growing, harvesting, and transportation. Methanol from biomass or flue gas CO₂ is at least 2-3 times more expensive than the fossil-fuel based methanol [13, 64, 70].

Table 7.6 Methanol costs and emissions¹ from various productions process [13,22,71].

Process	Production cost \$/mt methanol ²	Emissions kg CO ₂ /kg methanol	Energy efficiency %
Natural gas based syngas	170	0.5-1.6	75
Coal based syngas	432	2.8-3.8	48-61
Biomass based syngas	723	0.2	51
CO ₂ from flue gas	973	0.8	46

¹This emissions account for methanol production process as well as the emissions occurring with the utilization of methanol.

²The cost data [13] for 2005 has been updated using: $\text{Cost}_{\text{new}} = \text{Cost}_{\text{old}} [\text{CEPCI}(2014)/\text{CEPCI}(2005)]$
CEPCI (2014) = 595 and CEPCI (2005) = 468 [70].

7.3.2. Methanol from CO₂ and H₂

Converting CO₂ into chemicals is thermodynamically challenging, and inherently carries costs for the energy and hydrogen supply [22]. The conversions of reactions (1) to (3) with catalyst of Cu/ZnO/Al₂O₃ are limited by the chemical equilibrium of the system. The temperature rise must be minimized in order to operate at good equilibrium values. However selectivity for methanol is high with a value of 99.7% at 5 MPa and 523 K with a H₂/CO₂ ratio of 2.82 [63]. The energy efficiency for the concentrated CO₂ and hydrogen based methanol is around 46%. Figure 7.5 shows a schematic of renewable hydrogen production.

Methanol synthesis from water, renewable electricity, and carbon may lead to renewable energy storage, carbon recycle, fixation of carbon in chemical feedstock, as well as extended market potential for electrolysis. For methanol production with coal as carbon source, 23.7 GJ/mt methanol and with CO₂ as carbon source 35.5 GJ/mt methanol are required.

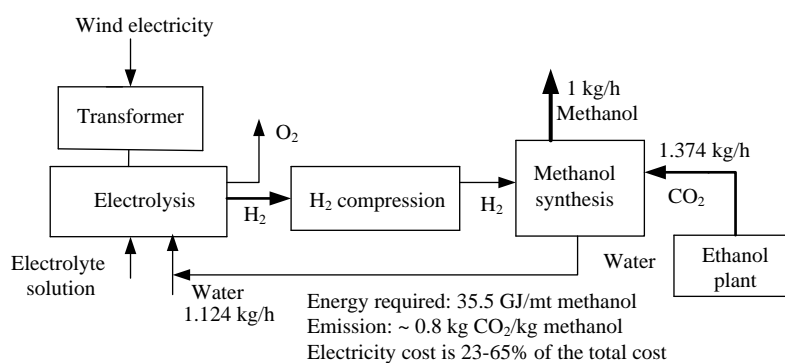


Figure 7.5 Schematic of methanol production using renewable hydrogen and CO₂ [13,63,22].

Currently the cost for hydrogen from electrolysis is roughly twice of that from natural gas steam reforming. Therefore, methanol production from renewable hydrogen would increase the energy consumption; however, a significant GHG reduction may be possible [22]. Clausen et al.[70] used electrolytic H₂ in methanol production using the post combustion captured CO₂. The alkaline electrolyzer is operated at 90 °C and atmospheric pressure with an electricity consumption of 4.3 kWh/Nm³ H₂ corresponding to an efficiency of 70% (LHV). With underground storage for hydrogen and oxygen and the electricity price during the off-pick hours of operation, the costs are estimated as \$15.0/GJ, \$20.0/mt CO₂, and \$217/mt methanol (2010 \$), respectively. The electricity cost is around

23% - 65% of the methanol production cost because of high stoichiometric hydrogen demand in the synthesis [66-68].

7.3.3. CO₂ capture and compression

Some of the available sources for CO₂ are fermentation processes such as ethanol production plants, fossil fuel-based power stations, ammonia, and cement plants. Table 7.7 shows the equipment and operating costs to capture and liquefy 68 mt CO₂/day and 272 mt CO₂/day (the maximum capture rate for a typical 40 million gal/year ethanol plant). The estimated costs are for food grade CO₂ (99.98% minimum and < 0.4 ppmv of sulfur) and also for less purified CO₂ suitable for enhanced oil recovery or sequestration [25].

Table 7.7 Estimated cost of CO₂ recovery options from ethanol plant (\$ 2006) [25].

Cost	68 mt CO ₂ /day beverage grade	272 mt CO ₂ /day beverage grade	272 mt CO ₂ /day Non-beverage grade
Capital cost, \$	2,530,000	5,770,000	4,700,000
Capital cost, \$/mt CO ₂	37205	21213	17279
Electricity ¹ , \$/mt CO ₂	19.46	18.8	18.9

¹Electricity cost: \$0.10/kWh

7.3.4. Methanol production plant

We designed and simulated a methanol plant using renewable electrolytic H₂ and CO₂ supplied from an ethanol plant. The RK-SOAVE equation of state is used. The plant uses 19.1 mt H₂/day and 138.4 mt CO₂/day, and produces 99.9 mt methanol/day at 99.7-wt% together with 57.3 mt/day 98.3-wt% of waste water.

Figure 7.6 presents the process flow diagram for the methanol plant using CO₂ and H₂. The feedstock is at the conditions associated with typical storage, with H₂ at 25 °C and 33 bar and CO₂ at -25.6 °C and 16.422 bar (liquid phase) [7,8,25]. The ratio of H₂ to CO₂ is held at of 3:1 to promote methanol synthesis. In the feed preparation block, the renewable

H₂ and CO₂ are compressed to 50 bar in a multi-stage compressor and pump, respectively, and mixed with the recycle stream S9 in mixer M101. Stream S4 is the feed of the plug-flow reactor R101 where the methanol synthesis takes place. This multi-tube reactor has 15 tubes with a diameter 0.127 m and a length of 5 m, loaded with a total of 250 kg of catalyst. The reactor operates at 50 bar with a constant temperature of 235 °C representing the Lurgi's low pressure isothermal system [66].

Langmuir-Hinshelwood Hougen-Watson (LHHW) kinetics formulations, with fugacities, are used for reactions (1) and (2). LHHW kinetics considers the adsorption of the reactants to the catalytic surface, the surface reactions to synthesize the methanol and water, and the desorption of the products from the catalytic surface [66,47]. The reactor output stream S5 is expanded in a turbine in order to cool down the outlet and produce power. This turbine produces 0.69 MW of electrical energy which can be fed back into the process or sold for a revenue. In flash drum F101, stream S6 is separated into liquid (S6) and gas streams (S7). Stream S7 is the crude methanol, which is separated from the water in the distillation tower T101. The product methanol is the distillate, while the wastewater is the bottoms flow of T101. The streams of methanol and water are cooled by the heat exchangers of E101 and E102, respectively, and are stored. Gas stream S8 is sent to a flow splitter SF101, in which 90% of S8 is recycled to the reactor after it is compressed in the multi stage compressor REC-COMP. Stream S9 is chosen as a tear stream. The mole fraction of methanol in the distillate is controlled by varying the reflux ratio and the ratio of bottoms flow to feed flow rate by using two design specifications in the Radfrac column T101. The column has 20 stages with a feed stage 17 and partial condenser. Methanol production has the potential for the best possible technology deployment ranging from 16%

to 35% [65]. Therefore the design reflects that potential in a simple design delivering almost pure methanol and waste water containing less than 1% methanol.

