Process Modelling, Characterization and Dynamic Analysis of Centralized Distillation System for Separation of Methanol and Water

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Process Modelling, Characterization and Dynamic analysis of Centralized Distillation System for Separation of Methanol and Water

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ZEF
ZERO EMISSION FUELS

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Abstract

Over the past few decades, there has been an increased awareness and concern about the rising pollution, global warming, sudden climatic changes, and the accelerating CO_2 emissions that have coerced people to shift to renewable resources and sustainable fuels. Zero Emission Fuels (ZEF) is a leading startup company that focuses on developing a sustainable methanol micro-plant that is powered by solar energy. CO_2 and H_2O are absorbed from the air (DAC system) and the extracted H_2O is split into H_2 (AEC system) in order to produce a methanol-water mixture where the mixture is then separated using a Distillation System (DS system). Each micro-plant operates for 7 hours per day and produces 600 g of methanol. with a distillate methanol purity of 99.8% (AA grade methanol) and in the future ZEF is planning to develop a 'methanol farm' with 13500 micro-plants.

Based on a previous study at ZEF, fractional distillation was seen as a potential system for separating methanol and water mixture with desired purity. On the other hand, it was also suspected that implementing multiple decentralized separation units could be expensive with higher energy consumption and therefore alternative methods of implementing the DS system were analyzed. For this purpose, 3 different schemes namely Decentralized (1 DS per micro-plant), semi-centralized (1DS per 1000 micro-plant) and centralized (1 DS per 13500 micro-plant) were analyzed. Furthermore, heat integrations were introduced as various literature pointed out that a significant improvement in the total cost and energy consumption was observed and hence they were adapted to ZEF requirements. Therefore, six different systems namely conventional distillation (base case), Feed pre-heating, Vapour recompression, Bottom flashing, External heat integrated distillation and Vapour compression systems were suggested. The primary focus of this research will be to analyze these different distillation designs for all the three schemes and recommend a feasible design for the DS sub-system that is both energy-efficient and economically viable along with analyzing the impact of varying ambient conditions on the DS system.

For this purpose, each of these systems was modelled in COCO and the modelling results obtained were used in analyzing the overall energy consumption and the total cost of each design. Different scenarios were analyzed, preliminary equipment designs were estimated. Each system was compared and evaluated in terms of energy and cost-saving and a quantitative and qualitative analysis was performed. Based on this analysis a centralized VRC and base case systems powered by solar PV operating for 7 hours were recommended. In order to understand the impact of fluctuating solar radiation and ambient temperature on the DS system, a MATLAB model was developed. From the results, it was evident that the fluctuating ambient conditions affected the product purities and the startup and shutdown of the DS system. A feed mass flow-temperature control was implemented for Centralized base case system, where the feed mass flow rate into the DS system was adjusted depending on the fluctuating power input. The control structure was able to effectively control the distillate and bottom purities by varying the feed mass flow rate.

Keywords: *Methanol-water mixture, Distillation System, Process modelling, energy and economic analysis, Dynamic analysis.*

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Venkatraman Raju
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Abbreviations and Nomenclature

Abbreviations and Molecular Structures

AEC	Alkaline Electrolysis subsystem
BF	Bottom Flashing
CAPEX	Capital expenditure
CCS	Carbon Capture and Storage
CCU	Carbon Capture Utilization
CH_3OH	Methanol
CO_2	Carbon dioxide
COCO	Cape Open- Cape open
DS	Distillation subsystem
ESH	Equivalent sun hours
Ext.HiDiC	External Heat integrated Column
FCI	Fixed Capital investment
FOB	Free On Board
GHG	Greenhouse Gas Emissions
H_2	Hydrogen
H_2O	Water
Hex	Heat exchanger
HK	Heavy key component
IPCC	Intergovernmental Panel on Climate Change
isc	Short circuit
LK	Low key component
LMTD	Logarithmic mean temperature difference
MeOH	Methanol
MS	Methanol synthesis subsystem
NRTL	Non-random Two Liquid model
O_2	Oxygen
OPEX	Operational expenditure
PSRK	Predictive Soave-Redlich-Kwong
PV	Photovoltaic
TAC	Total Annualized cost
TCPM	Total cost per ton of methanol
TEPA	Tetraethylpentamine
VC	Vapour Compression
VLE	Vapour-Liquid Equilibrium

VRC or MVR	Vapour Recompression or Mechanical vapour Recompression
ZEF	Zero Emission Fuels

Variables and General parameters

$\dot{m}$	Mass flow rate	kg/hr
$A_{condenser}$	Area of condenser	m^2
A_n	Feed flow rate of nth stage	kg/hr
A_{panel}	Solar panel area	m^2
B	Bottom flow rate	kg/hr
c_p	Specific heat capacity	J/kg.K
D	Distillate flow rate	kg/hr
D_c	Diameter of column	m
F	Feed flow rate	kg/hr
G	Solar Irradiation	W/m^2
h	Molar enthalpy	J/mol
h_{conv}	Convection heat transfer coefficient	W/m^2.K
h_{rad}	Radiation heat transfer coefficient	W/m^2.K
I	current	A
k	Thermal conductivity	W/m.K
K_i	Distribution coefficient	-
L_c	Length of column	m
L_n	Liquid flow rate of nth stage	kg/hr
N	Lifetime of DS system	years
n	Total number of systems	-
P	Pressure	N/m^2
P^{sat}	Saturated pressure	N/m^2
P_{total}	Total solar panel output	W
$Q_{condenser}$	Condenser duty	W
$Q_{dutycorrected}$	Corrected duty of solar energy systems	W
$Q_{reboiler}$	Reboiler duty	W
RR	Reflux ratio	-
T	Temperature	K
T_0	Initial column Temperature	K
T_e	Ambient temperature	K
$t_{startup}$	Time	s
$U_{overall}$	Overall heat transfer coefficient	W/m^2.K
V	Volume	m^3
V	voltage	V
V_B	Boil-up ratio	-
V_n	Vapor flow rate of nth stage	kg/hr
x	Liquid phase fraction	-
y	Vapour phase fraction	-

Greek Symbols

α	Absorptivity	-
γ	Activity Coefficient	-

ρ	Density	kg/m^3
ε	Emissivity	-
β	Fraction of feed that is vapourized	-
ϕ	Fugacity	-
α_{ij}	Relative volatility	-
σ	Stefan Boltzmann constant (5.67×10^{-8})	W/m^2.K^4
μ	Viscosity	Pa.s

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Chapter 1

Introduction

This chapter provides an overview of all the background information that is necessary for proceeding with the thesis. A general introduction to distillation systems and an outline of ZEF's distillation system is also presented. Later, problems associated with current ZEF distillation is mentioned and a possible solution with a short summary are presented (section 1.2.4.3). Then, a brief review of heat integration systems and dynamics of distillation column are also discussed (section 1.2.5). Finally, the chapter ends with research objectives (section 1.3.2) and report outline. (section 1.3.3).

1.1 Introduction

1.1.1 Cause and Effect: CO$_2$ Emissions and Climate Change

Over the 20th Century, the world has been witnessing a drastic increase in global population and eventually, this has led to an upsurge in global energy demand. Fossil fuel including coal, oil and natural gas has been considered as one of the major energy sources ever since the industrial revolution and the consumption of fossil fuels has seen a rise due to this surging global energy demand which had caused some serious impacts especially climate change and global warming on both human civilization and biodiversity [1].In the past few decades, there have been an increased awareness and concern about Global Climate change and its unremitting environmental and health impacts. Climate change results in a sudden shift in the weather pattern, the surging temperature of the Earth's atmosphere, pre-mature melting of glaciers and rises in sea levels, changing weather patterns, drought and the unprecedented catastrophic events and effect on food production, widespread losses of wildlife and ecosystem[2].

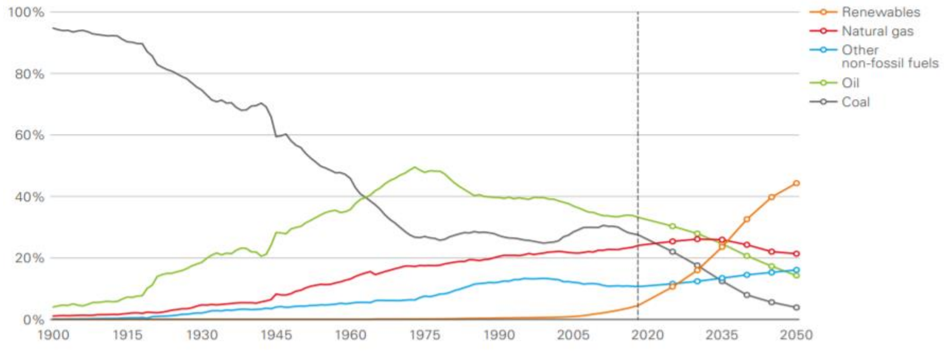


Figure 1.1. Global Primary Energy Consumption shares 2020[3]

Many scientists across the world have attributed Climate change and global warming to "Anthropogenic Carbon emissions" (emission pertinent to human activities) which are usually emitted from the combustion of fossil fuels for heat and electricity, burning of agricultural products, volcanic eruptions, industrial and transportation emissions [4]. Anthropogenic CO2 emissions were first acknowledged as the major contributor to Global Warming in the Kyoto Protocol of 1997. Intergovernmental Panel on Climate Change (IPCC), an internationally accepted authority on climate change have predicted that maintaining global warming below 1.5℃ is cardinal to mitigate Climate change and its repercussions [5]. Later Paris Agreement was signed in December 2015 between countries that contribute at least 55% of global emissions, the global warming should be maintained below 2℃ to avoid the detrimental impacts of global warming. As a part of the Paris Agreement, many countries and companies agreed upon certain mitigation strategies and has already started implementing them to reduce carbon emission [6].

1.1.2 Decarbonization and Green Methanol Production

1.1.2.1 Mitigation Strategies:

Continuous measuring and controlling of the carbon footprint are paramount and having a comprehensive understanding of the source of emissions is cardinal to propose a mitigation strategy for decarbonization. These mitigation strategies are majorly applied to four main sectors namely the industrial sector, transport sector, agricultural and building sector which are the major GHG emission contributors, and these mitigation strategies can be classified into three namely, Mitigation by shifting to renewable resources and sustainable fuels, mitigation through process and energy optimization, and mitigation through advanced decarbonization technologies

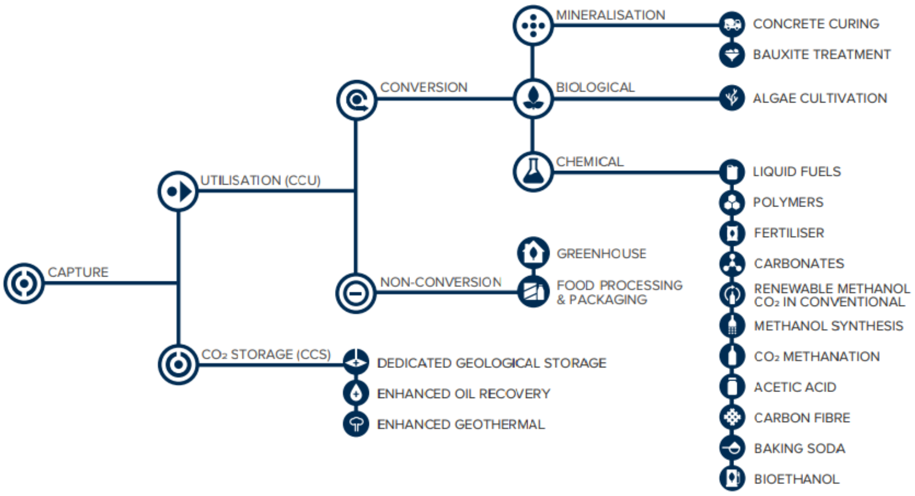
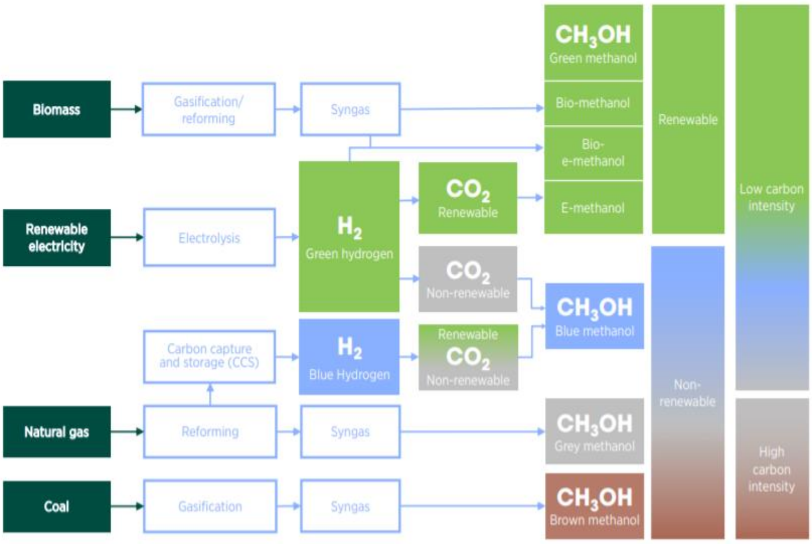


Figure 1.2. Classification of Carbon Capture storage and utilization[7]

Most of the industries have begun to switch from conventional energy sources to renewable energy sources such as solar photovoltaic, solar thermal, concentrated solar power, wind energy, geothermal, hydropower, biofuels, and biomass[8]. Out of these solar and wind powers are the most preferred energy sources as they offer the maximum decarbonization potential. Electric and hydrogen vehicles are quickly transforming the transportation sector. Biofuels especially the hydrogen produced through electrolysis is used in the production of various chemical in industries sustainably. Mitigation through advanced decarbonization technologies such as CCU/CCS, soil carbon sequestration, biochar, wetland restoration and process and energy optimizations have proved to be beneficial and a promising strategy to reduce CO_2 emission[9] Most of the industries have incorporated decarbonization technologies like Carbon Capture and Storage (CCS) and Carbon Capture Utilization (CCU). The waste CO_2 from factories and powerplants are captured, transported, and stored using CCS technology and with the help of CCU, these captured CO_2 are utilized in the production of zero-carbon fuels [10].

1.1.2.2 Carbon-neutral methanol - A sustainable link to the future:

Methanol is considered one of the most important industrial chemicals due to its vast application in the production of various chemical products such as paints, solvents, mattresses, fertilizers, adhesives, cosmetics, consumer products etc.[11]. The production of formaldehyde has been one of the largest applications of methanol. Methanol is one of the major feedstocks for the plastic and pharmaceutical industry and is a common fuel in the power generation industry. It can also be used as the source for Direct Methanol Fuel Cells which are considered as one of the solutions for the intermittency issue in renewable energy production and are viable replacements to costlier batteries. Methanol is seen as one of the alternative fuels which can be used in long-range vehicles such as ships, trains, aviation, and heavy good vehicles. In future, methanol will be used as a renewable fuel, energy storage and used for synthesizing hydrocarbons and their products and are suggested as a bridge to a sustainable future and a major alternative to fossil fuels. Methanol is bio-degradable and has a high-octane number and therefore it burns with no soot and low No_x and So_x emissions[12].The usage of methanol-based fuels has been increasing in Asia Pacific regions especially in India, China, and Japan.



Renewable CO_2: *from bio-origin and through direct air capture (DAC)*
Non-renewable CO_2: *from fossil origin, industry*

Figure 1.3 Various Methanol production routes[13]

But a major drawback is that in most cases methanol is produced from the combustion of non-renewable resources such as steam reforming natural gas. [Appendix A.1]. In China, more than 67% of industries produce methanol by burning coal and in Germany, more than 90% of the methanol industry uses natural gas steam reforming process.[14]. This contributed to global greenhouse gas emissions and therefore an alternative “green” process which involves the production of hydrogen from renewable energy sources and carbon dioxide from Carbon capture technology was developed. Studies from the literature [15] show that there are different methods to produce methanol and out of which the Two-step methanol synthesis method and direct methanol synthesis were predominantly used. The former method used Carbon dioxide and hydrogen to produce CO through reverse water gas shift. Later this CO was utilized to produce methanol by the addition of excess hydrogen into the second reactor. This method gave a higher yield of methanol where optimal productivity was achieved at 50-100 bar and 200-300 ^{o}C. In the second method, carbon dioxide and hydrogen were directly injected in the ratio of 1:3 to produce methanol and other by-products. The advantage of the latter method was its comparatively more economical.[16]. Therefore, Renewable methanol production was a game-changer in chemical industries and these reasons served as an impetus for the establishment of Company - “Zero Emission Fuels”.

1.2 Literature Study

1.2.1 Distillation Theory

Separation Techniques: Distillation Separation

The separation process has always been one of the most crucial and ineluctable methods in process and chemical industries where mixtures and products with two or more phases are separated. The separation techniques can be predominantly categorized into four: Gas-Gas separations, Liquid-Gas separations, Liquid-Liquid separations, and solid separations [17]. Liquid-liquid mixtures are ubiquitous in chemical industries and Distillation has been a default process for the separation of liquid-liquid mixtures. Various types of distillation such as simple distillation, extractive distillation, stripping distillation, etc. are used in industries. Barnicki & Fair [18]have proposed various methods for the separation of liquid-liquid mixtures depending upon the boiling and freezing point differences ranges, relative volatility, similarity in chemical family, polarity differences, temperature sensitivity and purity. At ZEF, Liquid-Liquid separation named Simple Distillation was considered for separation of methanol and water mixture and this distillation process was a continuous process. The methanol-water mixture was a binary, non-ideal, non-azeotropic and miscible liquid with relative volatility greater than 1.5. Distillation has always been energy-intensive technology that uses 50-70% of the total energy required in large industries and most of these energies were provided from the combustion of non-renewable fuels. But the research and innovations in distillation technologies in the past few decades have made this process a more energy-efficient and sustainable process. Implementation of solar energy in distillation [19], electrification of distillation columns [20], micro-distillation, heat integrations are some of the latest advancements in distillation. Micro-distillation is the technology that is currently implemented at ZEF.

Continuous Distillation System

Distillation is a process of separation of a liquid mixture into two or more components as distillate and bottom product depending on the relative volatility of components. The relative volatility depends on the differences in boiling points of each component. When the relative volatility is higher, better will be the separation of components. A multi-stage continuous distillation column consists of a column with a certain number of equilibrium stages with a reboiler and condenser attached to the bottom and top of the distillation column. The stages can be trays or packings [17]. The feed stage location plays an important role in the separation of liquid mixture and affects the column specifications and the energy consumption. Optimum feed stage location results in minimum energy consumption, reduced number of stages and high purity products. The feed phase conditions can range from subcooled liquid to superheated vapour.