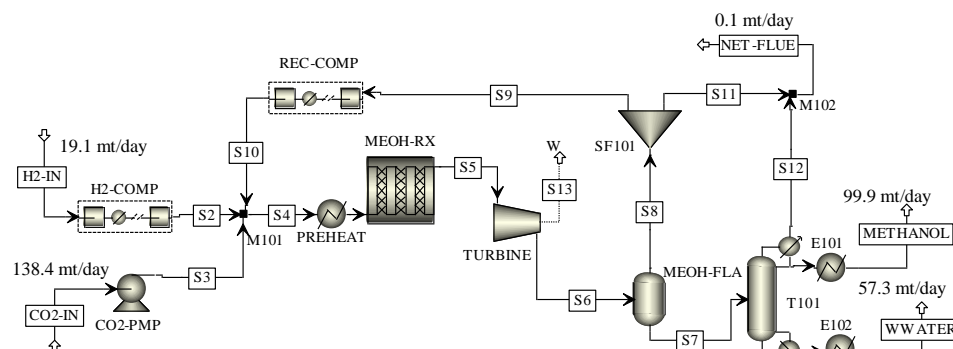
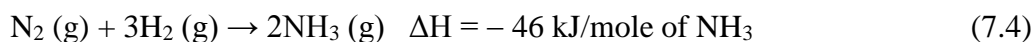


Figure 7.6 Conceptual process flow diagram of the methanol plant.

7.4. Ammonia Production

Ammonia is synthesized by the catalytic reaction of H₂ and nitrogen gas at around 400-600 °C and 200 – 400 atmospheres (Haber and Bosch process).



The sources of H₂ are steam reforming and/or water-gas shift from natural gas or gasification of coal, while an air separation unit (ASU) supplies the nitrogen [71-73]. Figure 7.7 shows the both processes of renewable H₂ based and syngas-based NH₃ production.

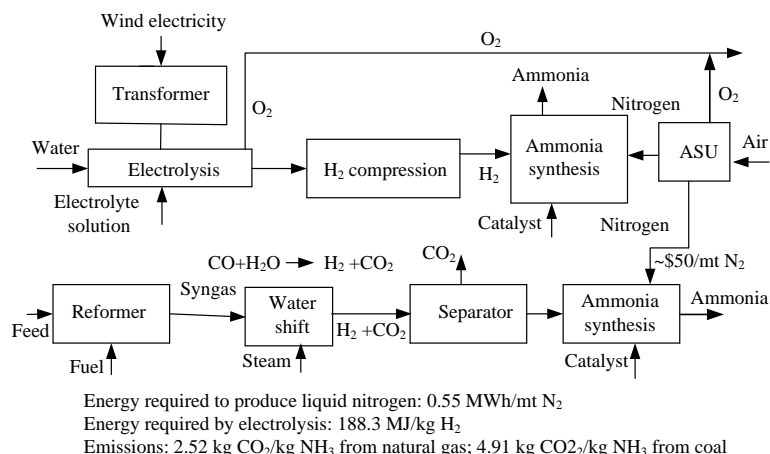


Figure 7.7 Schematic of processes of renewable H₂ based and syngas-based NH₃ production using an air separation unit [37-42].

7.4.1. Air separation unit

ASU can produce nitrogen (99.999% purity) and oxygen (98% purity) for synthesis of ammonia using the air (75.5% N₂, 23.2% O₂, and 1.3% Ar) [72,73]. Ambient air is compressed in multiple stages (accounting for 86% of the total energy consumption) with inter-stage cooling to 6.45 bar and sent into the molecular sieve to remove residual water vapor, carbon dioxide, and atmospheric contaminants. Table 7.8 shows typical power consumptions. A larger plant with efficiency improvements (energy consumption of less than 10%) and process optimization would deliver air liquefaction at around 0.4 MWh/mt liquid nitrogen. Operation and maintenance (O&M) costs typically amount to between 1.5% and 3% of the plant purchase price per annum. Production cost is around \$54/mt nitrogen for a 300 mt/day capacity and \$49/mt nitrogen for a 600 mt/day capacity [71-73].

Table 7.8 Specific energy consumptions for hydrogen and nitrogen [22,71-73].

Process Steps	kWh/Nm ³	MJ/Nm ³	MJ/kg	kg H ₂ /Nm ³	kg N ₂ /Nm ³	\$/mt N ₂
Electrolysis	4.7	17.0	188.3	0.09		
ASU	1.0	4.0	3.1		1.17	49(600 mt N ₂ /day)

7.4.2. Ammonia production plant

Figure 7.8 shows the process flow diagram for the ammonia plant. Production of ammonia is based on the Haber-Bosch synthesis process at high pressure in the presence of porous iron oxide. Typically for ammonia synthesis these conditions are about 150 atmospheres and 370 - 500 °C. Under equilibrium conditions the proportion of reactants and the product of a chemical reaction are balanced and determined by the existing physical conditions such as pressure, temperature and concentrations. Since the reaction is exothermic, lowering the temperature in the reactor will increase the yield of ammonia. However, this also slows down the reaction therefore, for higher efficiency, the temperature is kept as high as possible. Increasing the pressure will increase the yield of ammonia but there is a limit in pressure for safety reasons [41,42].

The nitrogen is supplied by an air separation unit SEP 101, to produce 1202.66 mt/day anhydrous ammonia. The ammonia process is designed and simulated by using the RK-SOAVE equation of state property method. The ammonia plant uses 217.71 mt/day H₂ and 1009.15 mt/day nitrogen, and produces 1202.66 mt/day 99.9 wt % ammonia. The flow rate of ammonia is maximized to be 2943 kmol/hr and its composition to be 0.99wt% NH₃, using the constrained optimization option. There is a slight loss of ammonia in the stream BLEED. Air is separated in SEP 101, and the feeds of nitrogen and hydrogen at 20.27 bar are mixed in M101. This mixture is compressed to about 212 bar in compressors C101 and C102. Temperature of this mixture is adjusted in heat exchanger E201. In reactor R201 the ammonia synthesis takes place at around 556°C and 212 bar with a platinum group metal such as ruthenium [40-42]. The reactor R201 is a RGIBBS reactor and estimates the

equilibrium composition of the reactor by Gibbs free energy minimization. The output of the reactor is conditioned in heat exchangers E202 and E203 and sent to adiabatic flash drums FL301 and FL302, which operate at 203 and 12 bar, respectively. The bottom flow of FL302 is the product ammonia at -26°C and 12.4 bar. There is a large energy difference between the input and output, and must be compensated by outside utilities in the form of cooling water, steam, electricity, and refrigeration.