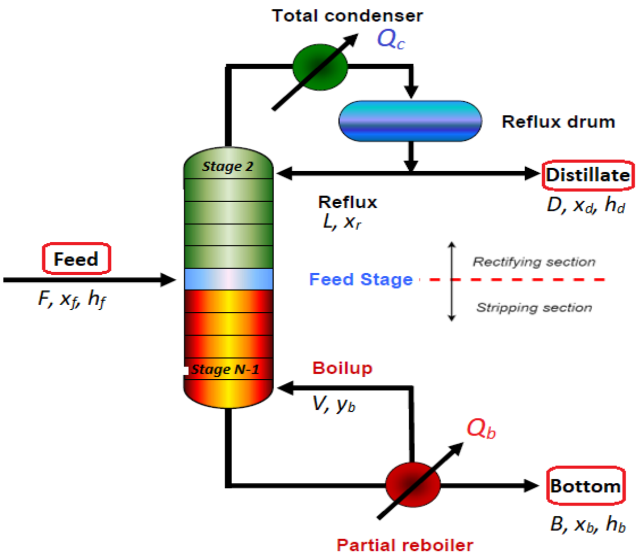


Figure 1.4. Conventional Distillation Column with total condenser and partial reboiler

The feed stage divides the column into Rectifying section and Stripping Section. The stripping section corresponds to the stages below the feed stage. The liquid mixture is partly heated in the partial reboiler to boiling temperature and due to differences in boiling point temperature, more volatile compounds, or light key compounds (LK) vaporize and these vapours flow to the top of the column. Thermosiphon, kettle and forced circulation are three different types of reboiler available [21]. The less volatile component or heavy key component (HK) with a high boiling point which are always in a liquid state are collected as bottom products. Rectifying section represents the stages above the feed stage and a reflux drum and total condenser with reflux are available at the top of this section. The vapour which is richer in more volatile components flows through the total condenser where it condenses completely to liquid. A part of the liquid is refluxed back into the column and the remaining liquid is extracted as a distillate or top product. Both the reflux and the boil-up ratio are necessary to improve the purity of top and bottom products [17]. The purity of products can be increased by increasing the reflux and boil-up ratio or by increasing the number of stages in the column [Refer Appendix A.3].

Energy Requirement of Distillation System

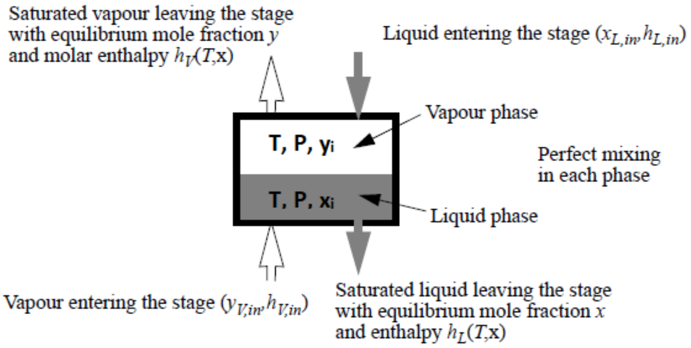
The total energy demand of a Distillation system generally depends on the four important parameters: Sensible energy, vaporization energy, reflux ratio and heat losses. Sensible energy is usually the energy required to rise the temperature of the fluid to the boiling point temperature and at this temperature phase change does not occur. The sensible heat depends on the mass flow rate, specific heat capacities and the temperature difference between the initial fluid temperature and boiling point temperature. Vaporization energy is the energy required to vaporize methanol from the liquid to the vapour phase in the reboiler. Heat losses to the surrounding also contribute to the total energy demand of the column and the intensity of losses depends on the insulation. Poor insulation leads to higher heat losses and therefore, the temperature within the column decreases. The maximum heat loss occurs at the reboiler and this is followed by the stages and as a result, excess energy needs to be supplied to overcome these heat losses. Reflux ratios also determine the total energy demand as higher condensed fluid is refluxed back, more sensible and vaporization energy needs to be supplied to evaporate this condensed fluid. As mentioned earlier, the ZEF sub-systems are powered by solar panels. Over the past few decades, there has been a dramatic drop in prices of solar thermal and solar PV panels and changing energy policies, government investments and financial incentives make solar energy one of the most preferred renewable energy. A major issue with solar energy is the intermittency issues which requires storage capacities such as batteries to store the produced energy which eventually increases the plant size and the total capital cost.

1.2.2 Vapour Liquid Equilibrium (VLE) of Binary Mixtures

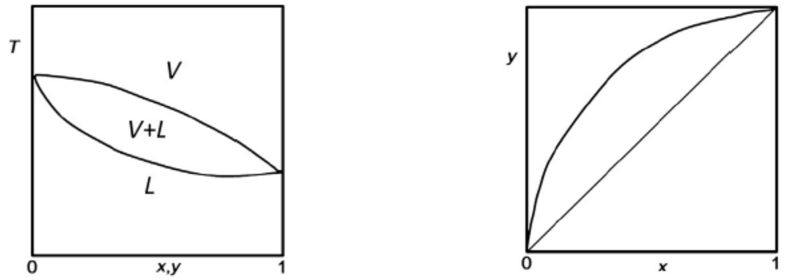
The separation of components in a system depends on the boiling point difference, vapour pressure, temperature, and compositions of the mixture. Therefore, understanding the distribution of chemical components in different is necessary. Depending upon variation in external conditions such as pressure, temperature, etc., a qualitative change will be observed in properties of system and system changes from one phase to another which is called phase transition or phase change. For example, the phase transition of a liquid to vapour by heating it to boiling point. In a system where phase transition occurs, given sufficient time an equilibrium will always be reached. A system is said to be at equilibrium if all physical properties remain unchanged with time and the interactions are zero. Equilibrium represents stability. Thermal, mechanical, chemical and phase equilibrium corresponds to temperature, pressure, chemical potential, and phase remaining constant throughout the system and together they form the thermodynamic equilibrium.[22] .The criterion for equilibrium is

$$\begin{aligned} T^I &= T^{II} =.....= T^n && (thermalequilibrium) \\ P^I &= P^{II} =.....= P^n && (mechanicalequilibrium) \\ \mu^I &= \mu^{II} =.....= \mu^n && (chemical\ equilibrium) \end{aligned} \tag{1.1}$$

A system is said to be in Vapor-Liquid equilibrium or VLE when both vapour and liquid phases of pure substance or mixture coexist under specific temperature and pressure conditions. In a Distillation system, VLE plays an important role as there is a mass and heat transfer taking place in each stage and therefore the knowledge of VLE is important for designing and optimizing the distillation column. VLE of the mixture can be easily estimated from important equations such as Antoine, Modified Raoult's equation, activity correlation and summation of vapour fraction as they are a function of pressure, temperature, and phase composition of mixture [23]. Figure 1.5a shows an equilibrium stage of a distillation column where the output liquid and vapour streams are in equilibrium. Pressure-mole fraction graph at constant temperature or Temperature-mole fraction graph at constant pressure or vapour and liquid mole fraction graph at constant pressure are some ways of depicting a VLE. T-xy graph and x-y graph are presented in Figure 1.5b. For binary mixtures, if any two parameters (pressure, temperature, or mole fractions) are known, the unknown quantity can be estimated using VLE. Accurate VLE plots help in the proper designing of the distillation column. VLE plots for mixtures are usually predicted using the Modified Raoult's Law and this law requires certain vital parameters for calculation which are elaborately discussed in Appendix A.4



(a)



(b)

Figure 1.5. a) vapour-liquid Equilibrium in Stage (b) VLE curve (T-xy and x-y plot) example [23]

1.2.3 Zero Emission Fuels

Zero Emission Fuels (ZEF B.V.) is a Dutch Startup company founded at Delft that is working on producing a low-cost commercial methanol synthesis plant that uses water to split hydrogen and air to capture carbon dioxide thereby turning them into methanol through direct methanol synthesis or CO_2 hydrogenation process [16]. The process is powered by 300W solar panels, and each micro-plant is equipped with three solar panels and therefore it's called a "3X System". The peculiarity of this project is that the methanol is developed sustainably with the use of renewable resources, produces valuable fuel which can be used in the transportation sector or chemical industry and it is a small scale and a compact micro plant that is automated with fast start-up procedure and faster response to dynamic fluctuations [10] Various other reasons for opting for micro-plants was that they are safer, improvements in yield, energy efficiency, easier controllability, scalability, it's easier to troubleshoot problems and has lower investment and operational costs

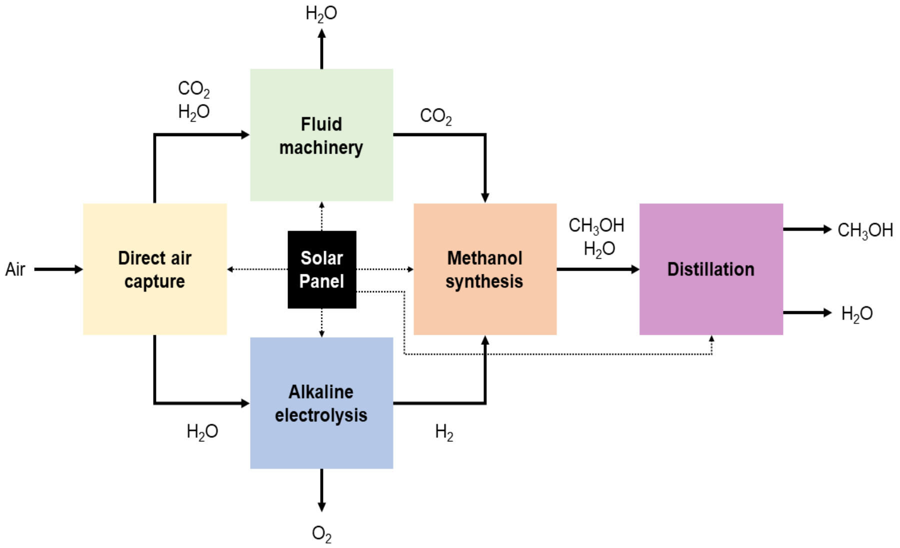


Figure 1.6 Schematic of ZEF micro plant [24]

Figure 1.6 represents an overview of the ZEF process. The ZEF micro plant consists of 5 sub-systems and each of these sub-systems has different purposes The main objective of the micro-plant is to produce AA-grade methanol through a direct hydrogenation process by capturing CO2 and splitting H2O. The methanol-water mixture produced by the methanol synthesis reactor is then separated using a distillation process. To achieve this objective, ZEF combines a series of sub-systems into a single micro-plant and each sub-system carries out different tasks. The rest of this section will provide an overview of the responsibilities of each of these sub-systems. Later, the detailed study of the Distillation sub-system at ZEF will be presented along with its drawbacks and alternative solution to the common problem faced by the DS sub-system.

1.2.3.1 ZEF Sub-systems

The entire methanol micro-plant can be divided into five sub-systems and each of these sub-systems play a unique role in the methanol production process. Figure 1.6 represents the various sub-systems in the ZEF micro-plant and each of these systems are explained below.

- **Direct Air Capture (DAC)** : DAC is the first unit of the plant and in this system carbon dioxide and water are absorbed from the air using liquid amine-based sorbent (TEPA-PEG). Then the loaded amine solution is fed into the stripper section where CO_2 is desorbed. This CO_2 is used in the production of methanol and the separate water is utilized by the AEC subsystem.
- **Alkaline Electrolysis Cell (AEC)** : This subsystem helps in splitting water which is captured from the DAC unit into hydrogen and oxygen. This is done using an alkaline electrolysis cell with KOH as an electrolyte and uses solar energy as the source of electricity. This system pressurizes the liquid H_2O captured by the DAC sub-system and decomposes it into H_2 and O_2 gases where O_2 is purged to the surrounding. The split hydrogen is used in the reactor unit to produce methanol
- **Fluid Machinery (FM)** : CO_2 and H_2 are compressed to 50 bar in multiple stages using the fluid machinery subsystem. The pressurized components are then fed into the reactor system.
- **Methanol Synthesis (MS)** : In the methanol synthesis subsystem, the pressurized CO_2 and H_2 are synthesized with $Cu/ZnO/Al_2O_3$ catalyst in Lurgi reactor at 230-250°C to produce methanol as product and water as a by-product
- **Distillation System (DS)** : The methanol-water mixture from the MS sub-system is then fed into DS where methanol and water are separated with a distillate methanol purity of 99.8%.

1.2.3.2 ZEF Requirements

AEC system :

$$4H_2\mathrm{O} \leftrightarrow 4H_2 + 2O_2 \tag{1.2}$$

MS reactor :

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \qquad \Delta\mathrm{H}_{298} = -49.5\ \mathrm{kJ/mol} \tag{1.3}$$

$$CO_2 + 2H_2 \leftrightarrow CH_3OH \qquad \Delta\mathrm{H}_{298} = -92\ \mathrm{kJ/mol} \tag{1.4}$$

$$CO_2 + 3H_2 \leftrightarrow CO + H_2O \qquad \Delta\mathrm{H}_{298} = -41\ \mathrm{kJ/mol} \tag{1.5}$$

The main goal of ZEF is to produce 600 g of “AA grade (99.8% purity)” methanol per day per micro plant which is equivalent to 18.75 mol of methanol. Usually, in direct hydrogenation of CO_2 reaction, 1 mole of carbon dioxide combines with 3 moles of hydrogen to produce 1 mole of methanol and therefore to produce 18.75 mol of methanol and water, we need 18.75 mole and 56.25 moles of carbon dioxide and hydrogen respectively which is equivalent to 824.56 g of CO_2 and 112.5 g of H_2. The plant is designed to work for 7 hours per day. Methanol is usually produced from a direct methanol synthesis reaction which is shown in equation 2.3-2.5 [15] The current research is related to the Distillation System and therefore, the rest of the sub-systems will not be discussed.

1.2.4 DS system at ZEF

Distillation is an energy-intensive system, but it has always been the most preferred process for the separation of liquid mixtures. Over the years, there has been tremendous improvement in the Distillation technology and one of the latest advancements which are the micro-distillation systems were implemented at ZEF. As mentioned earlier, the ZEF DS system is the final sub-system of micro-plant which is responsible for the separation of a methanol-water mixture produced from a Methanol Synthesis reactor. Table 2.1 in Section 2.1 provides an overview of the requirements and specifications of the ZEF DS System.

1.2.4.1 Micro-Distillation and its Classification

Micro distillation is one of the latest advancements in distillation process intensification that has been widely researched for the past few decades. These systems are safer with efficient mass and energy transfer, consumes less energy consumption, offer a high contact area to volume ratio and have high driving force gradients with short transport distances. A major advantage is a reduction in the size of equipment, cost, ease of maintenance and response time. [25]. In this type of distillation, surface forces such as capillary forces dominate over gravitational forces. Various types of micro-distillation systems are available, but they can be majorly classified into two types: Concurrent flow distillation and Countercurrent flow distillation. Microdistillation with segmented flow and bubble assisted distillation belongs to concurrent flow whereas membrane distillation, microchannel, sieve-tray micro rectification, rotating microchannel and zero-gravity distillation with heat pipe falls under counter-current distillation. The schematics and detailed working principles of all the types of micro distillation systems are presented in Appendix A.5.

Out of all these types, Capillary distillation or zero gravity distillation developed by Seok and Hwang [26] was found to be one of the most efficient distillation systems which produce products with high purity and higher throughputs with high efficiency. Due to this reason, this method was implemented at ZEF to separate methanol and water. A plot representing the level of purities achieved by each distillation type has been presented in the report and they conclude that the design by stating that Seok and Hwang achieve the highest methanol purity. The principle behind this concept is explained in the next section.

1.2.4.2 ZEF DS System

Zeok and Hwang Design: The first operational zero-gravity distillation was proposed in 1985 by Seok and Hwang [26]where they experimented with two different mixtures: Methanol-water and Ethanol water. The adiabatic section was made of a glass tube with an inner diameter of 10.5 mm and a length of 100mm. Several layers of fibreglass material with a thickness of 1.2 mm which acted as a wick material was attached to the wall. Copper tubes were used for both evaporator and condenser. The feed position was at the middle of the column and constant heat flux was supplied. It was observed that a high separation with methanol purity of 99% and ethanol purity of 74% was achieved and concluded that separation predominantly occurs in the adiabatic section and high reflux leads to better separation. A similar system was implemented at ZEF for the separation of methanol and water.