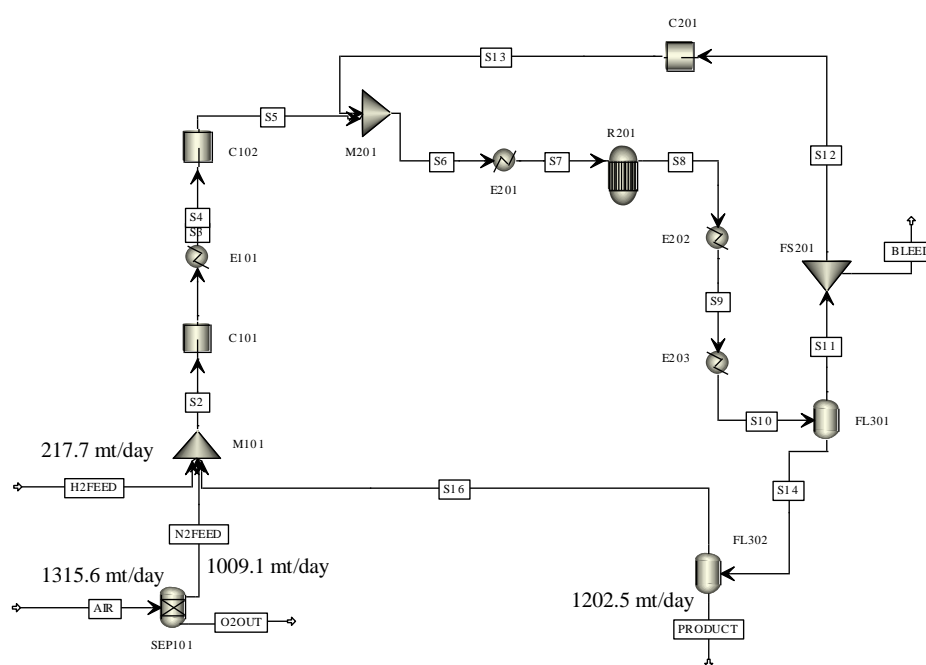


Figure 7.8 Process flow diagram for the ammonia plant.

7.5. Sustainability and Economic Analyses

7.5.1. Sustainability analysis

The integral methanol production facility consists of three units: an electrolytic hydrogen production, CO_2 capture and storage, and the methanol production. Similarly, the

integral ammonia production facility consists of three units: an electrolytic hydrogen production, ASU, and the ammonia production. Figures 30 and 31 show these integral facilities subject to sustainability and economic analyses. Table 7.9 shows the main results of the material and energy usages, as well as the CO₂ emissions for the integral facilities. The energy costs are estimated by the unit cost of utilities listed in Table 7.10.

The integral methanol facility requires 19.08 mt H₂/day and 138.38 mt CO₂/day in total. The total emissions of CO₂ from each unit are –111.54 mt CO₂/day, 18.51 mt CO₂/day, and 8.77 mt CO₂/day for the methanol production, H₂ production, and CO₂ capture and storage, respectively. The net carbon fee is –\$9.3/h for the methanol facility and \$69.89/h for the ammonia facility based on a set value of \$2/mt CO₂e. As Table 7.11 shows, the values of net duty and cost are the highest for the hydrogen production units used in methanol and ammonia productions.

The integral ammonia facility requires 217.72 mt H₂/day and 1009.15 mt N₂/day in total. The total emissions of CO₂ from each unit are 838.78 mt CO₂/day, 211.18 mt CO₂/day, and 111.47 mt CO₂/day for the ammonia production, H₂ production, and ASU, respectively.

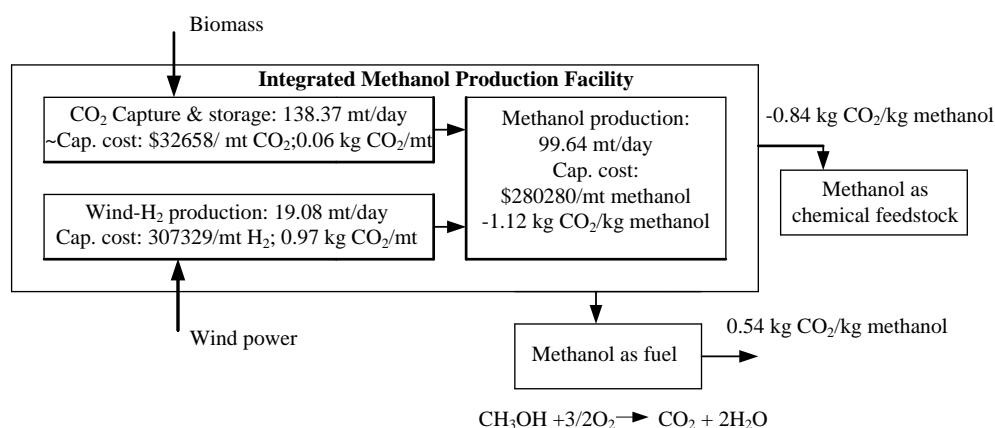


Figure 7.9 Economic and sustainability indicators in the integral methanol production facility.

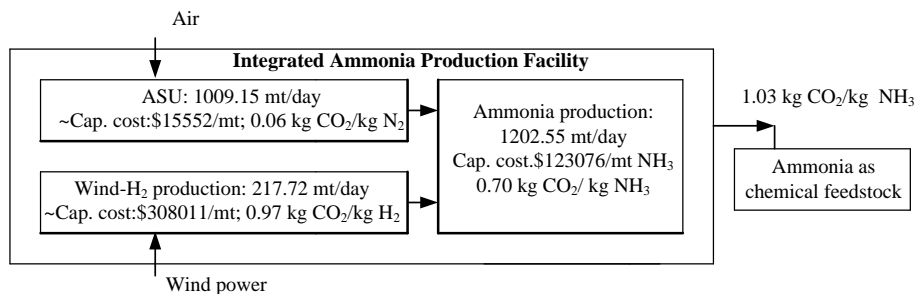


Figure 7.10 Economic and sustainability indicators in the integral ammonia production facility; ASU: air separation unit.

Table 7.11 presents the following sustainability metrics that are estimated for the integral methanol and ammonia facilities:

- Material intensity (nonrenewable energy/unit mass of product)
- Energy intensity (nonrenewable energy/unit mass of product)
- Potential environmental impact (pollutants and emissions/unit mass of product)

The overall facility emissions of CO₂ are normalized with respect to methanol and ammonia capacities. The material intensity metrics show that the methanol facility requires 1.39 mt CO₂/mt methanol. The environmental impact metrics shows that the integral methanol facility reduces −0.84 kg CO₂/kg methanol when utilizing it as a chemical feedstock, and recycles 0.53 kg CO₂/kg methanol after its complete combustion, as seen in Figure 5.6. On the other hand, the environmental impact metrics for the integral ammonia facility is 1.03 kg CO₂/kg ammonia, as seen in Figure 7.10. The duty (heating – cooling) becomes negative due to excessive cooling required in the ammonia facility.

Table 7.9 Sustainability indicators for the methanol and ammonia plants¹.

Material metrics	Integral methanol production			Integral ammonia production		
	Methanol prod.	H ₂ prod.	CO ₂ C&S	NH ₃ prod.	H ₂ prod.	ASU
CO ₂ Input, mt/day	138.37					
H ₂ Input, mt/day	19.08			217.72		
N ₂ Input, mt/day				1009.2		
Methanol production, mt/day	99.66					
Ammonia production, mt/day				1202.6		
Energy intensity metrics						
Total heating duty, MW	4.60	42.49	1.05	103.54	484.89	23.08
Total cooling duty, MW	2.93	0.12	0.03	162.32	1.40	0
Net duty (heating - cooling), MW	1.67	42.37	1.02	-58.78	483.49	23.08
Total heating cost flow, \$/h	59.18	3292.83	81.31	2648.9	37579	1789
Total cooling cost flow, \$/h	2.24	0.09	0.02	1236	4.85	
Net cost (heating + cooling), \$/h	61.42	3292.92	81.33	3885	37584.08	1789.04
Environmental impact metrics						
Net stream CO ₂ e, mt/day	-138.37	0	0	0	0	0
Utility CO ₂ e, mt/day	26.83	18.51	8.77	838.78	211.18	111.47
Total CO ₂ e, mt/day	-111.53	18.51	8.77	838.78	211.18	111.47
Net carbon fee, \$/h	-9.29	1.54	0.73	69.89	17.60	9.29

¹US-EPA-Rule-E9-5711; natural gas; carbon fee: \$2/mt.

Table 7.10 Unit energy cost for various utilities with energy source of natural gas for 2014 [47].

Utilities	Energy price, \$/MJ	T_{in} °C	T_{out} °C	Factor ¹	U^2 kW/m ² K
Electricity	\$0.0775/kW h			0.58	
Cooling Water	\$0.09/mt	20	25	1	3.75
Medium Pressure Steam	2.2×10^{-3}	175	174	0.85	6.00
High Pressure Steam	2.5×10^{-3}	250	249	0.85	6.00
Refrigeration	3.3×10^{-3}	-39	-40	-1	1.30

¹CO₂ energy source efficiency factor; ² Utility side film coefficient for energy analysis.

Table 7.11 Sustainability metrics for the integral methanol and ammonia plants.

Material metrics	Integral methanol plant	Integral ammonia plant
CO ₂ used/Unit product	1.39	
N ₂ used/Unit product		0.84
H ₂ used/Unit product	0.19	0.18
Energy intensity metrics		
Net duty/unit product, MWh/mt	9.55	-1.17
Net cost/Unit product, \$/mt	828.67	863.33
Environmental impact metrics		
Total CO ₂ e/Unit product	-0.85	1.03
Net carbon fee/Unit product, \$/mt	-1.70	2.07

7.5.2. Economic analysis

The economics analyses of the integral methanol and ammonia plants are based on the discounted cash flow diagrams (DCFD) prepared for a ten-year of operation using the current economic data. Based on the equipment list from the process flow diagrams (Figures 7.6 and 7.8), bare module costs are estimated and used as fixed capital investments (FCI). Chemical Engineering Plant Cost Index [47] (CEPCI-2014) (= 576.1) is used to estimate and update the costs and capacity to the present date by

$$\text{Cost}_{\text{New}} = \text{Cost}_{\text{New}} \frac{\text{CEPCI}_{\text{New}}}{\text{CEPCI}_{\text{Old}}} \left(\frac{\text{Capacity}_{\text{New}}}{\text{Capacity}_{\text{Old}}} \right)^x \quad (7.5)$$

where x is the factor, which is usually assumed to be 0.6. Working capital is 20% of the FCI. Depreciation method is the Maximum Accelerated Cost Recovery System (MACRS) with a 7-year recovery period [74]. After estimating the revenue and the cost of production, DCFDs are prepared. The details can be found within the ‘Supporting Information.’ DCFDs generate the three economic feasibility criteria that are Net Present Value (NPV), Payback Period (PBP), and Rate of Return (ROR). At least two out of three criteria should be favorable for the operation to be feasible. These criteria are favorable if $\text{NPV} \geq 0$, PBP

\leq useful operational years; and $ROR \geq i$, where i is the internal interest rate. In addition, the economic constraint (EC) and the unit product cost (PC) are also estimated

$$EC = \frac{\text{Average Discounted Annual Cost of Production}}{\text{Average Discounted Annual Revenue}} \quad (7.6)$$

$$PC = \frac{\text{Average Discounted Annual Cost of Production}}{\text{Capacity of the plant}} \quad (7.7)$$

The PC takes into account the operating and maintenance (O&M) costs. An operation with $EC < 1$ shows the opportunity to accommodate other costs and improve the cash flows of the operation toward a positive NPV.

The estimated approximate values of the FCIs are \$5.87 million for the wind-based electrolytic H_2 production unit, \$4.52 million for the CO_2 production unit, and \$28 million for the methanol production unit. The H_2 production includes the compression, storage, and dispensing from a centralized production facility with an average electricity cost of 0.045/kWh. Therefore, the total value of the FCI is around \$38.39 million.

The distribution of unit capital costs for the integral methanol production facility shows that the contribution from wind-based H_2 is the highest (Figure 7.9). The cost of H_2 , which makes the $NPV = 0$, is \$0.88/kg H_2 when the selling price of methanol is \$600/mt with the corresponding values of $EC = 0.85 (< 1)$ and $PC = \$518/\text{mt}$ methanol ($< \$600/\text{mt}$). Global prices of methanol change widely; the prices in 2014 are \$435/mt in Europe, \$482/mt in North America, \$410/mt and in Asia Pacific [75]. Compared with natural gas-based methanol, renewable methanol production costs almost five times as much. Only the biomass production cost is comparable, as seen in Table 6.7. The cost of renewable hydrogen and the selling price of methanol affect the economics of the renewable methanol.

The approximate value of FCI for the ammonia process is around \$148.5 million, while the values of FCIs for the ASU and wind-based electrolytic H_2 production unit are around

\$15.6 million and \$66.9 million, respectively. The capital cost of the integrated production, including the ammonia process, the ASU, and the H₂ production unit, becomes \$231.0 million. An average selling price of ammonia is around \$700.0/mt (2014 \$) [76]. The cost of H₂, which makes the NPV = 0, is \$2.33/kg H₂ when the selling price of ammonia is \$700/mt with the corresponding values of $EC = 0.95$ (< 1) and $PC = \$662.9/\text{mt}$ methanol ($< \$700/\text{mt}$). The details of the economic analysis of the ammonia plant are given in Appendix B.

7.5.3. Assessment of methanol and ammonia-based electricity storage

The economics of electricity storage are influenced by the type of storage technology, electricity price, the requirements of each application, the frequency of charging and discharging cycles, and the system in which the storage facility is located. Besides, one needs to consider direct and localized impacts of the technology and the generation source used [77].

Main chemical storage of electricity involves the production of hydrogen, synthetic natural gas, and chemicals, which are mainly methanol and ammonia. Combination of several storage applications together may help electricity storage to be more feasible. The initial investment requires a cost per unit of power (\$/kW) and a cost per unit of energy capacity (\$/kWh), which are technology dependent [77].