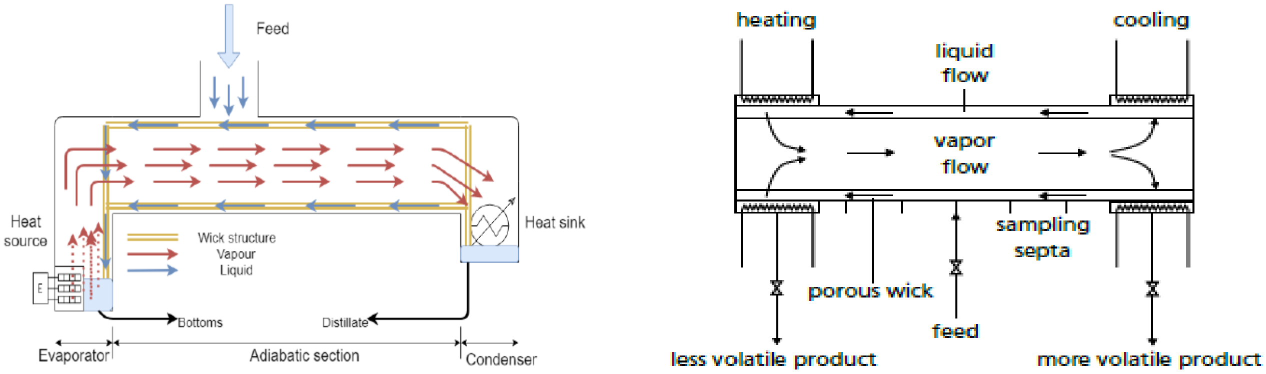


Figure 1.7. (a) Zero Gravity or Capillary distillation (b) Schematic of distillation apparatus designed by Seok and Hwang [26]

- Zero gravity distillation is also called capillary distillation is a micro distillation that utilizes the heat pipe principle and primarily works on capillary action. The system is divided into three parts: Evaporator zone, Adiabatic section, and Condenser zone.
- The system consists of a closed heat pipe with an evaporator attached to the heat source at one end and a condenser on the other side. The system is oriented in the horizontal direction. A wick material is provided which acts as a reflux system and this wick is made up of metal or ceramics and is placed inside the pipe connecting the condenser and evaporator region.
- The wicks are porous material that transfers liquid between two zones and mass transfer takes place between two phases. The feed inlet is at the middle of the pipe in the adiabatic section. The feed mixture from the Methanol synthesis reactor enters the distillation system and flows to the evaporator zone which acts as a reboiler in conventional distillation.
- The fluid is heated, liquid vaporizes and the vapour flows through the adiabatic zone and gets condensed in the condenser. More volatile products are obtained here, and the fewer volatile products are extracted at reboiler.
- The wick which is saturated with liquid refluxes part of liquid obtained at the condenser to reboiler due to capillary pressure. Therefore, capillary forces dominate gravitational forces. The capillary distillation can be regarded as continuous distillation due to this constant counter-current flow
- Various developments were made to this micro-distillation system, and they are explained elaborately in Appendix. A.6. A summary is presented in Table 1.1

1.2.4.3 Problem and Alternative Solution: Current DS System

Problems with current micro-distillation system:

Table 1.1. Drawbacks of different ZEF Designs and recommended solutions

Design	Salient Features	Purity	Major drawback	Solution
D1	• Seok and Hwang Design • Feed inlet position -above the hot end • Sorbo Absorber cloth-wick material • Polycarbonate body and copper joints • 200g methanol production	Distillate-77.37% Bottom-N/A	Distillate purity	• Changed polycarbonate body and feed position • Hot and cold end slightly bend
D2	• Copper body and copper joints • Feed inlet position -middle • Sorbo Absorber cloth-wick material • 200g methanol production	Distillate-95.77%	Distillate purity Energy losses	• Changed body material • Changed wick material • Added insulation
D3-(1)	• Stainless steel body (resulted in fewer energy losses) and aluminium tubes • Kevlar fiberglass wick • Feed pre-heated and proper insulation provided • Reboiler duty-37.4 W • 200g methanol production	Distillate-93% Bottom- 97%	Distillate purity Energy losses	• Changed the piping material • Tilted the setup • Increased reboiler temperature to compensate for losses

D3-(2)	• Silicon tubing • Tilted setup by 10° • Increased reboiler temperature to 115°C and duty is 50W • 200g methanol production	Distillate-99.9% Bottom-N/A	Energy loss for all micro distillation unit-very high Unstable product - when run over a longer period 3-4 hr operation	
D3-(3)	• Microdistillation was expensive and high energy consumption • Proposed Fractional Distillation – 600g of methanol production • 7 hr operation	Distillate-99.8%	Higher reflux ratio recommended and therefore reboiler duty increased (112.2 W) Lower feed flow rate recommended	• Suggested conventional distillation system

Summary:

[1] According to Siepel's report [11] , ZEF prototype 3 was **designed for total methanol production of 200 g per** day and the total energy consumption was approximately 37.4 W with losses whereas **as current ZEF requirement is 600 g/hr**. Therefore, producing 600 g of methanol per day with current specifications became a highly energy-intensive process thereby increasing the energy cost which is one of the main disadvantages with the present micro distillation system.

[2] It was also mentioned that a **product with desired purity was not achieved when the system ran for a longer period**.

[3] The **energy losses in these systems were found to be high** and therefore heat losses for the entire park with 13500 plants were found to be huge. Heat integration was recommended to reduce the duty but implementing it was complicated. A large ZEF farm consists of 13500 plants and **implementing a micro-distillation system for each plant was found to be expensive**.

Alternative solutions:

[1] A conventional **Fractional Distillation** system was seen as a potential solution to **address the high cost, product purity and energy issues**. In Gokberk's report [27] a decentralized fractional distillation system was modelled in COCO for a 7-hour operation period. It was observed that there was a significant reduction in the energy consumption where the total reboiler duty decreased to 57.9 W by considering energy loss. Moreover, as this is a conventional distillation system, the problem of selection of perfect wick material was avoided. This **system produced products with desired purity**

[2] The report also **recommended a Centralized Distillation system** where instead of multiple decentralized distillation units, separation of methanol and water was done by sending the products of all the Methanol reactor sub-systems to a single centralized conventional distillation unit was found to be one of the feasible solutions. The main reason was the losses in the centralized distillation system was smaller when compared to losses of 13500 decentralized DS systems.

[3] Another **major advantage with a conventional distillation system was that the implementation of heat integration was possible** and numerous literature with satisfactory results pertinent to heat integration in methanol-water distillation were available. Therefore, these systems needed to be studied and analyzed to design a stable, cost and energy-efficient Distillation system. [21].

1.2.5 Heat Integrated Systems

Heat pump-assisted distillation technology is one of the latest inventions that solve the problem of high energy consumption, high cost and low energy efficiency of the conventional distillation columns. In this technology, the low-temperature heat rejected in the condenser will be used as an energy source to heat the reboiler thereby effectively reducing required energy and cost. Various designs such as VC, MVR, HiDiC, cyclic, divided wall and Kaibel column, CRHP, TAHP are available across numerous literatures and a few out of those designs which are suitable for methanol-water distillation (binary separation) are discussed in this section. Kiss et.al [28] had classified various heat integrated systems pertinent to binary distillation. Based on the classification, Cyclic, DWC and Kaibel columns are used for multi-component separation whereas VC, MVR, HiDiC, TAHP, etc. are implemented with binary distillation systems. In this thesis the simplest and commonly used heat integrated designs that were found to be most efficient for binary distillation columns were considered.

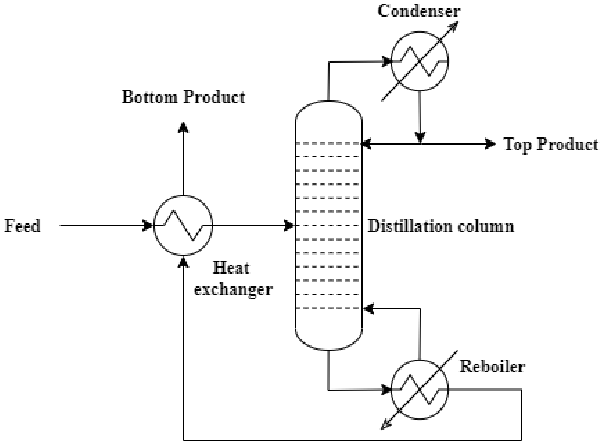


Figure 1.8. Feed-preheating system

Feed-Preheating systems: This design is the simplest out of all the heat integrated designs **where a heat exchanger is used to preheat the feed mixture**. Pratibha et.al [29] simulated a 30 tray distillation model that separated methanol and water with a methanol distillate purity of 99.9% and reported an average energy saving of 2.32% for a methanol-water distillation system with pre-heater.

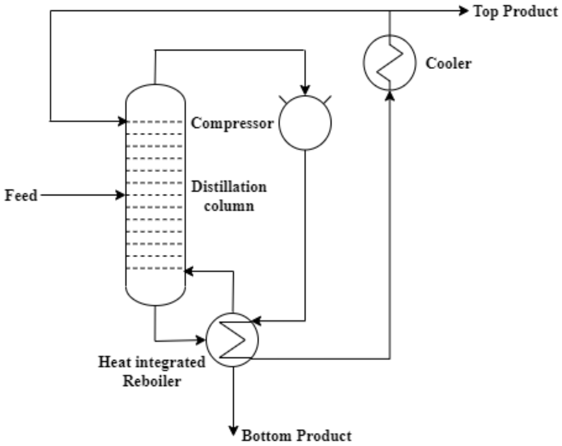


Figure 1.9. Mechanical Vapor Recompression system

Mechanical Vapor Recompression: In MVR, **the vapour coming out from the top of the distillation column is used as an energy source to heat the fluid mixture in the reboiler**[28]. This technology uses compressors and heat exchangers for heat integration. A major concern with this technology is that a high-pressure ratio is required to create a positive heat transfer in the heat exchanger and often two compressors are required to create this high pressure [30]. It is also called a vapour recompression column (VRC). Most literature reported a significant reduction in energy consumption and total annual cost.

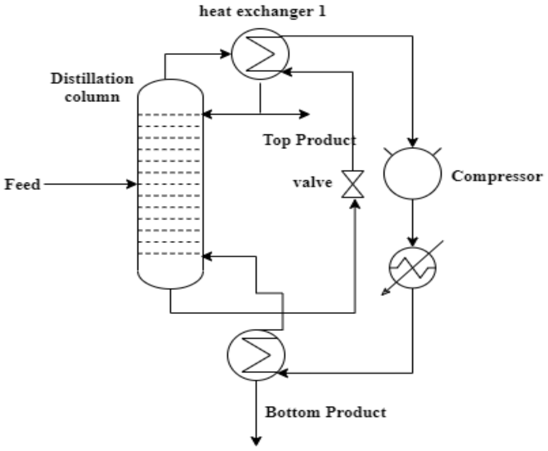


Figure 1.10. Bottom Flashing systems

Bottom Flashing: Another configuration is the bottom flashing **where the bottom product temperature is decreased by using an expansion valve and utilizing this low-temperature liquid to cool the hot vapour**. After cooling the overhead vapour, the bottom product becomes a saturated vapour, and this vapour is then compressed back to initial pressure thereby increasing the vapour to a higher temperature [31]. The vapour is returned to the bottom stage of the column as a boil-up. This was found to be less efficient than VRC and capital costs were found to be close to the base case distillation column column considered in the literature [29]

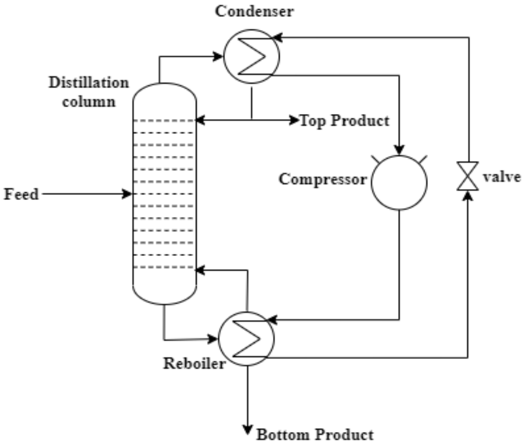


Figure 1.11. Vapor Compression system

Vapour Compression Distillation (VC): In this type of system, **an external loop containing a compressor and an expansion valve with specific heat transfer fluid such as refrigerant is heat integrated with a conventional distillation column.** Heat exchangers are used to transfer heat in the reboiler and condenser. Pratibha et.al [29]used R-114 refrigerant and reported an average energy saving of 78% with respect to conventional methanol-water distillation system. VC systems are one of the classical and proven concepts, but a major drawback is the usage of compressors and refrigerants which are hard to maintain and not sustainable. Kiss et al. concluded MVR was more energy-efficient and requires less CAPEX compared to VC [28]

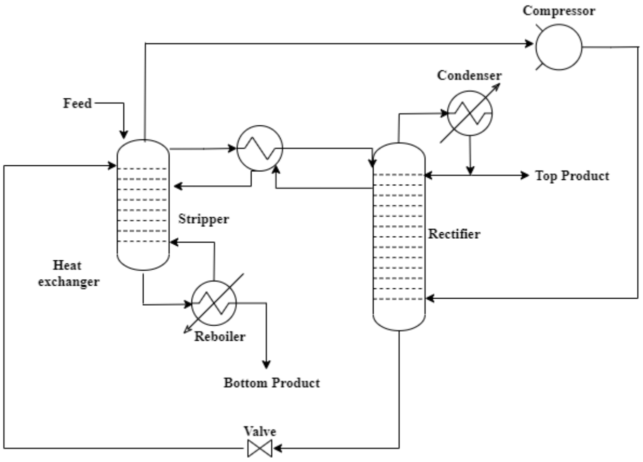


Figure 1.12. External Heat integrated Distillation system

External Heat integrated Distillation column (Ext.HiDiC): In these types of systems, the **distillation is divided into two columns: rectifier section and stripping section** and it is normally divided along the feed location. The **rectifier** is normally at a **higher pressure** than the stripper and therefore rectifier acts as a heat source and the stripper as a heat sink where **heat integration is made possible by utilizing a heat exchanger and compressor**. There are two different types of HiDiC: Internal and External. [32] and concluded that the internal HiDiC with rectifier placed inside a stripper with heat integration through heat panels are less efficient than external HiDiC with two separate columns heat integrated using a heat exchanger. The total annual cost of external HiDiC was less and they can be easily designed and controlled. In external HiDiC, the overhead vapour of the stripper is compressed using the compressor and fed into the rectifier and this is the reason for high pressure in the rectifier. Due to this heat exchange, a part of reboiler duty is reduced [30]. A significant drop in total annual cost and energy consumption was observed due to effective heat integration

Table 1.2. Comparison of energy-efficient heat integrated Methanol-water distillation technologies

Literature	Technology	Energy Saving (%)	Total Cost reduction (%)	Payback time (yrs)
Kiss et. al [28]	VC	46*	43	0.9
	HiDiC	41	-	-
	MVR	69	67	0.7
Pratibha et.al [29]	MVR	82	67	0.48
	VC	78	44.7	0.81
	Feed preheat-bottom	2.32	1.05	0.01
Shahandeh et.al [30]	VRC	49.6	3.1	7.54
	Ext.HiDiC	56.4	27.2	3.48
Harvindran et.al [33]	HiDiC	71.2	4.32	7
(*) denotes average value from different sources and all values are compared with values of conventional distillation mentioned in specified papers				

1.2.6 Dynamic Behaviour analysis of DS system

1.2.6.1 Influence of Dynamic Environment on the DS system

One of the major fluctuating disturbances for the DS powered by solar PV is dynamic solar radiation. In ZEF's distillation column the fluid mixture in the reboiler will be heated directly by introducing heating elements into the reboiler. It is a well-known fact that large fluctuations in solar radiation can be observed between different hours of the day, between consecutive days or between different seasons which directly affects the solar PV output. Figure 1.13 depicts a weekly variation in solar radiation across months. These variations highly influence the purity of methanol, cost, and performance of the distillation system. Another factor that needs to be considered is the geographic location and changing weather patterns. Poor selection of geographical location may result in increased investment costs as more solar energy systems are necessary to produce the minimum energy required for the distillation process. Varying weather patterns can influence the availability of sunlight, air temperature and humidity.

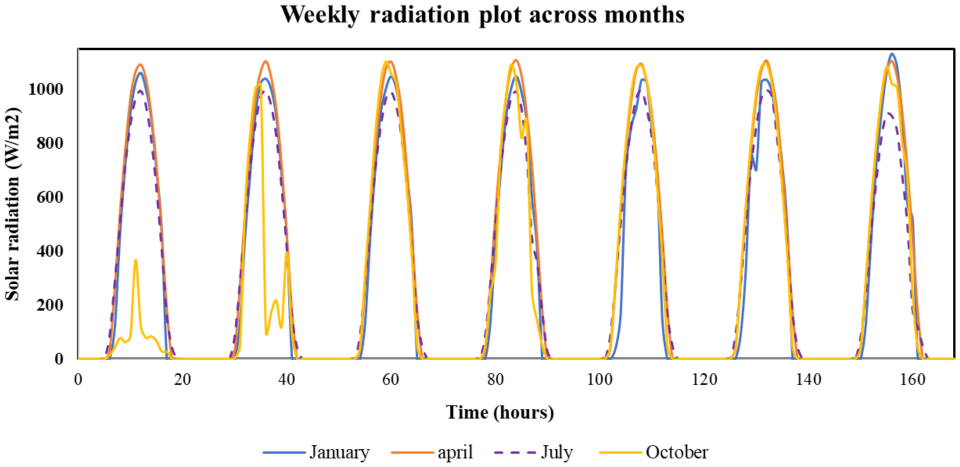


Figure 1.13. Solar radiation fluctuation across months

Another disturbance that can affect the DS system will be the feed compositions. Feed composition to distillation system depends on the product produced from the methanol synthesis reactor. An increase or decrease in air temperature or relative humidity affects the performances of the DAC and MS sub-system which in turn influences their end products. Even though these dynamic changes will be addressed by respective systems as each system will have a control scheme, modelling the distillation system for varying feed is recommended. Therefore, these perturbations will play a crucial role in the performance of the system. It is important to implement a control scheme in such a way the distillation system can withstand these fluctuations without breaking down and produce the required amount of methanol of specified purity without any interruption. Hence, investigating the dynamic changes in the environment and identifying the important parameters is necessary to model the dynamic behaviour of the distillation column.

1.2.6.2 Startup and Shutdown effect on the DS system

The startup of the large-scale column is a long process where the system is transformed from shutdown state to operational state and a significant amount of energy is necessary for this process. Owing to this reason, in large scale industries startup processes are infrequent and occur for a short duration. An important parameter is the startup time which is defined as the optimal time taken by the distillation column to reach the desired steady-state and during this startup process, there is no flow in the inlet and outlet streams of the distillation system. Heat losses take place in the column and due to this a large amount of energy is spent in heating the system during startup. The heat losses not only influence the energy consumption but also determine the startup time. Startup time is usually influenced by the scale of the DS system, hold-up time of the mixture in the reboiler and the thermal mass of the column. Therefore, time and energy are the two main parameters that need to be considered. The distillation system should always be designed in such a way that these two parameters remain minimum. As the DS system at ZEF will be powered by solar PV, it is a known fact that the total sunshine hours per day is limited and hence starting the DS system with minimum startup time becomes essential. On the other hand, Shutdown is the reverse sequence where a large substantial portion of the energy is lost when the system is shut off. Usually, the column does not operate below a certain threshold power limit and this limit depends on the heat losses, feed flow rates, column internals etc. A column is shut down when the feed flow rate or the reboiler duty is below the threshold limit. During these shutdown processes, the solar energy which is continuously produced can be stored in batteries or can be diverted to other sub-systems. Hence investigating the influence of dynamic changes in the environment on the DS system and identifying the important parameters during Startup and Shutdown process is essential to designing an optimum DS system for ZEF.

1.3 Research Objectives, Scope and Thesis Outline

1.3.1 Scope of thesis

The above section described previous research carried at ZEF, various literature pertinent to the distillation system and based on this knowledge and recommendation, the major focus of thesis is chalked out.