Minimum and maximum current world-wide productions of methanol are around 55 to 5000 mt/day. Methanol has half of the volumetric energy density relative to gasoline or diesel; however, it can be used in the direct methanol fuel cell [13-15,20,21,29,34,36]. Renewable hydrogen-based methanol would recycle carbon dioxide as a possible alternative fuel to diminishing oil and gas resources [78,79]. It is also used as a chemical

feedstock to ultimately fix the carbon. This would lead to a “methanol economy” [18,19]. There are already vehicles which can run with M85, a fuel mixture of 85% methanol and 15 % gasoline [1,18-22]. Methanol can be used with the existing distribution infrastructure of conventional liquid transportation fuels. In addition, fuel cell-powered vehicles are also in a fast developing stage, although they are not yet available commercially [1,2,19].

Table 7.12 shows the specific energy consumptions and emissions in producing methanol and ammonia by various feedstocks [22]. The coal-based process has the emissions of 3.8 kg CO₂/kg methanol, while natural gas-based process leads to 1.6 kg CO₂/kg methanol. Lifecycle CO₂ emission is around 0.8 kg CO₂/kg methanol for the flue gas based methanol. Around 50% of these emissions are due to the CO₂ capture processes [22,80].

Current capacities for ammonia vary from 1,000 to 2,000 mt/day or 360,000 to 720,000 mt/year. NH₃ can be used as fertilizers, industrial chemicals, and fuel. Ammonia cracking is endothermic and depends on the catalyst [37,38]. Ammonia has a capacity of 17.6 wt% for H₂ storage; however, considerable energy is required to release H₂ from ammonia. Ammonia synthesis coupled with hydrogen production may increase efficiency. Ammonia can burn directly in an internal combustion engine and can be converted to electricity directly in an alkaline fuel cell, or converted to H₂ for non-alkaline fuel cell. However, polymer electrolyte membrane (PEM) fuel cell technology is incompatible in the presence of ammonia (> 0.1 ppm) [37]. For sites in a remote island, ammonia fuel may become competitive around \$10/gallon of diesel fuel [39-41].

Table 7.12 Specific energy consumptions and emissions for ammonia and methanol productions [22].

Process	kg H ₂ / kg prod.	H ₂ prod. /comp.	Average prod.	BPT	Theor min.	Average kg CO ₂ /kg prod.
Methanol from CO ₂	0.189	37.06				
Syngas-coal methanol	0.126	24.20	24.0	20.1	5.1	2.83
Syngas-NG methanol			13.9	9.0-10	5.1	0.52
Ammonia	0.178	35.57				
syngas-NG Ammonia			15.4	7.2-9.0	5.8	2.52
Syngas-coal Ammonia			27.9	22.0	8.1	4.91

SEC: Specific energy consumption that includes fuel, steam and electricity for the process.

BPT: Best possible technology; GHG: greenhouse gas emissions as CO₂ equivalent per ton of product; the CO_{2e} includes CO₂, CH₄, and NO_x.

When it is produced from natural gas, ammonia production cost depends on the price of natural gas; for example, for \$4.5/MMBtu natural gas, NH₃ production cost is around \$180/mt, while for \$7.0/MMBtu natural gas, NH₃ production cost becomes \$260/mt at 2006 \$. Only 60-65% of the energy input of natural gas to the process is contained in the product ammonia. Replacing natural gas with coal as the feedstock increases energy consumption and production costs 1.7 times and the investment cost 2.4 times [37-39,73]. The cost of ammonia from renewable hydrogen ranges between \$660/mt and 1,320 \$/mt, which is higher than both coal and natural gas based-ammonia production costs [22].

Emission for a natural gas-based ammonia is around 2.52 mt CO₂/mt NH₃, while coal-based ammonia produces nearly 4.91 mt CO₂/mt NH₃. The emission of CO₂ based on natural gas represents a lower limit for the GHG emissions from ammonia production. Some of the CO₂ emitted is captured and subsequently used for the production of urea [22,37,38,77]. Energy consumption, as well as the capital cost, in ammonia production is higher than of that for methanol production [22]. The best possible technique for NH₃ production uses H₂ from renewable energy sources. Hydrogen production is one of the largest energy-consuming steps in the production of ammonia and methanol. Capital cost for a centralized 20000 mt H₂/year plant is around \$ 60 million (2011 \$) with operational

cost estimated at \$3.3 million/year. Investment costs of a centralized water electrolysis plant are roughly one third of the investment costs of a conventional natural gas based plant of equivalent production capacity [22]. As Table 6.7 shows, this is by far the highest energy consuming process step in the overall scheme and dominates all subsequent steps, such as hydrogen compression and, in the case of ammonia production, the air separation unit for production of nitrogen from air [22].

Tallaksen and Reese [38] compared the renewable and with fossil-based ammonia productions in terms of energy use and carbon emissions using the life cycle assessment (LCA) methods. Renewable ammonia production requires around 60 GJ of electricity/mt ammonia. This is considerably more total energy than conventional fossil fuel based produced ammonia, however it requires less fossil energy and results in less GHG emissions. The boundary of LCA for the wind to ammonia contains wind power, water electrolysis, hydrogen compression, nitrogen separation and compression, ammonia production and ammonia storage. LCA is more focused on environmental issues rather than raw material depletion [38].

7.5.4. Assessment of chemical processes by a decision matrix

Beside the economics analysis, sustainability metrics should also be used to evaluate the feasibility of chemical processes [81-84]. Table 7.13 shows a Pugh decision matrix [85] developed using ‘+’ and ‘-’ for the ratings to assess the methanol and ammonia production facilities. Four scores generated show the number of plus scores, minus scores, the overall total, and the weighted total. The weighted total adds up the scores times their respective weighting factors. The totals are guidance only for decision making. If the two top scores

are very close or very similar, then they should be examined more closely to make a more informed decision. Renewable energy-based systems may require the combined use of scenario building and participatory multi-criteria analysis for sustainability assessment [84].

Table 7.13 indicates the weighted decision matrix used to compare the plants producing methanol and ammonia from fossil and non-fossil resources. The weight factor can be adjusted with respect to the location, energy policies, and energy costs and security. With the weight factors adapted and the combined economic and sustainability indicators, the decision matrix has estimated the highest weighted scores for the methanol and ammonia production facilities based on non-fossil resources. This shows the impact of sustainability indicators in evaluating the feasibility of chemical processes requiring large investments and renewable energy resources.

7.6. Conclusions

Renewable energy-based hydrogen, methanol, and ammonia productions may lead to renewable electricity storage and reduce the carbon emissions either by recycling and/or fixation of the carbon. The cost of renewable hydrogen production plays an important role within the economics of the methanol and ammonia productions and determines the scope of improvements necessary for economic feasibility of the integral facilities. The economic analysis shows that the cost of electrolytic hydrogen is critical in the economics of methanol and ammonia plants at the capacities assumed in this study and using the currently available technologies. Supply of low cost hydrogen, much less than \$2/kg H₂, may lead to feasible processes for conversion of carbon dioxide into methanol and of nitrogen into ammonia.

Despite its poor overall efficiency and high up-front capital costs, chemical storage may provide the large-scale and long-term storage requirements of a mixed renewable power generation. Multi-criteria decision matrix, containing the sustainability indicators, show that chemical processes that use non-fossil fuels may achieve better overall assessment scores. This helps accounting the cost of environmental damage from using fossil fuels, in the overall assessment of feasibility for chemical process and energy systems. This is in line with the need for the development of low-carbon chemical processes and energy technologies in order to address the global challenges of energy security, climate change, and economic growth.