[1] The primary focus of this research will be to **analyze different distillation designs including the heat integrated distillation columns** (Chapter 2) for decentralized, Semi-centralized and Centralized schemes and **finalize an feasible design for the DS system** that is both **cost and energy efficient**.

[2] Another task will also be to **analyze the impact of varying ambient conditions** especially the solar radiation and ambient temperature on the distillation system and to build a model that can control these fluctuations and achieve the ZEF target.

Based on this primary focus of thesis the following scope of the thesis were framed

- The current thesis is limited to only the DS sub-system of ZEF and only involves process modelling of DS systems and does not include experimental work. Although the designs proposed in Chapter 2 are based on the literature and the designs are specifically modelled for ZEF requirements. The operating conditions of DS systems are decided based on the ZEF's criteria (Section 2.1.2).
- Even though for economic analysis, a preliminary design calculation was carried, the thesis does not involve detailed designing of DS system equipment. The preliminary design calculations are based on assumptions, and they are mentioned in respective chapters.
- For economic analysis, a factorial method approach that involves Lang factors (accuracy: ±40% [34]) were used and therefore cost presented in this thesis does not represent the exact cost of the final ZEF DS system. This approach was followed to decide the feasible and optimal design and the designs will be selected based on the cost per ton of methanol.
- The dynamic analysis is only limited to the DS system and the analysis is based on MATLAB models. The dynamic analysis will be carried for the system selected based on the economic and energy analysis. The influence of other sub-systems on DS will not be analyzed and solar radiation and temperature are the two dynamic fluctuations considered.

1.3.2 Research Objective

The following research questions will be answered during this thesis

[1] What are the most promising heat integrated configurations that could be recommended to the proposed methanol-water distillation system to reduce energy consumption?

[2] What is the economic performance of the proposed designs for Decentralized, Semi-centralized and centralized schemes? How does operating conditions such as energy source, geographic location and operating hours influence the cost?

[3] How do the different configurations of 3 different schemes compare to each other in terms of energy consumption? Based on the energy and economic performances, which design could be a possible option for the operating conditions considered?

[4] What are the impacts of fluctuating ambient conditions (solar radiation and temperature) on the performance of the distillation system? How does it affect the start-up of the column?

[5] What could be the final recommended distillation design that meets the ZEF's requirements

1.3.3 Report Outline

The report is divided into 6 chapters and this thesis is structured as follows

- Chapter 1 provides general information about the company and gives theoretical background into research topics pertinent to the distillation system. This chapter also reviews in brief different types of heat integrated systems and the effect of the dynamic behaviour of the environment.

- Chapter 2 describes the basis of the design and operating conditions of the DS system at ZEF. The chapter also introduces different distillation designs where each design is explained in detail and modelling of these designs were carried out in COCO. The simulation results were also presented, and these results were the basis for Techno-economic analysis. This Chapter is also related to Research Objective 1

- Chapter 3 presents the techno-economic analysis of the selected designs. It also explains the methodology followed to analyse the cost and energy results of these designs. The chapter ends with the selection of the most feasible designs that can be implemented at ZEF. This Chapter provides a solution for Research Objective 2 and 3

- Chapter 4 is related to analyzing and modelling the influence of the dynamic environment on the DS system. Startup and shutdown characteristics are also presented in this chapter and this Chapter answers the last Research objective

- Finally, the final recommended Distillation system that meets the ZEF's requirement was proposed in Chapter 5 and Chapter 6 provides a conclusion and presents a few possible recommendations for future work.

Chapter 2

Process Modelling

From the previous chapter, it became clear that a conventional distillation system was seen as a possible alternative to separate methanol and water and on the other hand, a centralized distillation system was also recommended as the energy losses were less. Therefore, it was important to analyse these systems and for this purpose, the distillation systems were modelled for 3 different schemes: Centralized, Semi-Centralized and Decentralized.

This chapter primarily focuses on the modelling of these simple conventional distillation systems. Furthermore, to these designs, heat integration was introduced as literature presented that heat integration resulted in reduced energy consumption COCO and Chemsep software were used to model the chemical process and the simulation results are presented in Section 2.3 of this chapter.

2.1 Basis of design

The basis of design is considered as one of the important aspects of process modelling and it is the first step in designing a process plant. A typical basis of design combines different project parameters such as process requirements and expectations, assumptions, input and output structures, constraints and limitations, battery limits, etcetera. A battery limit is often defined as an imaginary boundary that separates two responsibilities and setting up a battery limit helps in the design, construction, economics, maintenance, and safety of the plants. Fig 2.1 represents the process flow diagram of the distillation subsystem with boundaries highlighted. In our thesis, the distillation column and its equipment excluding pumps were considered for analysis.

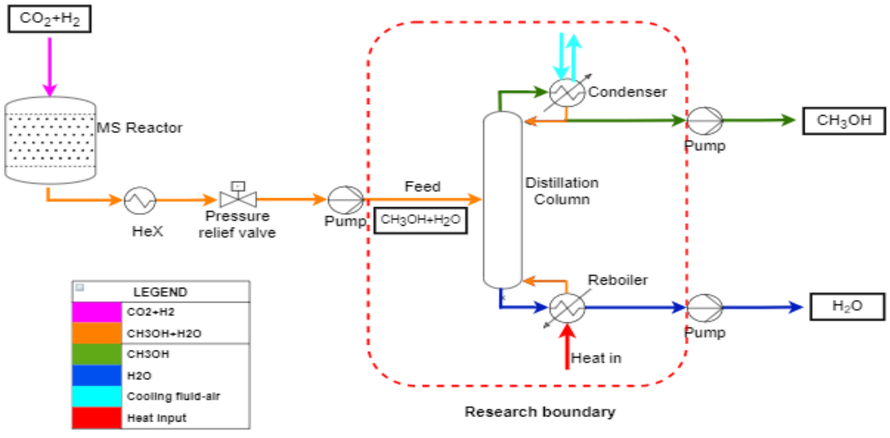


Figure 2.1. Process flow diagram of Methanol Synthesis and Distillation subsystem

2.1.1 Decentralized, Semi-Centralized and Centralized Distillation Schemes:

The current research primarily focuses on three different schemes: Decentralized, Semi-Centralized and Centralized. All these designs are classified based on the feed flow rates which depends on the number of micro plants connected to the DS system. In future, ZEF is planning to develop a ZEF park with approximately 13500 micro plants where each micro-plant has all the 5 sub-systems and will be equipped with 3 solar panels. The

- **Decentralized scheme** - a scenario where **every micro plant has a small-scale or lab-scale fractional distillation system** and therefore, the entire ZEF park contains around 13500 DS systems. The mixture from 1 micro plant will be fed into the DS system and the **feed flow rate will be 135.71 g/hr**
- **A semi-Centralized scheme**-a scenario where **every 1000 micro-plants (1000 is an assumption) will have 1 DS system** and therefore the ZEF park will approximately have 14 medium-scale DS units. Whereas the feed flow rates for a single semi-centralized DS system will be 1000 times higher than the flow rate of a single decentralized DS system and this is because the methanol-feed mixture from 1000 plants is fed into the DS system. The mixture from 14 micro plants will be fed into the DS system and the **feed flow rate will be 135714.29 g/hr**
- **Centralized scheme** - a scenario where **one large-scale DS unit is installed for the entire park** with 13500 micro-plants and therefore, the methanol-water mixture from all 13500 micro-plants will be fed into this DS system. Hence the **feed flow rate will be 1.83E+06 g/hr**

2.1.2 Input and Output Structures:

As mentioned earlier, the CO_2 and H_2 from DAC and AEC subsystem are compressed to 50 bar and fed into the reactor system which is at 230-250°C. In the presence of the catalyst, a mixture of methanol and water was produced in an equimolar ratio of 1:1. The produced methanol-water mixture is cooled using a heat exchanger and then decompressed and are fed into the distillation system to separate the mixture. The main objective of this system was to produce distillate methanol and water with a purity of 99.8% and 0.2% respectively. The temperature and pressure of the feed mixture were reduced to 35°C and 1 bar and therefore, the feed mixture was in the liquid state. As already stated in Chapter 1, a total of 600 g of methanol needs to be produced in 7 hours and therefore 18.75 moles of methanol and water mixture was fed into the distillation system for the 7-hour period which corresponds to 135.71 g/hr [Refer Appendix B.1].

Table 2.1. ZEF Distillation System Requirements

Parameters	**ZEF Specifications**	**Units**
Plant operating hours	7	hrs
Production rate of methanol	600	g/day
Minimum Operating Pressure of Distillation Column	1	bar
Feed flow rate from MS reactor	135.71 (decentralized) 135714.29 (Semi-Centralized) 1832142.86(Centralized)	g/hr
Feed conditions from MS reactor	35°C, 1bar, 50%-50% methanol-water mixture	
Molar Fraction of Distillate product (Purity of Distillate)	Methanol - 0.998 (99.8%) Water - 0.002 (0.2%)	
Expected Cost of Methanol produced at ZEF	350	€/tonne

2.2 COCO Modelling

For this research, two free open source software called “Cape Open- Cape Open and Chemsep”[35] was used for designing the distillation column. Various unit operations such as splitters, mixers, heat exchangers, separators which includes distillation columns and flash tanks, reactors, etc. are available and based on the selected EOS and thermodynamic models [Refer Section 2.2.1] and with necessary inputs such as feed conditions and product purities, the distillation column can be modelled and analyzed at steady-state condition. COCO and Chemsep are steady-state software that uses MESH equations [Appendix B.2] to solve and calculate all the necessary results including flow rates, temperatures, ratios and duties.

2.2.1 Process Description and Methods

Various researchers have proposed different mathematical models to estimate the physical and thermodynamic properties of components in the mixture. For simulating distillation column in COCO, 5 important thermodynamic properties need to be selected and they are: K-value models: These models are used to determine the distribution coefficient and relative volatility for a given specific component. K-models are used in estimating the VLE Equation of state models: Equation of state models provides a relationship between temperature, pressure and volume and these models help in predicting the physical properties of particular components. Equation of state can be majorly classified into four categories: Ideal, Cubic, non-Cubic and Virial equations. A detailed description of all the EOS is provided in literature [36].Activity models predict the activity coefficients for non-ideal liquid solutions which are necessary for plotting VLE. Wilson, Margules, Van Laar, Non-Random-Two-Liquid equation (NRTL), Universal Quasi Chemical (UNIQUAC) are a few examples of Activity models. Vapour pressure and enthalpy models: Vapor pressure plays an important role in estimating the VLE and enthalpy models were required for the calculation of energy balance equations Specific models suited for methanol-water mixture were chosen based on the suggestions provided in Chemsep software.[36] and the selected models are explained in Table 2.2

Table 2.2. Selection of Thermodynamic Models

Thermodynamic Model	Selected model	Reason	Source
K-value	$\gamma - \phi$	A good approximation of VLE for low-pressure systems recommended for non-ideal mixtures	[36]
EOS	PSRK	Non-electrolyte, non-ideal and polar mixture, recommended for alcohol mixtures, can be used for liquids and vapours	
Activity	NRTL	Recommended for water, alcohols, dilute systems, predicts VLE and LLE more accurately	
Vapour Pressure	Antoine	γ-ϕ model recommended	
Enthalpy	PSRK	Preferred if PSRK EOS model is chosen	

2.2.2 Process Assumptions

- The model is assumed to be at a steady-state condition. The vapour and liquid phases are assumed to be homogeneous in all stages and an equilibrium is achieved between the liquid that flows to the below stage and vapour that flows to the above stage. A partial reboiler and total condenser were assumed.
- The pressure inside the distillation system is assumed to be constant and the assumed column pressure was 1 bar. Even though in reality there will be a pressure gradient between the bottom reboiler and top condenser, these pressure fluctuation effects are assumed to be negligible.

- A constant liquid hold-up is assumed, and the vapour hold-up is negligible and the effects due to column internals (occlusion, weeping flooding, etc.) are neglected. Constant relative volatility is assumed.
- The flows are assumed to be completely mixed, in steady-state and there is no accumulation in trays. No other reactions and heat losses are occurring in the column. It is assumed that the heat transfer takes place only in the reboiler and condenser. Even though in reality, there are fluctuations in reboiler duty as the reboiler is powered by solar panels, for the steady-state calculation, the energy source is assumed to be constant.

2.3 Design Cases and Model results

Based on the literature study, 6 different designs namely base case, feed heating, VRC, external HiDiC, Bottom Flashing and VC were chosen and some of these technologies such as VRC, VC systems and feed heating are well established in industries. In this section, a single distillation unit from each of these designs was modelled and analysed for all the 3 schemes depending upon the ZEF's requirement [Table 2.1] and the simulation results are also presented.

2.3.1 Base Case Design

The simple distillation column with 19 trays, a total condenser and a partial reboiler was chosen as a base case. The initial reflux and boil up ratio, feed stage and the total number of stages were chosen by using the FUG method [36] and later they were optimized to achieve the target of 99.8% methanol purity and 0.2% water purity in the distillate product.

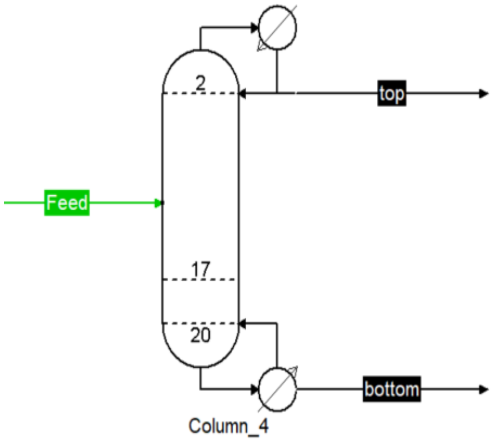


Figure 2.2. Base-Case COCO model

The base case model separated methanol and water at the temperature of 98.7°C which can also be observed from the VLE curve [Appexdix B.3]. The feed stream is a methanol-water mixture at 35°C and its mole fraction is 0.5. The feed flow rate varies for different schemes, and they are presented in Table 2.3. The thermodynamic properties mentioned in Table 2.2 were chosen and with all the input parameters, the COCO model calculated the flow rates and duties of the distillation column. The results are presented in Table 2.3

Table 2.3. Base-Case Model Results

Parameters	**Units**	**Decentralized**	**Semi-Centralized**	**Centralized**
Feed flow rate	g/hr	**135.71**	**1.35E+05**	**1.83E+06**
Column Pressure	bar		1	
No. of rectifying stages			15 (excl.cond)	
No. of Stripping stages			4(excl.reb)	
Feed stage			16th	
Distillate flow rate	g/hr	86.62	8.66E+04	1.17E+06
Bottom Flow rate	g/hr	49.09	4.91E+04	6.62E+05
Reflux Ratio			1.29	
Boil-up ratio			2.13	
Distillate temperature	℃		64.29	
Bottom temperature	℃		98.70	
Reboiler Duty	W	**65.49**	**6.55E+04**	**8.84E+05**
Condenser Duty	W	**-62.93**	**-6.29E+04**	**-8.49+05**

2.3.2 Feed Pre-heating Design

- This is one of the simplest heat integrated designs that were proposed. Heat exchangers are used to preheating the feed mixture thereby effectively reducing the sensible energy that decreased the reboiler duty. On the other hand, hotter feed resulted in higher heat removal in the condenser and increased vapour flow and therefore reflux ratio had to be increased to maintain the purity.
- The same distillation column with 19 trays, a total condenser and a partial reboiler that was used for the base case was chosen.

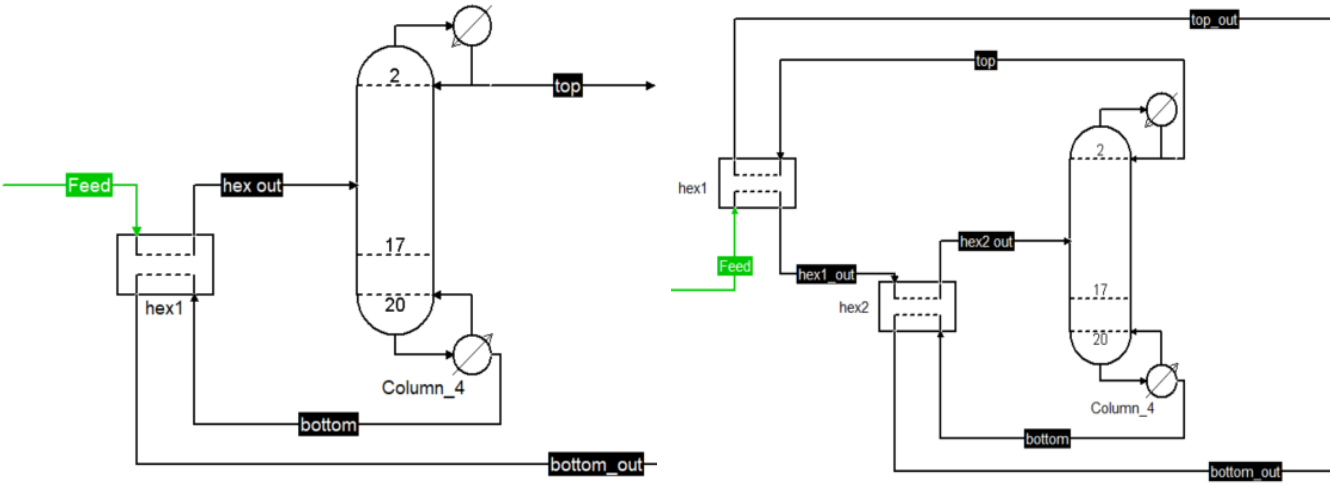


Figure 2.3. (a) Feed pre-heating 1-hex COCO model (b) Feed pre-heating 2-hex COCO model

- Two different designs were proposed: In the **first design, a single heat exchanger was used** where the heat transfer takes place between the bottom product which is at 98.7℃ and the feed which is at 35℃. The reflux and boil-up ratio were optimized to reach purity.
- Similarly, **for the second design, two heat exchangers were used.** One heat exchanger was used to exchange heat between the top product and feed and the second heat exchanger was used to heat the outlet stream of the first heat exchanger with the bottom product.

- For both the designs, a minimum temperature approach between 5°C was assumed for the counter-flow heat exchanger where the temperature difference between the hot fluid outlet and the cold fluid inlet was 5°C. Even though the results showed decreased reboiler duty, the energy reduction wasn't that significant**. The energy-saving was comparatively higher for the second design** These results are presented in Appendix B.4[1].

2.3.3 Vapour Recompression Column Design

- The third design is the mechanical vapour recompression system, and the main advantage of this design is that the **total energy required to heat the mixture in the reboiler is provided by hot compressed overhead vapour.**
- This design is similar to the base case, but one major change is the addition of a heat exchanger and compressor. The same distillation column with 19 trays, a total condenser and a partial reboiler that was used for the base case was chosen. The partial reboiler was replaced with a flash tank.
- It must be noted that for initial start-up, an additional reboiler or immersion heater will be provided and once enough vapours are produced, they will be switched off. A major assumption made is that the vapour and liquid flow rates in the distillation column are constant and continuous and only vapour enters the compressor. In reality, condensation might occur in the pipe connecting compressor and distillation column, but this can be solved by introducing a superheater before the compression stage.

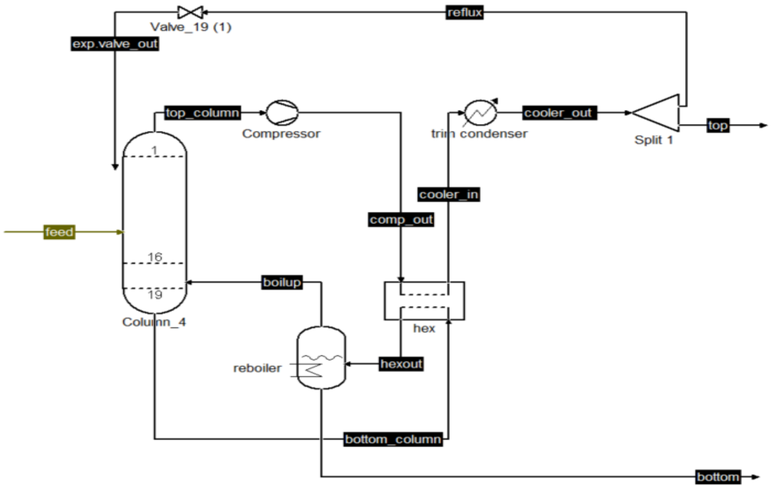


Figure 2.4. VRC COCO model

- To provide the required heat to reboiler, a high-pressure ratio of 4.38 was necessary which was calculated from sensitivity analysis and a compressor efficiency of 0.9 was assumed.
- Due to this high-pressure ratio, **the compressed overhead vapour temperature increased drastically which provided the necessary heat for heating the feed mixture in a heat exchanger**. The heat exchanger operates as a combination of both condenser and reboiler. The feed mixture is heated, and it exits the heat exchanger as a vapour liquid mixture where the vapour and liquid are separated in a flash tank.
- On the other hand, complete condensation of overhead vapours does not occur and therefore **an extra trim condenser was required to cool the liquid.** A minimum temperature approach of 5°C was assumed for counter-flow heat exchangers and all the heat is utilized in heating the liquid mixture. The results presented in Appendix B.4 [2] show a significant reduction in total energy consumption of the column and this was considered as one of the efficient heat integrated designs.

2.3.4 Bottom Flashing Design

- The bottom flashing is one of the theoretical concepts presented in the literature. The same distillation column used for the base model was considered and the assumptions similar to VRC was assumed. Unlike VRC, **bottom flashing uses the liquid exiting from the bottom stage of the column to cool the hot overhead vapour where the liquid temperature is reduced using an expansion valve. Heat transfer takes place in a heat exchanger**.

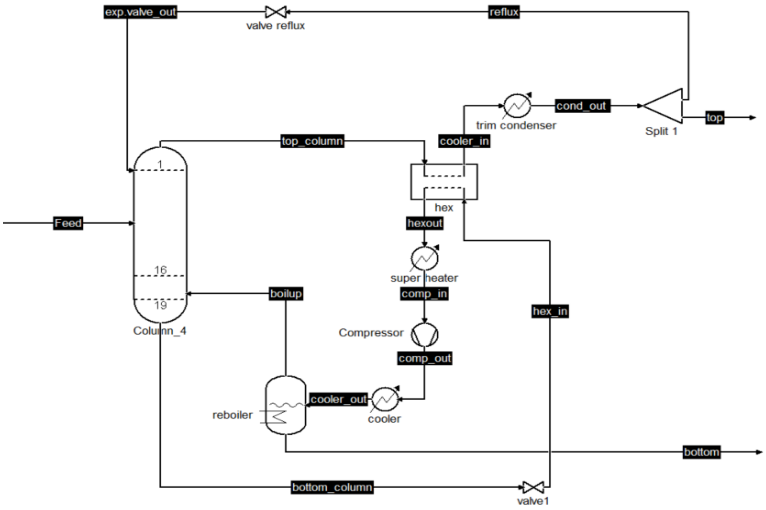


Figure 2.5. Bottom Flashing COCO model

- As this liquid exiting the heat exchanger are not completely vaporized, an additional superheater was necessary as the liquid in the compressor inlet stream would damage the compressor. This steam is then recompressed where the pressure is brought back to column pressure, and this also increases the temperature of the stream. Due to this reason, an additional cooler is required, and the vapour and liquid are separated in the flash tank. A high-pressure ratio of 4.49 was required and a minimum temperature approach of 5℃ was assumed.
- Even though the results showed reduced energy consumption, this design was found to be less efficient as this design requires extra components which may increase the capital cost and the energy consumption was higher compared to VRC systems. The results are presented in Appendix B.4 [3]

2.3.5 External HiDiC Design

- In the external heat integrated distillation column, the base case model was divided into two along the feed stage: the stages above the feed along with the condenser were named as rectifier and stages from the feed to reboiler was called a stripper.
- Therefore, the stripper had 4 stages and a reboiler whereas the rectifier had 15 stages and a condenser. The feed is provided at the top stage of the stripper and the vapours from the top stage of the stripper pass through a compressor and compressed vapour enters the bottom stage of the rectifier.
- It must be noted that the pressure of the rectifier column is higher than the pressure of the stripper column and a major assumption made is that no condensation of vapour occurs in the pipe connecting the stripper, compressor, and rectifier. An expansion valve was used to reduce the pressure of the rectifier liquid stream to stripper pressure and the liquid was sent to the top stage of the stripper.

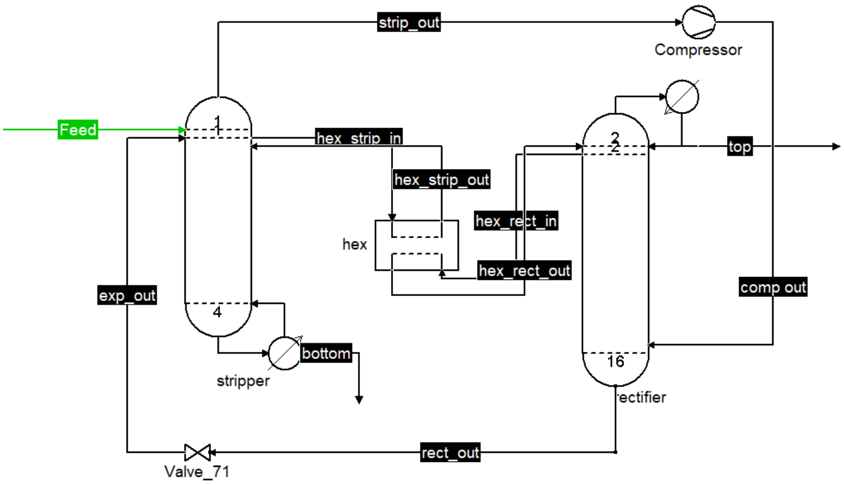


Figure 2.6. Ext.HiDiC COCO model

- A heat exchanger was introduced, where the main purpose was to transfer heat from hot vapours of rectifier column to cold liquid of stripper column. The compressor ratio, liquid and vapour side stream stage locations, flow rates were selected based on sensitivity analysis. Liquid and vapour side streams from top stage of the stripper and rectifier were found to be an efficient option and a maximum flow ratio of 1 was chosen[32].
- A compressor ratio of 2.13 was necessary to produce a significant reduction in reboiler and condenser duty. Compressor efficiency of 0.9 and 5°C minimum temperature was assumed for compressor and heat exchanger respectively. The results were tabulated and presented in Appendix B.4[4]. This design helped in reducing the total energy consumption, but the reduction was not as large as VRC systems.

2.3.6 Vapour Compression Design

- The vapour compression systems are the widely implemented heat integrated systems in industries **The heat integration in these systems is done by utilizing heat exchangers, compressors, refrigerants and expansion valves. Heat exchangers are used to transferring heat in the reboiler and condenser**.
- The saturated vapour refrigerant from the condenser is compressed to superheated temperature and this high-temperature vapour is used to heat the methanol-water mixture in reboiler. The refrigerant exiting the reboiler will condense to saturated liquid which passes through the expansion valve. The liquid-vapour refrigerant is then fed into the condenser where heat from the overhead methanol-water vapour is absorbed and therefore converts back to saturated vapour.

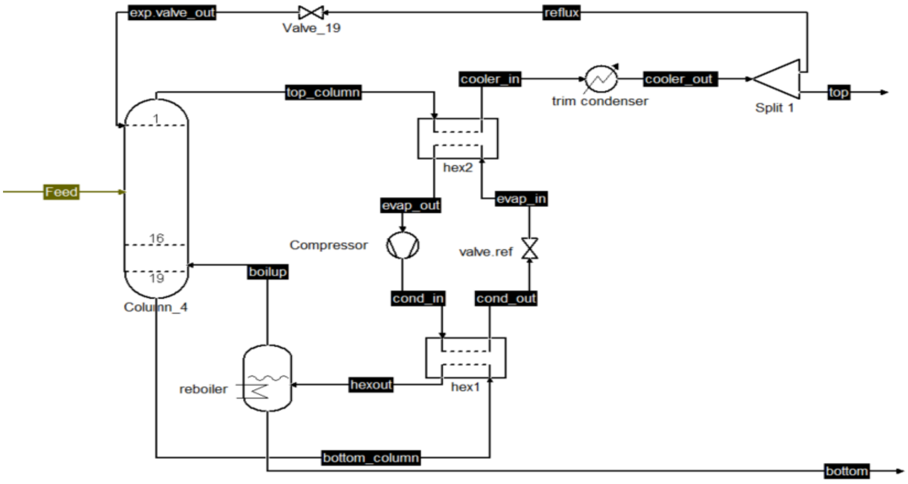


Figure 2.7. VC COCO model

- A major problem with these systems is the refrigerants. Most of the refrigerants used in industries such as CFC's, HCFC's, HFC's are non-ecofriendly. Therefore, proper selection of refrigerants is a challenge as these refrigerants need to be eco-friendly, should be a non-pollutant, non-toxic and non-flammable, should have low Ozone Depletion Potential (ODP) and Global warming potential (GWP) and should have good thermodynamic properties. Venkatarathnam et. al [37]has provided a comprehensive assessment of eco-friendly refrigerants used in industries and has classified refrigerants based on critical temperature, GWP, ODP and ASHRAE safety standards.
- Based on this assessment, Ammonia and Butane were chosen as refrigerants for our case [Appendix B.4[5]]. The simulation was carried out with the same distillation column with 19 trays, a total condenser and a partial reboiler chosen for the base case.
- A major assumption here was that an ideal vapour compression cycle was considered where refrigerants condense to saturated liquid after releasing the heat in the reboiler and the condenser, it becomes saturated vapour.
- 5℃ minimum temperature was assumed for both the heat exchangers and all the heat rejected by the refrigerant is utilized in heating the liquid mixture. An efficiency of 0.9 was assumed for the compressor. The model results for design with ammonia and butane refrigerants are mentioned in Table 2.8 and the vapour compression plots are presented in Appendix B.4. A significant reduction in reboiler and condenser duty was observed for both designs.

2.4 Energy comparison of different designs

In the previous section, the modelling results of different designs were presented, and it was observed that different designs had different energy requirements. As reported in the literature, heat integrated designs had a huge influence on the total energy demand of the system. This section provides an overview of the total duties required for each design and also describes how the implementation of heat integration influences the total energy demand. **For this analysis, a Centralized distillation system was chosen, and the heat losses were not considered. Therefore, the trends were similar for all three schemes**. Fig.2.8 shows a comparison of the total duties required by each design of the Centralized scheme.

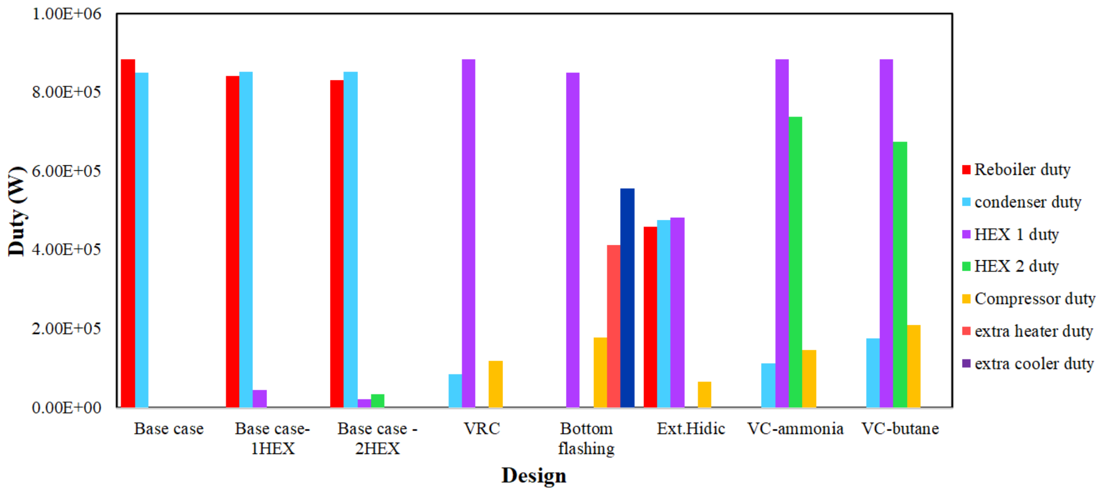


Figure 2.8. Comparison of the duties of different designs of Centralized Scheme

[1] Base Case:

- The **base case system** required a **total reboiler duty of around 8.84E+05W** and the **condenser duty was found to be 8.50E+05W**. The base case does not have a compressor and therefore the **total energy consumption of the Centralized base case was 8.84E+05W**.
- It has to be noted that all the energy trends (increase or decrease in energy consumption) of designs discussed in this section will be compared with the reboiler, condenser duty and the total energy consumption of the base case.

[2] Feed preheating:

- The **feed preheating design 1** where one heat exchanger was implemented, showed a maximum **reduction** in **reboiler duty of approximately 4.8%** from the reboiler duty of the base case whereas the **condenser duty increased by 0.28%.**
- The **feed preheating design 2** reported a **5.9% reduction in reboiler duty and a 0.35% increase in condenser duty**. This shows that increasing the temperature of feed reduces the reboiler duty and increases the condenser duty.
- Pratibha et. al [29] simulated a 1hex design where a 22-tray column with the feed of 75% methanol and 25% water (by weight) at 35°C, 1bar and flow rate of 6000 litres per hour was fed. Reported a similar trend as our design where the reboiler duty reduction was 5.3% compared to reboiler duty of base case and condenser duty increased by 0.9%

[3] VRC:

- The **VRC systems** were found to be the most energy-efficient systems where a **100% reduction in reboiler duty** and a **90.1% reduction in condenser duty** was observed.
- A **compressor duty of 1.19E+05** was required and therefore the total energy savings (TES) of the VRC system was around 86.5%.
- The Total energy savings gives a measure of reduction in total energy demand of the system when compared to the total energy consumption of the base case. It includes compressor duty, heater duty and reboiler duty as these are the main energy-consuming systems. The base case is considered as a reference.
- A similar trend was reported by Pratibha et. al [29] where a 100% reduction in reboiler duty and 86.6% decrease in condenser duty were observed. Shahandeh et.al [32] simulated a 26-tray column used for methanol-water separation with a feed containing 70% methanol mole fraction at 35°C, 2 bar and flow rate

of 4968.4 kmol/hr. Reported a similar trend 100% reduction in reboiler duty and condenser duty decreased by 81.3%

[4] Bottom flashing:

- From Fig.2.8, it can be observed that the **reboiler duty and condenser duty decreased by 100%** but an **additional heater** with a heating duty of **4.1E+05W** and **cooler** with a cooling duty of **5.6E+05W** was necessary for this design.
- The compressor duty for this system was 49.6% higher than the VRC design and therefore the total energy saving was reduced to 33.1%.
- Sidek et.al [31]implemented VRC and bottom flashing designs for the separation of oleochemical fatty acids and the simulation results showed that VRC had a total energy saving of 82.4% whereas the bottom flashing reported 46.8% energy saving. Eventhough these designs were implemented for a distillation column operating for a different mixture, an energy-saving trend similar to our design was observed.

[5] External HiDiC :

- The external heat integrated distillation systems reported a **47.9% and 44.3% decrease in reboiler and condenser duty** respectively. Eventhough the compressor duty was 43% lower than the compressor duty of VRC systems, the total energy saving was just 40.6%.
- Shahandeh et al.[30] reported a total energy saving of 70% external HiDiC systems for methanol-water separation.