Table 7.13 Decision matrix for multi-criteria analysis and assessment of chemical processes and energy systems.

Economics and sustainability indicators	Weighting factor:0-1	Fossil-methanol	Non-fossil-methanol	Fossil-ammonia	Non-fossil-ammonia
Economic indicators					
Net present value NPV	1	+	–	+	–
Payback period PBP	0.8	+	–	+	–
Rate of return ROR	0.8	+	–	+	–
Economic constraint EC	0.9	+	–	+	–
Impact on employment	1	+	+	+	+
Impact on customers	1	+	+	+	+
Impact on economy	1	+	+	+	+
Impact on utility	0.7	–	+	–	+
Sustainability indicators					
Material intensity	0.7	–	+	–	+
Energy intensity	0.8	+	–	+	–
Environmental impact GHG in production	0.8	–	+	–	+
Environmental impact GHG in utilization	0.8	–	–	+	+
Toxic/waste material emissions Process safety and Public safety	1	–	+	–	–
Potential for technological improvements and cost reduction	0.8	–	+	–	+
Security/reliability	0.9	–	+	–	+
Political stability and legitimacy	0.8	–	+	–	+
Quality of life	0.8	–	+	–	+
Total positive score		8	11	9	11
Total minus score		9	–6	–8	–6
Net score (positive-minus)		–1	+5	+1	+5
Weighted total score		+0.2	+5.4	+2	+4

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CHAPTER 8. CONCLUSIONS AND RECOMMENDATIONS

Improvements in process design and optimization by thermodynamic analysis may have a positive impact on economic and sustainability of chemical processes. Column Targeting Tools (CTT) through thermal analysis and exergy loss profiles generated by the Aspen Plus simulation package, and energy analysis through pinch analysis and heat exchanger network system using Aspen Plus Energy Analyzer may be effective in improving existing and new designs of chemical processes. After the modifications that are suggested by the CTT and energy analyzer, the chemical processes became more efficient due to the minimization of the wasted energy, and friendlier to the environment due to the reduction of the CO₂ gas emission. Furthermore, the annual energy cost is reduced due to minimizing the energy and utilities that were consumed in the processes, which make these modifications economically feasible. A multi-criteria decision matrix, containing the economics and sustainability indicators, has been introduced for evaluation of the feasibility of chemical processes.

It is recommended that chemical process industries should be based on environmentally conscious processes design and development to achieve better overall assessment for economic and sustainability aspects. A multi-criteria matrix may help account for the cost of environmental damage from using fossil fuels in the overall assessment of feasibility. This is in line with the need for a better assessment of chemical processes and energy technologies in order to address the global challenges of energy security, climate change, and economic growth.

APPENDIX A. CHAPTER 5 SUPPLEMENTARY DATA

Table A1 Columns modified case summary: N: number of total stages; NF1, NF2, NF3 are the feed stages; RR is the reflux ratio; F is the total mass flow rate; P is the column pressure; TF1, TF2, TF3 are the feed temperatures, and PF1, PF2, PF3 are the feed Pressures.

Operation	Column 1		Column 2		Column 3	
	Base	Modified	Base	Modified	Base	Modified
N	50	55	50	55	60	66
NF	NF1=25	NF1=25	28	33	35	35
	NF2=15	NF2=15				
	NF3=10	NF3=11				
Mole RR	0.65	0.33	0.54	0.53	4.75	4.49
F (mt/hr)	F1=97.3	F1=97.3	175.86	175.86	173.23	173.23
	F2=59.82	F2=59.82				
	F3=3.74	F3=3.74				
P (bar)	35.15	35.15	23.9	23.9	16.87	16.87
TF (°C)	TF1= -37	TF1= -30	5	9	-24.6	-24.6
	TF2= -98	TF2= -98				
	TF3= -129	TF3= -129				
	PF1=37.3	PF1=37.30				
PF (bar)	PF2=37	PF2=37	35.15	35.15	17.6	17.6
	PF3=37	PF3=37				
Q _C (MW)	-0.29	-0.55	-6.38	-8.22	-37.81	-40.30
T _C (°C)	-99.58	-99.54	-13.68	-13.68	-35.92	-35.92
Reflux rate (mt/hr)	2.21	1.91	74.24	75.03	391.44	373.84
Distillate rate (mt/hr)	2.99	2.99	137.231	137.23	80.41	80.41
Q _R (MW)	9.33	9.68	16.26	18.09	32.2	34.34
T _R (°C)	5.53	5.53	74.41	74.41	-15	-14.93
Boilup rate (mt/hr)	138.75	128.10	204.07	204.92	329.2	308.33
Bottoms rate (mt/hr)	157.86	157.86	20.63	20.63	56.82	56.82

Table A2 Sustainability indicators for column 1 with modifications: N=50→55; NF1=25, NF2=15, NF3=11; RR=0.65→0.328; TF1= −37 °C →−30 °C.

Material intensity indicators	Column 1		
	Base Case	Modified Case	Change %
Feed 1 rate (mt/day)	2335.22	2335.22	0
Feed 2 rate (mt/day)	1435.73	1435.73	0
Feed 3 rate (mt/day)	89.66	89.66	0
Distillate rate (mt/day)	71.96	71.96	0
Bottoms rate (mt/day)	3788.66	3788.66	0
Energy intensity indicators			
Condenser duty, kW	−296.23	−286.83	−3.17
Reboiler duty, kW	9327.48	8769.74	−5.98
Feed conditioning duty, kW	0	548.28	–
Utility cost in condenser, \$/day	1083.41	1049.04	−3.17
Utility cost in reboiler, \$/day	2555.49	2402.68	−5.98
Utility cost in feed conditioning, \$/day	0	89.76	–
Total exergy loss, kW	1585.00	124.34	−92.15
Environmental impact indicators			
Condenser CO ₂ emission ¹ , mt /day	1.43	1.38	−3.50
Reboiler CO ₂ emission ¹ , mt /day	45.04	42.35	−5.97
Feed conditioning CO ₂ emission ¹ , mt /day	0	2.64	–

¹Emission based on US-EPA-Rule-E9-5711 and natural gas.

Table A3 Sustainability indicators for column 2 with the modifications: N=50→55; NF=33; RR=0.65→0.53; TF= 5 °C → 9 °C.

Material intensity indicators	Column 2		
	Base Case	Modified Case	Change %
Feed rate (mt/day)	3,788.66	3,788.66	0
Distillate rate (mt/day)	3,293.55	3293.55	0
Bottoms rate(mt/day)	495.10	495.10	0
Energy intensity indicators			
Condenser duty, kW	-6,384.75	-6,839.19	+6.64
Reboiler duty, kW	16,260.30	11,123.40	-31.60
Feed conditioning duty, kW	0	5591.27	-
Utility cost in condenser, \$/day	6,498.34	6,960.87	+6.64
Utility cost in reboiler, \$/day	2,663.15	1,821.82	-31.60
Utility cost in feed conditioning, \$/day	0	915.60	-
Total exergy loss, kW	3,726.13	2,343.95	-37.10
Environmental impact indicators			
Condenser CO ₂ emission ¹ , mt /day	30.83	33.02	+6.63
Reboiler CO ₂ emission ¹ , mt /day	78.52	53.71	-31.60
Feed conditioning CO ₂ emission ¹ , mt /day	0	26.88	-

¹Emission based on US-EPA-Rule-E9-5711, natural gas.