[6] VC systems:

- The VC systems were found to be the second most efficient design where a **100% reduction in reboiler duty** and **86.9% reduction in condenser duty** was reported for **ammonia design** whereas a **100% reduction in reboiler duty and 79.3% reduction in condenser duty** was observed for **butane design**. A total energy saving of 82.4% and 76.4% were observed for ammonia and butane design respectively.
- Pratibha et. al [29]presented a VC design for methanol-water distillation with R114 as working fluid and reported a 73.2% reduction in reboiler duty and 82.4% reduction in condenser duty

Chapter 3

Comparative Analysis and Discussion of selected designs

In chapter 2, the modelling results of various designs for three different schemes namely Centralized, Semi-Centralized and Decentralized were presented and the next main objective of this research was to figure out a feasible distillation design that is not just energy-efficient but also economically viable. In this chapter, simple energy and economic comparison between different designs are performed. Based on modelling results, preliminary equipment designing was carried out and each system was evaluated and compared in terms of cost and energy savings. The design which had the highest energy and cost savings was selected as the most preferred design. The methodology followed for the selection of feasible design is presented in Figure 3.1. Flowchart representing the methodology followed in the selection of final design

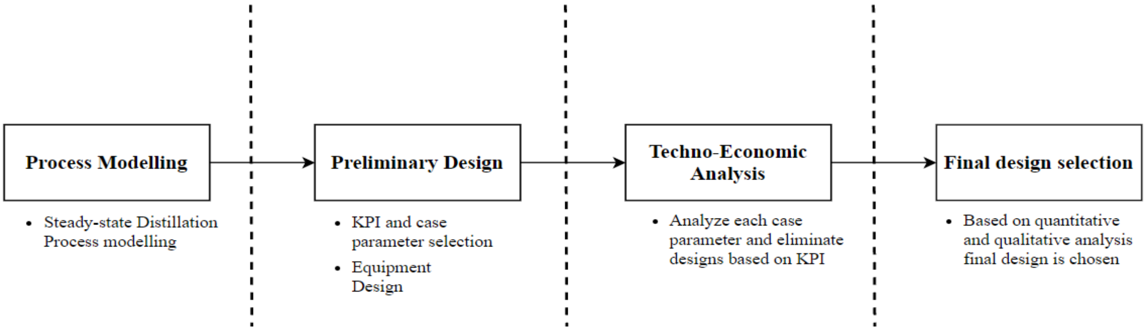


Figure 3.1. Flowchart representing the methodology followed in the selection of final design

3.1 Parameter Selection and Key Performance Indicators

Key performance Indicators: For this research, two key indicators namely the energy indicator and economic indicator were considered to evaluate all the proposed distillation designs and these performance indicators were used as a benchmark in assessing different systems and also in deciding the most effective design

- **Energy indicator**: The energy indicator represents the total duty that needs to be supplied to a particular system and can be determined by adding the reboiler, compressor and extra heater duty. These power-consuming systems will be powered by solar energy, and therefore analysing the energy demand and energy saving of all the proposed designs will be useful in selecting the feasible system. The design which has the lowest energy demand was chosen as the energy-efficient design

$$Total\ duty\ required\ (\mathrm{W}) = \ Reboiler\ duty\ +\ Compressor\ duty\ +\ Extra\ heater\ duty \tag{3.1}$$

- **Economic indicator:** The economic evaluation of each system was carried out by estimating the total cost per tonne of methanol in terms of total annualized cost. Annualized cost is the most commonly used function to evaluate the real cost of the system that is incurred each year. It takes capital cost, interest rates and operational cost into account [17]. The total cost per tonne of methanol can be estimated by dividing the total annualized cost by the total methanol produced within the system lifetime. The total cost per tonne of methanol (TCPM) was chosen as an indicator to gauge and evaluate the economic feasibility of different distillation designs. The design which had the lowest TCPM was selected as the most preferred design.

$$Annualized\ Cost\ (€/yr) = \ Operating\ Cost\ +\ \left(\frac{i\,(1+i)^N}{\left[(1+i)^N\right]-1}\ *\ Capital\ Cost \right] \tag{3.2}$$

$$Total\ Annualized\ Cost\ (€) = \ Annualized\ cost\ *\ t \tag{3.3}$$

$$Total\ Cost\ per\ tonne\ of\ methanol\ (€/ton\ methanol) = \frac{Total\ annualized\ Cost}{Total\ methanol\ produced\ in\ N\ yrs} \tag{3.4}$$

* i represents the interest rates and N represents the operating hours or the lifetime of the system.

Case Parameters: An important factors that needs to be considered for deciding the final design are the operating conditions of the distillation system and these conditions are denoted as case parameters. 5 different parameters were introduced: Energy source, location, operating hours, type of system and the scheme. Besides selecting the scheme and type of system as mentioned earlier, it is equally important to decide the energy source, location, and operating hours. All these different parameters influence the cost and energy of the system. Each of the parameters is separately analysed and based on KPI's an efficient scenario from each case parameter is chosen. The final distillation system will be designed based on this optimum case parameter and will represent a cost and energy-efficient design.

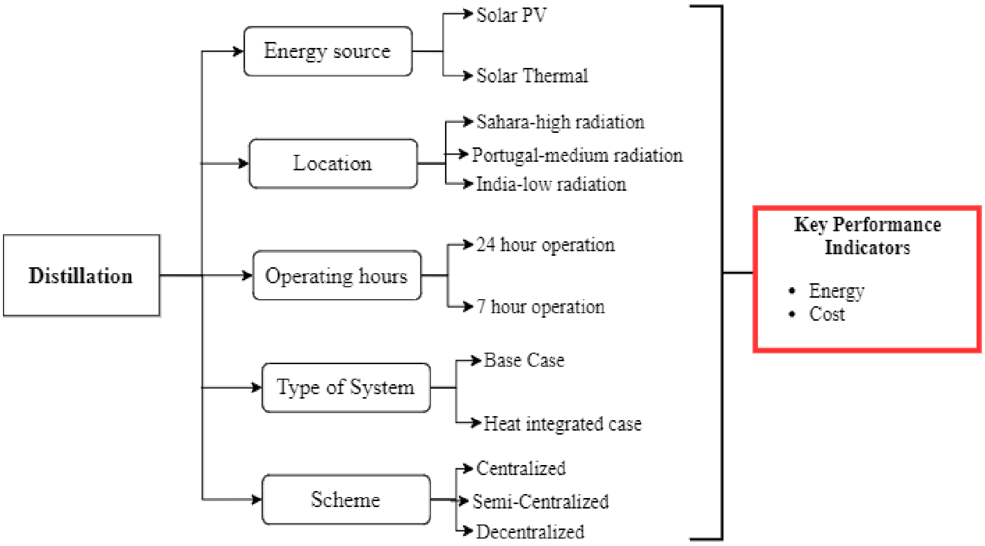


Figure 3.2. Flowchart representing case parameters and KPIs

3.2 Preliminary Equipment Design and Cost estimation

- To estimate the actual cost and energy consumption of the distillation system, it is important to have a rough estimate of the equipment sizes. The methods and formulas described in this section do not provide a comprehensive detailed design of process equipment. The idea here is to get a rough estimation of the equipment sizes or areas and based on these design parameters the preliminary cost analysis was performed. The cost of equipment mentioned in this section are Free On-Board cost which includes only the equipment cost and the transportation cost from the origin country, taxes and insurances are not considered.
- **The heat integrated designs for the decentralized scheme were not considered** due to difficulty in manufacturing components and unavailability of technology such as small-scale methanol compressors. Therefore, the only case considered for the energy-cost analysis is the decentralized base case. It must be noted that all the equipment mentioned in this section are within the battery limit (See Fig. 2.1). A major assumption here is that the piping and the pumping system in the distillation systems are not considered.

3.2.1 Condensers

- Condensers are one of the major components in the distillation system which are used to cool the overhead vapours. For our case, **natural air-cooled stainless-steel condensers were chosen**. The main reason for choosing air-cooled condensers was two-fold- one is the **unavailability of cooling fluids (eg: water) in locations such as Sahara and another reason was to reduce the fluid and the pumping cost**.
- To determine the cost of the condenser, a rough estimation of the area of the condenser was required which was found using equation 3.5 [17]. Flow stream temperatures and condenser duty data were extracted from the simulation results presented in Chapter 2 and the areas for all the designs were calculated. The cost per surface area range (€/m^2) were obtained from Alibaba and the cost of each condenser of different surface area was estimated by interpolation [Appendix C.1]
- **Assumptions:** [1] The overall heat transfer coefficient for natural air convection was reported to be between 3-25 W/m^2K[38] and for this analysis, an average of 14 W/m^2K was assumed

  [2] Column and piping heat losses were not considered and the overhead vapour flow rates and temperatures exiting the column were assumed to be constant at 64.33°Cand the ambient temperature was assumed to be 35°C

Total condenser area required,

$$A_{\text{condenser}}(m^2) = \frac{Q_{\text{condenser}}}{U_{\text{overall}} * LMTD} \tag{3.5}$$

where Logarithmic mean temperature difference,

$$LMTD = \frac{\left(T_{\text{hot vapour,in}} - T_{\text{ambient}}\right) - \left(T_{\text{hot vapour,out}} - T_{\text{ambient}}\right)}{ln\frac{\left(T_{\text{hot vapour,in}} - T_{\text{ambient}}\right)}{\left(T_{\text{hot vapour,out}} - T_{\text{ambient}}\right)}} \tag{3.6}$$

$$Condenser\ cost, (€) = cost\ per\ unit\ area * A_{condenser} * n \tag{3.7}$$

n- Number of units [Decentralized - 13500; Semi Centralized -14 units ; Centralized - 1 unit]

3.2.2 Immersion heaters

- The methanol-water mixture feed is heated in the reboiler of the distillation system where the necessary thermal energy is supplied by immersion heaters that are powered by solar PV.
- To determine the cost of immersion, an estimation of total reboiler duty was required, and this data was extracted from the simulation results presented in Chapter 2. The cost per wattage range (€/W) were obtained from Alibaba and the cost of each immersion heater for different designs was estimated by interpolation [Appendix C.1[2]].
- **Assumptions:** [1] The immersion heaters are powered by solar PV which is a fluctuating source and therefore this transient behaviour was neglected. The reboiler is assumed to be at a constant temperature of 98.7°C
  [2] Column and reboiler heat losses were not considered and the pressure inside the system is maintained at 1 bar, flow rate was assumed to be constant, other parameters such as residence time and volume inside reboiler were not considered.

$$Immersion\ heater\ cost, (€) = cost\ per\ unit\ wattage * Reboiler\ duty * n \tag{3.8}$$

3.2.3 Distillation column and reboiler

- The approximate size of the column can be estimated from flow rates and the number of stages obtained from COCO simulation and based on this sizing the cost of the distillation column was determined. The formulas used in Equation 3.9 are based on maximum vapour flow rates and velocity[17] and they provide a rough estimation of the diameter and height of the column for the centralized and semi-centralized systems. The important parameters necessary to calculate diameter and cost are mentioned in Appendix C.1[3]
- It should be noted that for the decentralized system ZEF had already implemented an experimental setup based on the COCO model and therefore the same dimensions were chosen for the decentralized base case system
- This rough estimate was sufficient for carrying out a preliminary cost evaluation. To determine the cost of the distillation column, an estimation of the total mass of distillation was required. For centralized and semi-centralized systems, the cost per mass (€/kg) of stainless-steel plates were obtained and for decentralized system cost per mass of sanitary tubing with estimated diameter were obtained from Alibaba [Appendix C.1[3]].
- **Assumptions:** [1] A steady liquid and vapour flow rates were assumed. In order to calculate the maximum vapour velocity, a flooding velocity of 85% was chosen. Usually, the acceptable flooding velocity ranges from 80 to 85%.
  [2] The equation 3.9 can be applied for a plate spacing range of 0.3-0.5 m and therefore a tray spacing of 0.5 and 0.3 were chosen for centralized and semi-centralized systems. Another major assumption here is that the reboiler height was taken as 2m.

The column diameter and height required can be calculated using

$$D_c(\mathrm{m}) = \sqrt{\frac{\mathrm{V_{vapour}}}{0.88\,\pi\,\mathrm{u_{max,vapour}}}} \tag{3.9}$$

$$L_c(m) = (Tray\ spacing * Number\ of\ stages) + assumed\ reboiler\ height \tag{3.10}$$

where $\mathrm{V_{vapour}}$ is the maximum vapour flow rate; $\mathrm{u_{max,vapour}}$ is the maximum vapour velocity

$$Distillation\ Column\ cost, (€) = cost\ per\ unit\ mass * Mass\ of\ column * n \tag{3.11}$$

3.2.4 Heat exchangers

- Heat exchangers are one of the vital components for the heat integrated designs where the heat exchange takes place between hot vapour and cold liquid (VRC, BF, ext.HiDiC, VC) or between hot and cold liquid. Two of the most predominantly used heat exchangers are the shell and tube and plate and frame heat exchangers. For our case, the shell and tube heat exchanger was chosen.
- The main reason for preferring shell and tube over plate and frame are shell and tube can be used for a wide range of temperature and pressure, a rigid design, easily cleaned, recommended heat exchanger for gases and phase changes. Even though plate and frame heat exchangers are comparatively cheaper, easier to maintain and scale up and offer better heat transfer they cannot be used for high pressure and high-temperature operations. Degradation and lifetime were other problems pertinent to plate and frame heat exchanger [17]A major disadvantage with this heat exchanger is the gasket. Vendors reported that gaskets suitable for methanol fluids and operation at high temperatures were not available.
- The cost per surface area range (€/m^2) of stainless-steel heat exchanger [Appendix C.1[4]] were obtained from Alibaba and the cost of each condenser of different surface area was estimated using equation 3.14
- **Assumptions:** [1] The major assumption here is the overall heat transfer coefficient and the coefficient ranges were obtained from the literature [39]. For preliminary analysis the average of these ranges is considered. Heat transfer coefficients of different designs are presented in Appendix C.1[4]. Heat losses were neglected.

Total heat exchanger area required,

$$A_{\text{heat exchanger}}\left(m^2\right) = \frac{Q_{\text{heat exchanger}}}{U_{\text{overall}} \ * \ LMTD} \tag{3.12}$$

where Logarithmic mean temperature difference,

$$\text{LMTD} = \frac{\left(T_{\text{hot fluid 1,in}} - T_{\text{cold fluid 2,out}}\right) - \left(T_{\text{hot fluid1,out}} - T_{\text{cold fluid 2,in}}\right)}{ln\dfrac{\left(T_{\text{hot fluid 1,in}} - T_{\text{cold fluid 2,out}}\right)}{\left(T_{\text{hot fluid1,out}} - T_{\text{cold fluid 2,in}}\right)}} \tag{3.13}$$

$$Heat\ exchanger\ cost, (€) = \ cost\ per\ unit\ area \ * \ A_{\text{heat exchanger}} \ * \ n \tag{3.14}$$

3.2.5 Compressors

- The compressors used in heat integrated designs need to be specifically designed to handle methanol fluids. The heat integrated designs for decentralized systems were omitted as designing and manufacturing small, customized compressors were difficult and the technology was unavailable.
- The cost of the compressor can be estimated using equation 3.15. The cost of compressors per unit is presented in Appendix C.1[5]

$$Compressor\ cost, (€) = \ cost\ per\ unit\ of\ compressor * \ n \tag{3.15}$$

3.2.6 Solar energy systems

As mentioned earlier, it was decided that the ZEF DS systems will be powered by solar energy systems. In the previous DS system, the reboiler was heated using immersion heaters powered by solar PV. These solar PV systems were cheaper with a longer lifetime which needed little maintenance.

But one of the major problems with solar energy systems are the intermittency issues and therefore storage devices were necessary to solve this issue. But storage systems for solar PV such as batteries were found to be expensive and therefore an alternative source of solar energy system which was solar thermal systems was analysed. Thermal energy storage such as solid or liquid storage medium (liquid, molten salts, etc.) effectively stores a large amount of energy and the cost are relatively cheaper than batteries. Therefore, investigating the economic impacts of both solar PV and solar thermal systems are important to figure out the most efficient energy source for our DS system.

Solar PV system

- The cost of solar PV systems mainly depends on the total number of solar panels required which can be estimated based on the equivalent sunshine duration available, watt peak of solar panel and the total duty required for specific distillation design. The equivalent sunshine duration varies with different locations and for our case, 3 locations were considered - Sahara (high radiation), Portugal (medium radiation) and India (low radiation)
- The equivalent sunshine duration and the solar Watt peak of solar panel was extracted from SolarAtlas[40]and Alibaba respectively and the total cost of the solar PV system was determined using equation 3.16
- The cost per wattage (€/W) of monocrystalline solar panels were obtained from Alibaba and the methodology and terminology for estimating the cost are mentioned in Appendix C.1[6]
- **Assumptions:** [1] The DS system was assumed to operate within the equivalent sunshine duration and a constant irradiance of 1000 W/m^{2}K was assumed. A solar PV system loss of 20% was considered and the solar panel frame and land cost of the solar module was assumed to be 2 times the cost per unit wattage of solar panel [Appendix C.1[6]]
  [2] The median cost of 0.31 €/W was assumed for the monocrystalline solar panel. The methodology for this assumption is explained in appendix C.1[6]

Total duty of particular design,

$$Duty_{total}(\mathrm{W}) = Reboiler\ duty + Compressor\ duty + Extra\ heater\ duty \tag{3.16}$$

Corrected Duty after considering losses and equivalent sunshine duration (ESH),

$$Duty_{corrected}(\mathrm{W}) = \left(\frac{Duty_{\mathrm{total}} * DS\ operatinghours}{ESH}\right) * \left(1 + (energy\ loss\%)\right) \tag{3.17}$$

The total cost of solar panels (including frame and land cost)

$$Solar\ panel\ cost, (€) = cost\ per\ unit\ wattage\ of\ solar\ panel * Duty_{\mathrm{corrected}} \tag{3.18}$$

Inverters and controllers: Two additional components which are important for the solar PV systems are the inverters and controllers which are used for changing the direct current of solar panels to alternating current and also for safety purposes. These systems are specifically required for centralized and semi-centralized systems as high voltage components such as immersion heaters and compressors will be used in these systems. For the decentralized systems, the inverter cost was not considered as PCB boards with in-built inverters were implemented and these PCB boards were inexpensive compared to inverters used for the semi-centralized and decentralized systems. The cost per unit wattage of inverters is presented in Appendix C.1[6]and the total cost of the inverter is estimated using equation 3.19

$$Inverter\ and\ controller\ cost, (€) = cost\ per\ unit\ wattage\ of\ inverter * Duty_{\mathrm{corrected}} \tag{3.19}$$

Batteries: One of the important case parameters that need to be analysed are the operation hours of the DS system and therefore the economic impact of incorporating batteries with the DS system needs to be investigated. For this purpose, the cost of batteries was estimated using equation 3.20. 20% energy losses and 50% depth of discharge was assumed [Solar photovoltaic course]. The cost per energy range of the battery is presented in Appendix C.1[6]

$$Battery\ cost, (€) = \ cost\ per\ unit\ energy\ of\ battery\ *\ (Duty_{corrected}\ *\ DS\ operating\ hours) \quad (3.20)$$

Solar thermal system:

- Similar to solar PV, the solar thermal cost also depends on the total number of panels. In order to determine the total number of panels, formulas from ICC-SRCC [41] solar rating sheets were used. Initially, a suitable solar thermal brand- Apricus 30 tube panel was chosen. Based on the radiation intensity obtained from Solar Atlas, the temperature of the fluid entering and exiting the solar thermal panel and ambient temperature, the total thermal yield per panel per day was estimated. It must be noted that the thermal fluid temperature and ambient temperature influences the panel output. The total cost of a solar thermal panel was estimated using equation 3.21.
- It must be noted that even if solar thermal systems are implemented in the DS system to heat the mixture in reboiler, the solar PV systems are necessary to power other electrical components such as compressors.
- **Assumptions:** [1] A heat exchanger was used to transfer heat between the hot thermal fluid and the mixture in the reboiler. The reboiler temperature of distillation system was at 98.70°C and 5°C approach temperature was assumed between the mixture in reboiler and the thermal fluid leaving the reboiler. Therefore, the thermal fluid exiting the reboiler was at 103.7°C. The temperature of thermal fluid entering the reboiler was fixed constant at 125°C These are the two major assumptions made in this analysis [Appendix C.1[7]]

  [2] 20% heat losses were considered. The average ambient temperature for Sahara, Portugal and India were assumed to be 35°C, 25°C and 19°C and was extracted from Solar Atlas. Apricus 30 tube unit with a cost of 323.6 €/set was assumed.

Corrected Duty after considering losses and equivalent sunshine duration (ESH),

$$Duty_{corrected}(\mathrm{W}) = \left(\frac{Duty_{\mathrm{total}}\ *\ DS\ operatinghours}{ESH}\right) * \left(1 + (energy\ loss\%)\right) \quad (3.21)$$

The total number of panels required

$$No\ of\ panels\ = \left(\frac{Duty_{\mathrm{corrected}}\ *\ DS\ operatinghours}{Yield\ per\ panel\ per\ day}\right) \quad (3.22)$$

The yield per panel per day can be estimated using the ICC – SRCC solar rating report

The total cost of the solar panel (including frame and land cost)

$$Solar\ thermal\ system\ cost, (€) = No\ of\ panels\ * 323.6 \quad (3.23)$$

Buffer tanks and thermal fluid: Buffer tanks were introduced which was used as an intermediate storage tank to store the thermal fluid. As the inlet temperature of the thermal fluid into the reboiler was 125°C, the thermal fluids should be stable at high temperatures and be able to transfer heat efficiently. The most commonly used heat transfer fluid was ethylene glycol. To estimate the buffer tank volume, a residence time of 5 minutes was assumed, and this was the minimum time required for buffer tanks [42]. The total volume of glycol was assumed to be 2 times the volume of the buffer vessel. Based on the estimated buffer vessel volume, the cost of cylindrical vessels was obtained from Alibaba

Reboiler Heat exchanger: Earlier, in solar PV systems, the immersion heater was used to heat the mixture in the reboiler, whereas for thermal energy systems a heat exchanger was used. This was assumed to be an external shell and tube heat exchanger where the heat exchange takes place between the reboiler mixture and thermal fluids. The heat exchanger cost can be estimated using the equation 3.12-3.14. The hot fluid in our case is the thermal fluid from solar thermal systems and the cold fluids are the mixture within the reboiler which is at 98.7°C. Sinnott et.al [17]reported an overall heat transfer coefficient for boiling aqueous and thermal fluid of 700-1000W/m^{2}K and for our case an average of 850 W/m^{2}K was assumed

3.3 Methodology

This section provides an overview of the methodology followed in assessing and evaluating different designs based on energy and economic parameters. Various assumptions considered in estimating the cost and energy are presented in this section.

3.3.1 Economic Analysis

- As mentioned earlier in Section 3.2, for the economic analysis an important performance parameter which is the total cost per tonne of methanol is used in assessing the designs.
- It gives a measure of the total cost required per tonne of methanol produced in designing, procuring equipment, building, installing, and operating the DS system for a specific plant lifetime. It takes the total plant cost and interest rates into account and the formula for calculating this parameter are mentioned in Equation 3.4.
- The Total plant cost can be divided into two: Total capital cost and total operating cost [17]. Figure 3.3 provides a clear classification of the total plant cost.

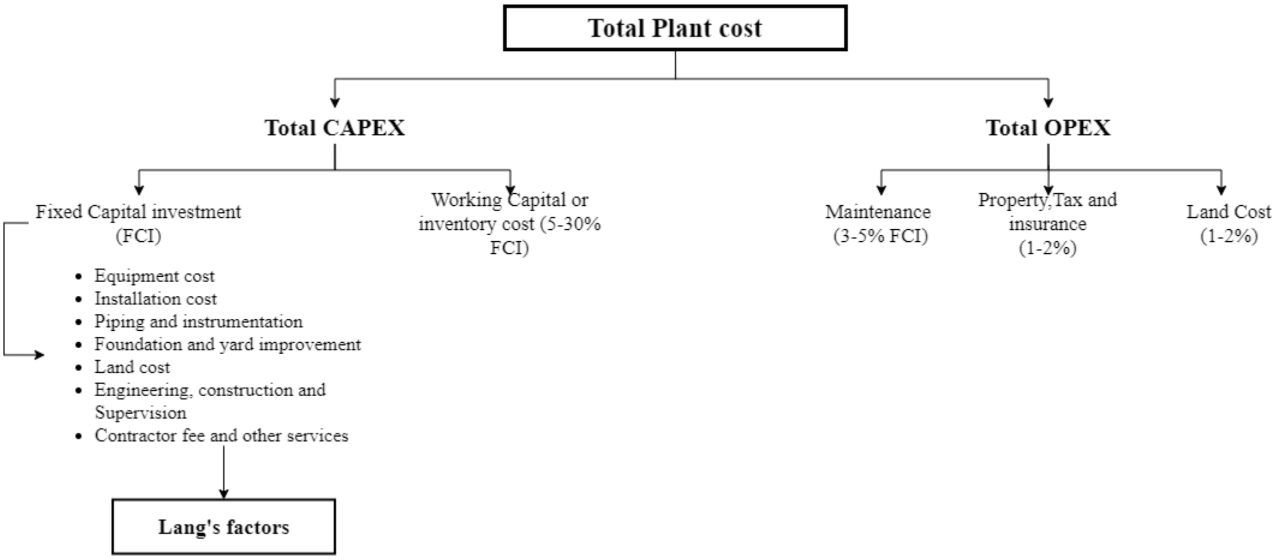


Figure 3.3. Flowchart representing the methodology for estimating the Total plant Cost

Total CAPEX estimation and assumptions:

- The total CAPEX cost is the initial investment required in procuring, building, and installing the necessary equipment for the plant. It consists of fixed capital investment and working capital.
- The fixed capital investment includes the equipment cost, construction, installation, and other essential costs. Factorial method [34]approach was followed in estimating FCI where specialized factors such as Hand and Lang factors are considered to account for these additional costs besides the equipment cost.

- The FOB prices estimated from the previous section are considered and **transportation, insurance, and import tax cost of 15% FOB** [34]were assumed in calculating the equipment cost. The equipment cost is then multiplied by the special factors to estimate the total fixed capital investment. The FCI data of DS system powered solar PV and solar thermal with an operating duration of 7 hours are presented in Appendix C.2
- The range of Lang and Hand factors are presented in Appendix C.2. It must be noted that the lang factors mentioned in the literature [34]are for large-scale systems and therefore these lang factor ranges were considered for centralized and semi-centralized systems. For the decentralized systems, the lowest range of 2 was chosen as this value was lower than the lang factors of all the large-scale equipment.
- The factorial method approach is not very accurate, but this method was sufficient for the preliminary analysis and to eliminate a few designs.
- The **Working capital** usually denotes the additional cost required for the inventory which mainly includes spare parts and raw material inventory. Sinnott et. al [sinott towler] had proposed a working capital range of 5-30% of FCI and for our case, the lowest range of **5%FCI** was chosen.

$$FCI\ (€) = \ [(FOB * Transportataion\ and\ Tax\%) * Langfactors] \tag{3.24}$$

$$Total\ CAPEX(€) = \ FCI\ +\ Working\ Capital \tag{3.25}$$

Total OPEX estimation and assumptions:

- The **total OPEX can be subdivided into fixed and variable operating costs**. The variable operating cost usually includes electricity cost, utility cost, raw material cost, and other miscellaneous costs. But **for our case, this variable operating cost can be neglected** as electricity is directly obtained from solar PV and utility costs were not considered as the condenser was cooled by natural convection and cooling water was not necessary. Therefore, these additional costs were not necessary
- The fixed operating cost can be subdivided into three namely the operating and maintenance cost, property tax and insurance cost and land cost. Sinnott et. al provided a feasible range for all these parameters where maintenance cost ranged from 3-5%FCI, tax and land cost for 1-2%FCI. For our case, the lowest of these ranges were selected and **therefore 3% and 1% were chosen for the maintenance, tax, and land costs**.
- The total lifetime of the system was assumed to be 12 years

$$Total\ OPEX(€) = \ [Maintenance\ cost + Property\ tax\ and\ Insurance\ Cost + \ Land\ Cost] * \ N \tag{3.26}$$

$$Total\ plant\ Cost(€) = \ Total\ CAPEX\ +\ Total\ OPEX \tag{3.27}$$

N represents the operating hours or the lifetime of the system- assumed as 12 years.

Total Cost per tonne of methanol estimation and assumptions:

- The total cost per tonne of methanol is calculated by substituting the estimated CAPEX and OPEX cost in Equation 3.2-3.4. The **total plant lifetime of 12 years was assumed and an interest rate of 3%** was considered. **The total methanol production per day of 600 g was assumed**
- Later, after the selection of the design, a sensitivity analysis was carried to analyse the impacts of all the considered assumptions. **ZEF** already expected the **total cost per tonne of methanol** which was approximately around **25€/ton** and this range was necessary to fetch profits. This value was considered as a benchmark to assess different designs.
-

3.3.2 Energy Analysis

- For the energy analysis, the selected performance indicator was the total duty required for the DS system which includes the duties of three components namely the reboiler, compressor and the extra heater and these systems were selected as they were power-consuming systems. The energy and cost are interconnected, **as reducing the energy consumption of the system decreases the solar energy cost and eventually reduces the total cost per tonne of methanol**.
- Equation 3.1 was used in calculating the total duty required and the design which had the lowest energy demand was chosen as the energy-efficient design. For this analysis, heat losses were considered and are added to the reboiler duty. The assumptions and the approach followed in calculating the energy losses are mentioned in Appendix C.2

3.4 Results and discussion

The previous section mentioned the methodology and assumptions considered for calculating the total CAPEX, OPEX and total cost of the system per tonne of methanol. In Section 3.1, 5 different case parameters for our analysis namely the geographical location, energy source, system operation, the scheme and the type of system were presented. Based on the methodology, all the necessary economic and energy parameters were estimated for all these different cases and were compared to assess the system. The results from this comparative analysis are presented and discussed and later at the end of this section a feasible design was recommended.

3.4.1 Economic analysis

3.4.1.1 Effect of Geographical Location

- As the Distillation system will be powered by solar energy, the geographical location plays a cardinal role in deciding the cost of solar energy systems. **The cost of solar energy systems is less for a location with high irradiance and equivalent sunshine duration** when compared to the location with low irradiance and equivalent sunshine duration. The main for this trend is that location with low irradiance and sunshine duration requires a greater number of panels to produce the required duty which eventually increases the cost of solar energy systems.
- To validate this trend, 3 different locations of varying irradiance were chosen, and the FOB price was analyzed for two different cases: DS system powered by solar PV, and another is DS system powered by solar thermal systems.
- Figure 3.4 shows the FOB price of solar PV and solar thermal systems for different designs of the 3-scheme operating for 7 hours. It must be noted that the energy losses are not considered and therefore the total energy demand is same for all the 3 schemes. Based on the COCO results and the formulas and assumptions mentioned in Section 3.2.6, the cost of solar energy systems is calculated.

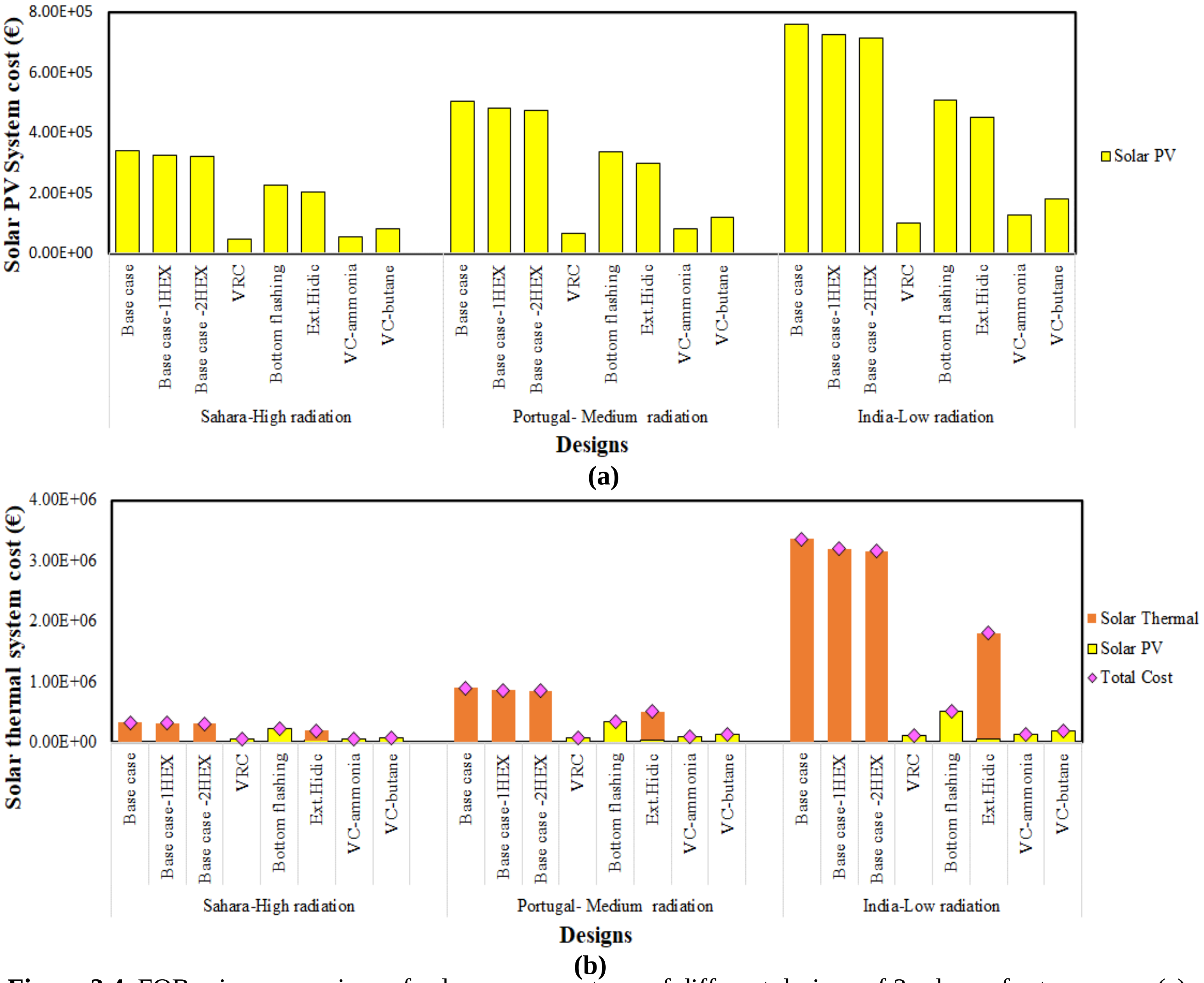


Figure 3.4. FOB price comparison of solar energy systems of different designs of 3 scheme for two cases: (a) Solar PV case (b) Solar Thermal case

- It must be noted that **for the solar thermal case** (Figure 3.4b), **both solar thermal and solar PV is necessary as the reboiler is powered by solar thermal and other systems such as compressor will be powered by solar PV**. **Assumption**: The column heat losses are not considered.
- For E.g. When the base case design was considered, the FOB cost of solar PV systems in Portugal and India were 48% and 123.5% higher than cost of solar PV systems in Sahara. A similar trend was also observed for Solar thermal systems. When base case of solar PV and solar thermal in Sahara location are compared, the FOB cost of solar thermal was 4% higher than solar PV.

- Two conclusions can be drawn from Figure 3.4

[1] **Both solar PV and solar thermal systems follow the above-mentioned trend.** The solar energy systems were expensive in the location where the irradiance and equivalent sunshine hours were lower.

We can observe that in both cases, the cost of all the designs was comparatively larger in medium radiation and highest for low radiation cases. Therefore, a geographical location with high radiation is preferred if the cost of the DS system needs to be minimized

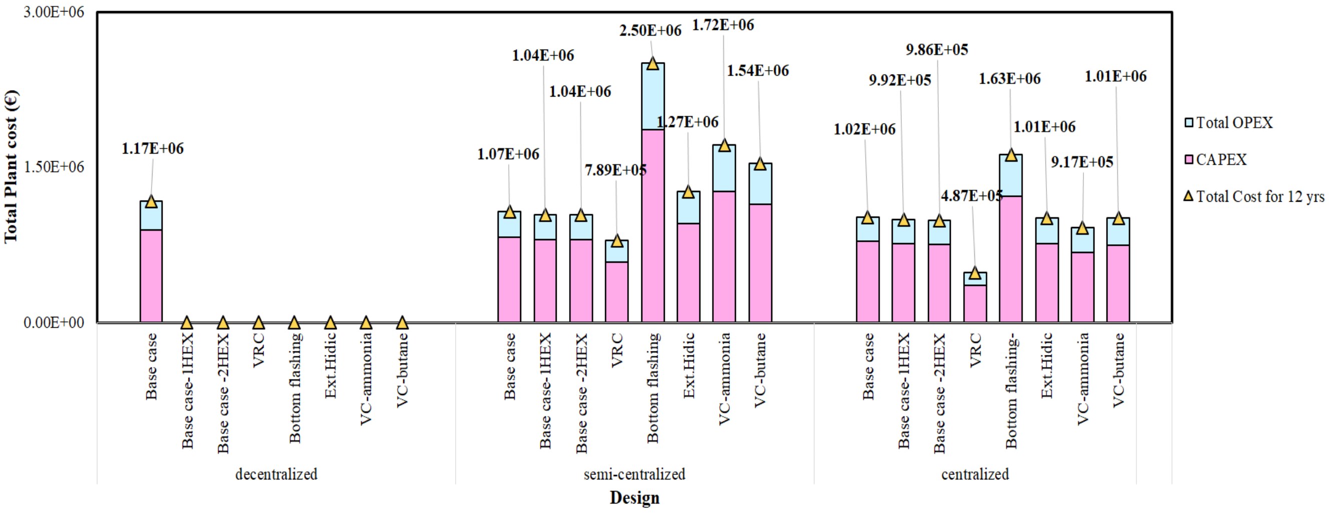
[2] For **the high radiation region, in both cases**, we can observe that the **FOB cost of the solar energy system for VRC and VC designs were less compared to other designs**. This was because of the reduction in reboiler duty. Both these designs require only the compressor and the cost denoted in the plot for these designs, represents the cost of solar energy systems required for powering compressors whereas for other systems both reboiler, and compressor duty was high, therefore more solar panels was required which increased the cost.