Table A4 Sustainability indicators of column 3 with modifications: N=66; NF=35; RR=4.49.

Material intensity indicators	Column 3		
	Base Case	Modified Case	Change %
Feed rate (mt/day)	3,293.62	3,293.62	0
Distillate rate (mt/day)	1,929.82	1,929.82	0
Bottoms rate (mt/day)	1,363.80	1,363.80	0
Energy intensity indicators			
Condenser duty, kW	-37,814.20	-35,080.10	-7.23
Reboiler duty, kW	32,198.80	29,125.50	-9.54
Utility cost in condenser, \$/day	55,312.80	51,313.50	-7.23
Utility cost in reboiler, \$/day	8,821.66	7,979.65	-9.54
Total exergy loss, kW	1,681.69	1,389.02	-17.40
Environmental impact indicators			
Total condenser CO ₂ emission ¹ , mt /day	182.60	169.39	-7.23
Total reboiler CO ₂ emission ¹ , mt /day	155.48	140.64	-9.54

¹Emission based on US-EPA-Rule-E9-5711 and natural gas.

NQ curve analysis:**Column1:**

Table A5 show four different cases of NQ curves analysis, each case gave different number of total stages, feed stage, duties, and reflux ratio. Table A5 is based on feed 2 (DEC1-F2) optimization with an objective function of minimizing the duties so case number 1 is the objective case.

Table A5 Column1 NQ curves result summary [1].

Case No.	Feed Stage	Total stages	Condenser duty, MW	Reboiler duty, MW	Reflux ratio, mole
➔1	15	55	-0.272	9.303	0.382
2	12	53	-0.276	9.308	0.387
3	12	51	-0.280	9.311	0.393
4	14	49	-0.296	9.326	0.418

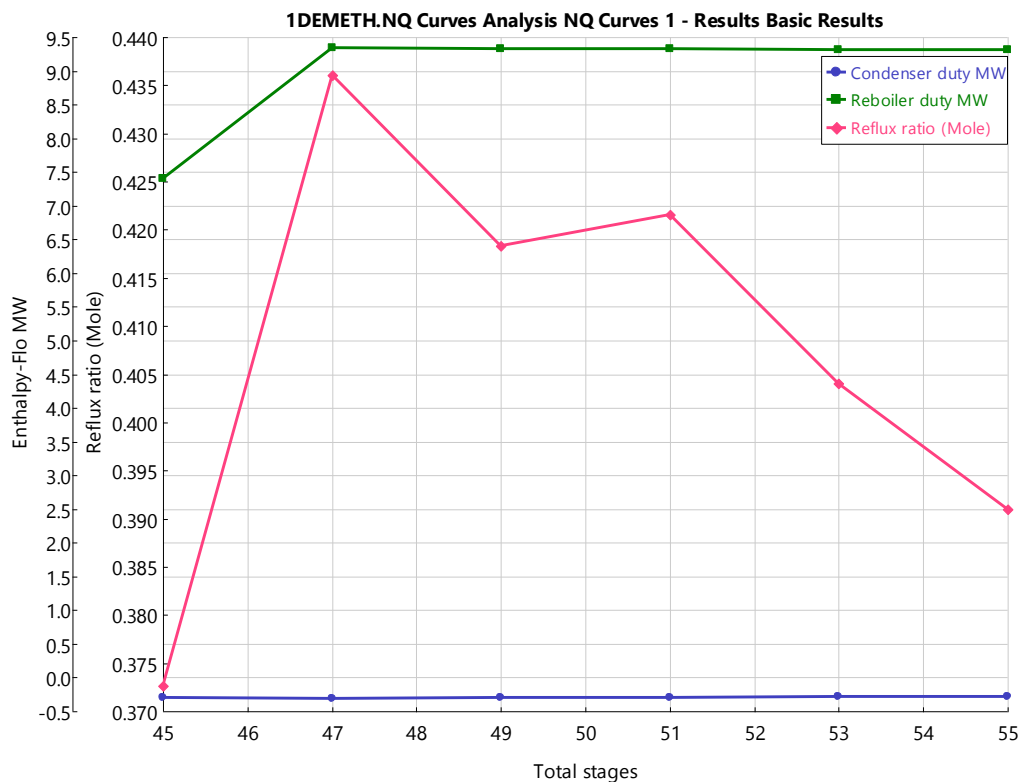


Figure A1 Column 1 NQ curve curves results.

Column 2:

Table A6 show four different cases of NQ curves analysis, each case gave different number of total stages, feed stage, duties, and reflux ratio. Table A6 is based on bottom feed of column 1 (1BOT) optimization with an objective function of minimizing the duties so case number 1 is the objective case.

Table A6 Column 2 NQ curves result summary [1].

Case No.	Feed stage	Total stages	Condenser duty, MW	Reboiler duty, MW	Reflux ratio, mole
→ 1	33	55	-6.316	16.192	0.531
2	31	53	-6.338	16.214	0.533
3	30	51	-6.366	16.242	0.535
4	28	49	-6.399	16.275	0.538
5	26	47	-6.442	16.317	0.542

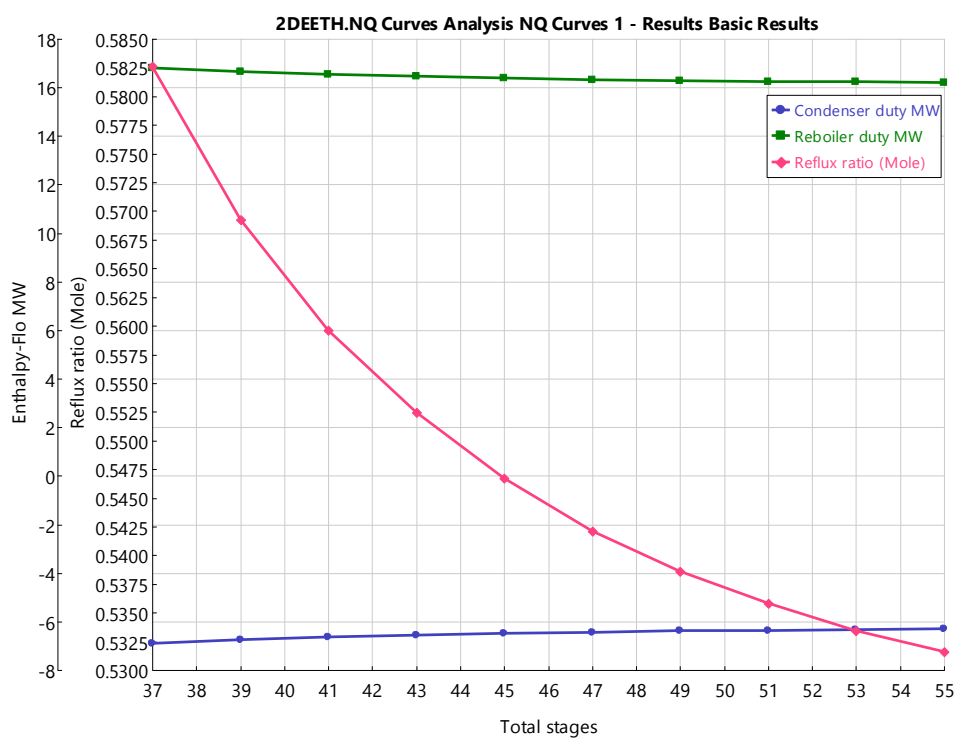


Figure A2 Column 2 NQ curve curves results.

Column 3:

Table A7 shows three different cases of NQ curves analysis, each case gave different number of total stages, feed stage, duties, and reflux ratio. Table A.7 is based on feed

3 (C2FRAC-1) optimization with an objective function of minimizing the duties so case number 1 is the objective case.

Table A7 Column 3 NQ curves result summary [1].

Case No.	Feed stage	Total stages	Condenser duty, MW	Reboiler duty, MW	Reflux ratio, mole
→ 1	35	66	-34.911	29.296	4.494
2	35	64	-35.553	29.937	4.576
3	34	62	-36.361	30.746	4.681

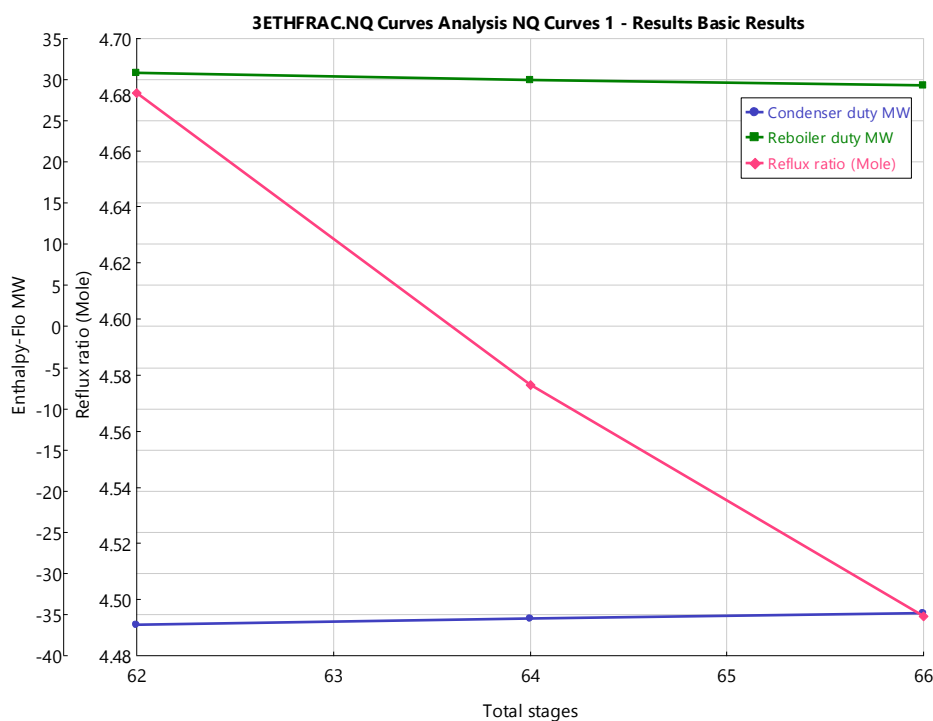


Figure A3 Column 3 NQ curve curves results.

References

1. Aspen Technology: <http://www.aspentech.com/products/aspen-plus.aspx>; accessed in 2013.

APPENDIX B. CHAPTER 7 SUPPLEMENTARY DATA

Methanol Plant Discounted Cash Flow Diagram.

Table B1 Methanol plant DCFD data.

Year	Investment	d_k	BV ^a	R	COM _d	NP ^b	Cash Flow	Cumulative Cash Flow
0	2.00		38.50				2.00	2.00
1	46.20		38.50				44.00	46.00
2		5.51	32.99	20.55	14.04	6.16	5.59	40.41
3		9.43	23.56	20.55	14.04	7.53	6.51	33.91
4		6.74	16.82	20.55	14.04	6.59	5.42	28.49
5		4.81	12.01	20.55	14.04	5.92	4.64	23.85
6		3.43	8.59	20.55	14.04	5.43	4.05	19.80
7		3.43	5.16	20.55	14.04	5.43	3.86	15.94
8		3.43	1.73	20.55	14.04	5.43	3.68	12.26
9		1.73	-	20.55	14.04	4.84	3.12	9.14
10			-	20.55	14.04	4.23	2.60	6.55
11			-	20.55	14.04	10.63	11.89	5.34

^aBV= Book Value = $FCI_L - Sd_k$.

^bNP= Net Profit = $(R - COM - dk) \times (1 - t) + dk$.

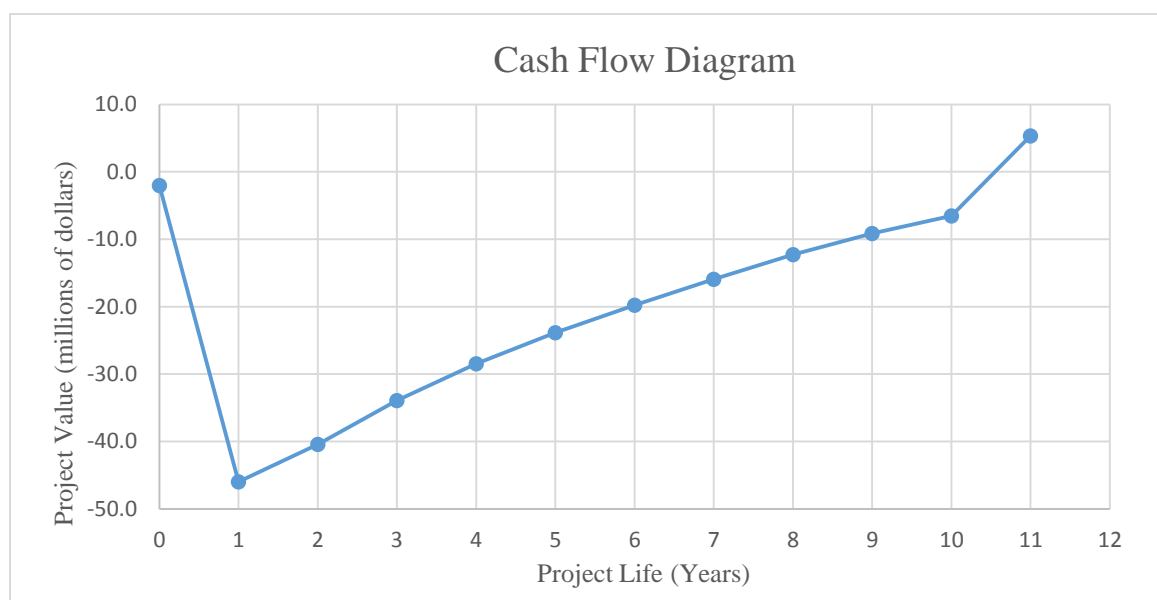


Figure B1 Methanol plant DCFD.

Table B2 Discounted Profitability criterion.

Net Present Value (millions)	5.34
Discounted Cash Flow Rate of Return	7.09%
Discounted Payback Period (years)	7.9