[3] For **the high radiation region (Sahara), the cost of solar PV and solar thermal systems were closer** and therefore to decide the energy source, other component costs need to be considered.

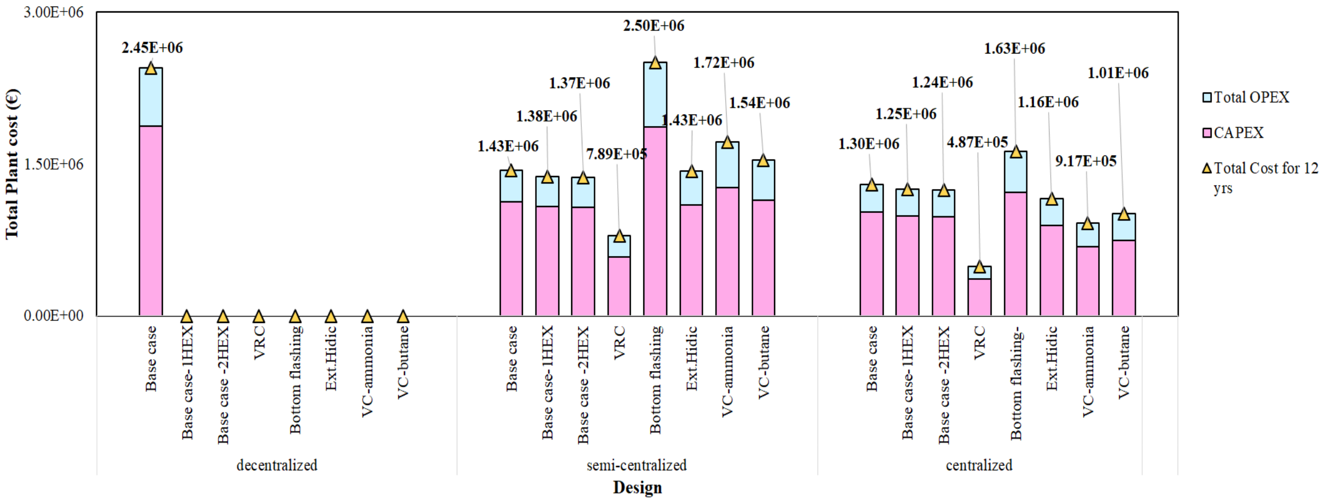
- Hence **the high radiation region (Sahara) was chosen as the preferred location** and all the analyses carried in upcoming sections are based on this Sahara location.

3.4.1.2 Effect of Energy source

- Another important parameter that needs to be decided is the energy source. From the previous analysis, the FOB price of solar PV and solar thermal were closer. In this analysis, a feasible energy source was selected based on the total cost per ton of methanol.
- Both the cases (solar PV case and solar thermal case) require different components and the FOB price of each of these components was calculated using the formulas mentioned in Section 3.2. Then, based on the economic methodology and assumptions, the total plant cost and total cost per ton of methanol were calculated. Fig C.7 presented in Appendix C.2 represents the fixed capital investment that includes the lang factors and transportation cost. It gives a breakdown of the individual cost of components.
- Figure 3.5 represents the total plant cost without interest rates for different designs across three schemes that are operating for 7 hours in the Sahara location and this analysis was done for two cases: Figure 3.5a-Solar PV and Figure 3.5b-Solar thermal case. This plot provides a breakdown of the total CAPEX and OPEX cost of each design across 3 different schemes.



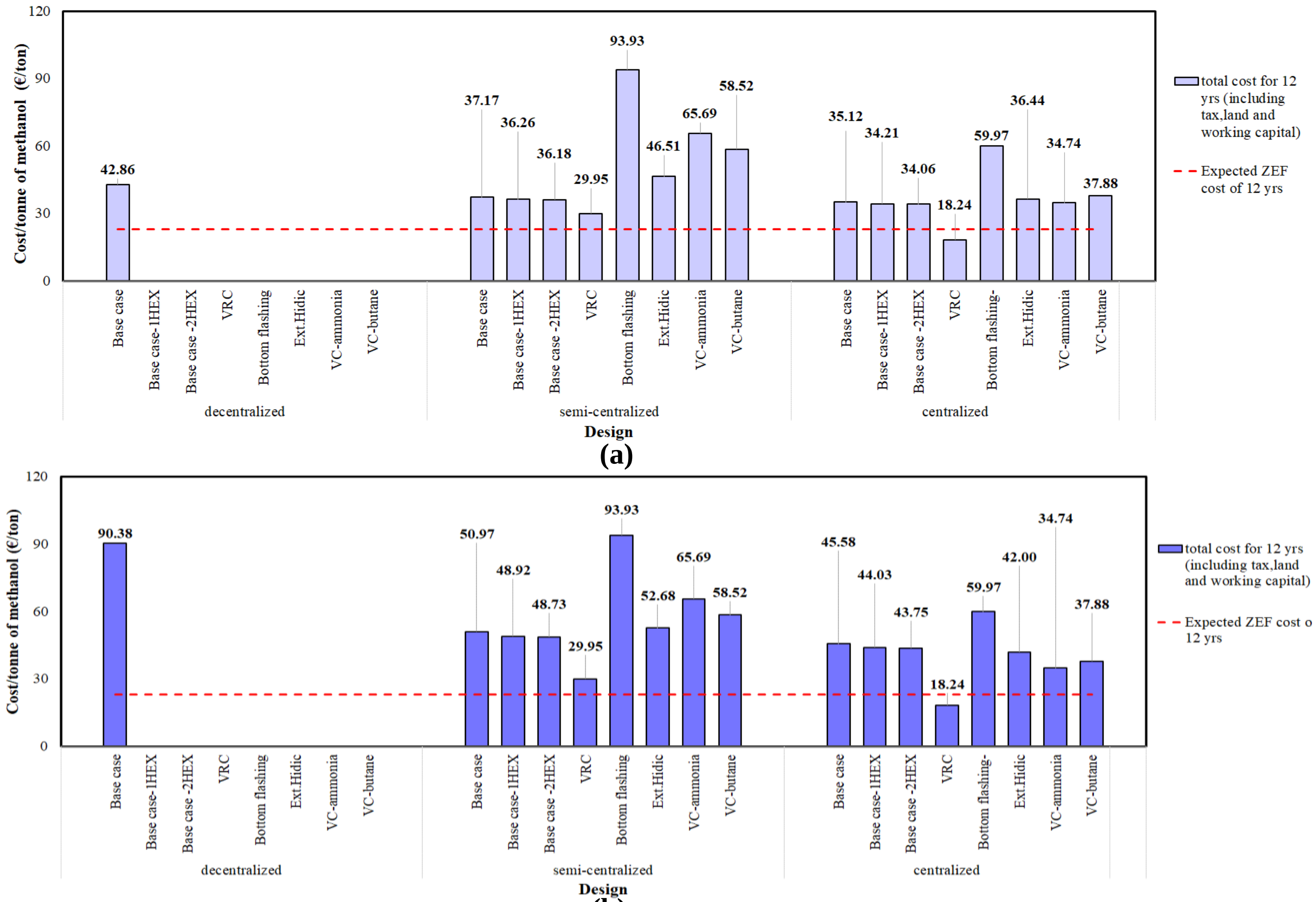
(a)



(b)

Figure 3.5. Total Plant cost comparison of solar energy systems of different designs operating for 7 hours in Sahara location for two cases: (a) Solar PV case (b) Solar Thermal case

- Based on the estimated CAPEX and OPEX cost and using equation 3.4, the total cost per ton of methanol was calculated and presented in Figure 3.6. The first plot represents the DS system powered by solar PV and the bottom plot denotes the DS system powered by solar thermal.



(a)

(b)

Figure 3.6. Total cost per ton of methanol comparison of solar energy systems of different designs operating for 7 hours in Sahara location for two cases: (a) Solar PV case (b) Solar Thermal case

- The conclusions drawn from the above-mentioned plots

  [1] From Figure 3.5, it can be observed that the **CAPEX cost of DS systems powered by solar thermal systems was higher than solar PV systems**. The component cost split up is presented in Fig.C.7 in Appendix C.2, An important reason for this trend is
  - For solar thermal cases, both solar thermal and solar PV systems are required for powering reboiler and compressor respectively which increased the cost. The solar thermal panels were found to be expensive than solar PV panels
  - For solar thermal cases, additional components such as heat exchangers in reboilers, thermal fluids, buffer tanks were required, and this increased the total cost of the system.
  - For solar thermal cases, designs such as VRC and VC, the cost per ton of methanol was the same as the solar PV case and this was because these designs did not require a solar thermal system as the reboiler duty is 0. Only solar PV panels were required to power the compressors.

  [2] Due to the high CAPEX and OPEX cost for the solar thermal case, the cost per ton of methanol also increased and it was higher than the expected ZEF range of **25€/ton.** This can be observed in Fig.3.6**.** On the other hand, the **cost per ton of methanol for solar PV cases was much closer to the expected range despite being higher than expected**.

  [3] Another reason for choosing a PV system is the learning curves of solar PV. **Solar PV cost is reducing every year** and in near future, it might reduce to 0.05€/W. Moreover, the DS system design is simple and requires fewer components when powered by Solar PV.

- Hence **preferred energy source is Solar PV** and all the analyses carried in upcoming sections are based on this energy source.
- From Figure 3.6, the impact of the design and schemes on the total cost of the system can also be analyzed and the observations are presented in the next section. As solar PV was chosen, this analysis is based on Fig.3.5a

3.4.1.3 Effect of Scheme and type of system

Effect of Scheme

- The conclusions are drawn from Figure 3.6a

  [1] We can observe a **decreasing cost per methanol trend when the size of the plant increases**. The **cost per methanol value was lower for centralized systems when compared with decentralized systems**. Fig.C.7a (in Appendix C.2) shows that cost of individual components of a decentralized system was higher than the cost of components used in centralized systems. Therefore, building a large-scale centralized system was found to be more cost-effective when compared to building multiple decentralized units.

  [2] Another reason **for not opting for decentralized systems is the energy or heat losses in the Distillation System.** Decentralized DS units were found to have higher energy losses compared to centralized units. The assumptions and methodology for calculating the energy losses in Distillation systems are presented in Appendix C.2.
  An energy analysis considering the energy losses for all the designs across 3 schemes are presented in Section 3.4.2 and it also mentions that the energy savings are higher in Centralized systems.

- Hence, **Centralized systems are the preferred most preferred scheme**.

Effect of designs

- The following observations and conclusions are based on Figure 3.6a

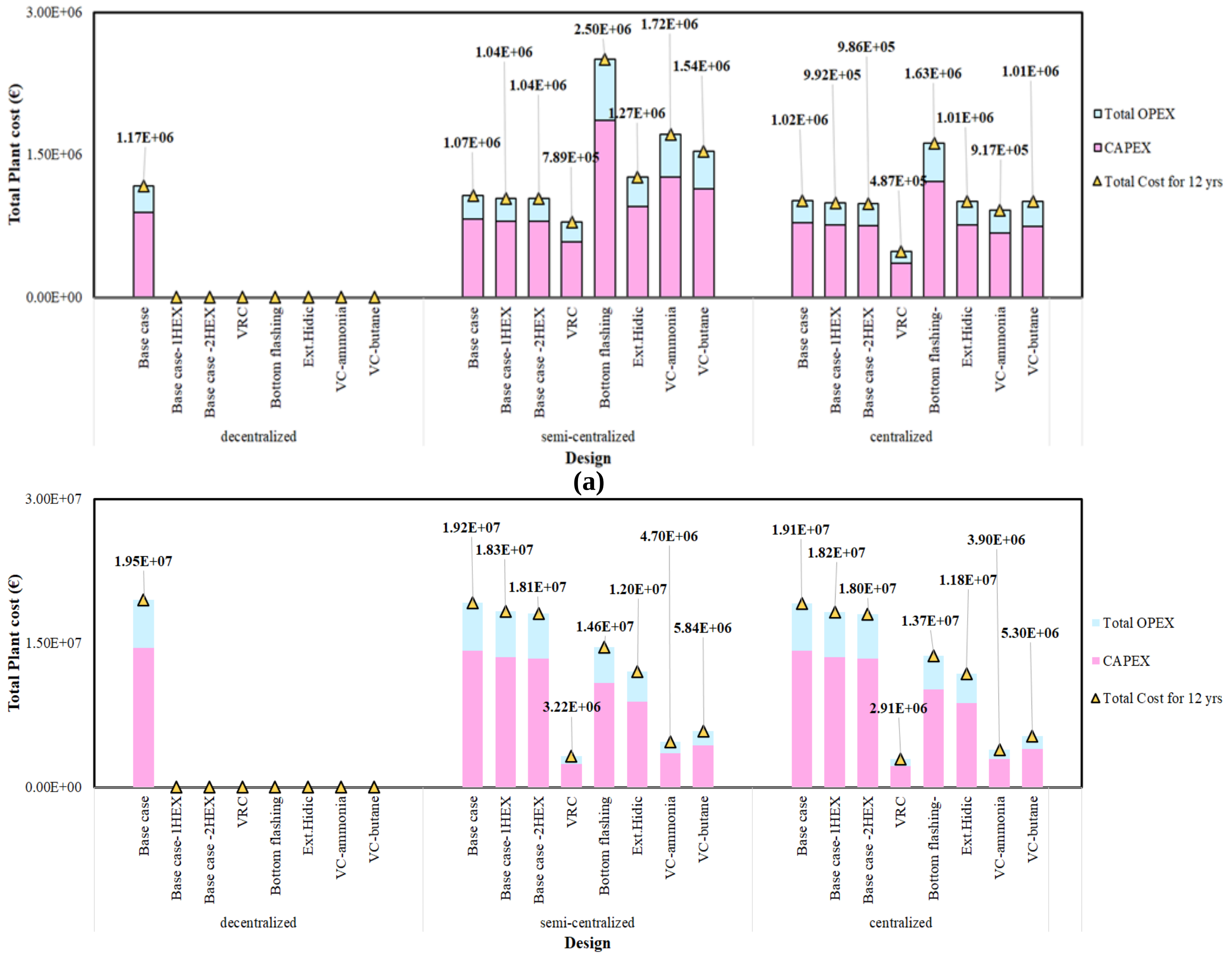
[1] **For a centralized scheme**, among all the designs the cost of the **bottom flashing design was the highest and this was because of the compressor and additional components** such as an extra heater and cooler. Fig.C.7a in Appendix C.2 shows a clear breakdown of all the components of the proposed designs across different schemes. The **cost per ton of methanol of the remaining designs was higher than the base case value**. Even though the Base case-1HEX and Base case-2HEX designs had a comparatively lower cost per ton value, the reduction from the base case wasn't significant. A similar trend was also observed for **semi-centralized systems but the cost per ton of methanol was higher than the centralized scheme and lower than the decentralized base case**.

[2] The **Centralized VRC design was found to be a cost-effective design**. Due to the low compressor, reboiler and condenser duty of VRC systems and the low energy losses for centralized schemes, the cost of the expensive component such as compressors, solar PV systems, etc. was reduced. The **cost per ton of methanol for the Centralized VRC system was much lower than the expected ZEF limit**. A similar trend was observed in most of the literature [43] where the VRC system was mentioned as a cost-efficient design that had the highest cost saving when compared with other designs. It must be noted that the columns used in this literature are conventional industrial columns with different column specifications.

- Therefore, for this particular design, a quantitative and qualitative analysis was performed to assess whether this system can be a potential design for our ZEF requirement

3.4.1.4 Effect of Operating Hours

- All the previous analyses carried out were related to a 7-hour operation, but ZEF was already planning to run the entire ZEF micro-plant for 24 hours to increase the production of methanol and profit. Therefore, this **section deals with the 24-hour operation of the DS system where the same feed flow rate used in a 7-hour operation is provided but instead of producing 600g of methanol in 7 hours, the distillation system will now be operating for 24 hours and will be producing 2057 g of methanol per day**. The analysis in this section will be related to the DS system powered by solar PV and the Sahara location was selected. For this analysis, the energy losses in DS systems are not considered.
- One of the major issues faced when the DS system operates for 24 hours is the energy source. As solar PV produces energy only for a specific sunshine duration, it is important to store sufficient energy so that the stored energy can be used to power the DS system during the night. Therefore, in this case, batteries need to be used. The cost of batteries can be calculated using the formulas mentioned in Section 3.2.6
- As there is no change in the feed rate, the energy and the column specifications remain the same. But the total plant cost and cost per ton of methanol changes because excess solar PV systems are required to store the energy in batteries and also simultaneously supply energy to the DS system during the daytime. Therefore, this increases the total cost of solar panel systems, but other equipment cost remains the same as flow conditions and energy demands are the same. **An average solar battery cost of 142.7€/kWh was considered which was closed to the value reported in the literature[44]**
- An approach similar to a 7-hour operation was followed in estimating the cost where equations and methodology from Section 3.2 were used in calculating the cost of equipment. Figure 3.7 provides a comparison of the Total Plant Cost between a 7-hour and 24-hour operation that includes the total CAPEX and total OPEX of different designs and schemes (solar PV and Solar thermal) without the interest rates.



(a)

(b)

Figure 3.7. Total Plant cost comparison of DS system powered by Solar PV for different designs across 3 schemes operating in Sahara location for two cases: (a) 7-hour operation (b) 24-hour operation

- The total cost per ton of methanol for both these cases was also calculated and the plots are presented in Figure 3.8. Figure 3.8a presents the 7-hour operation case and Figure 3.8b represents the 24-hour operation case.

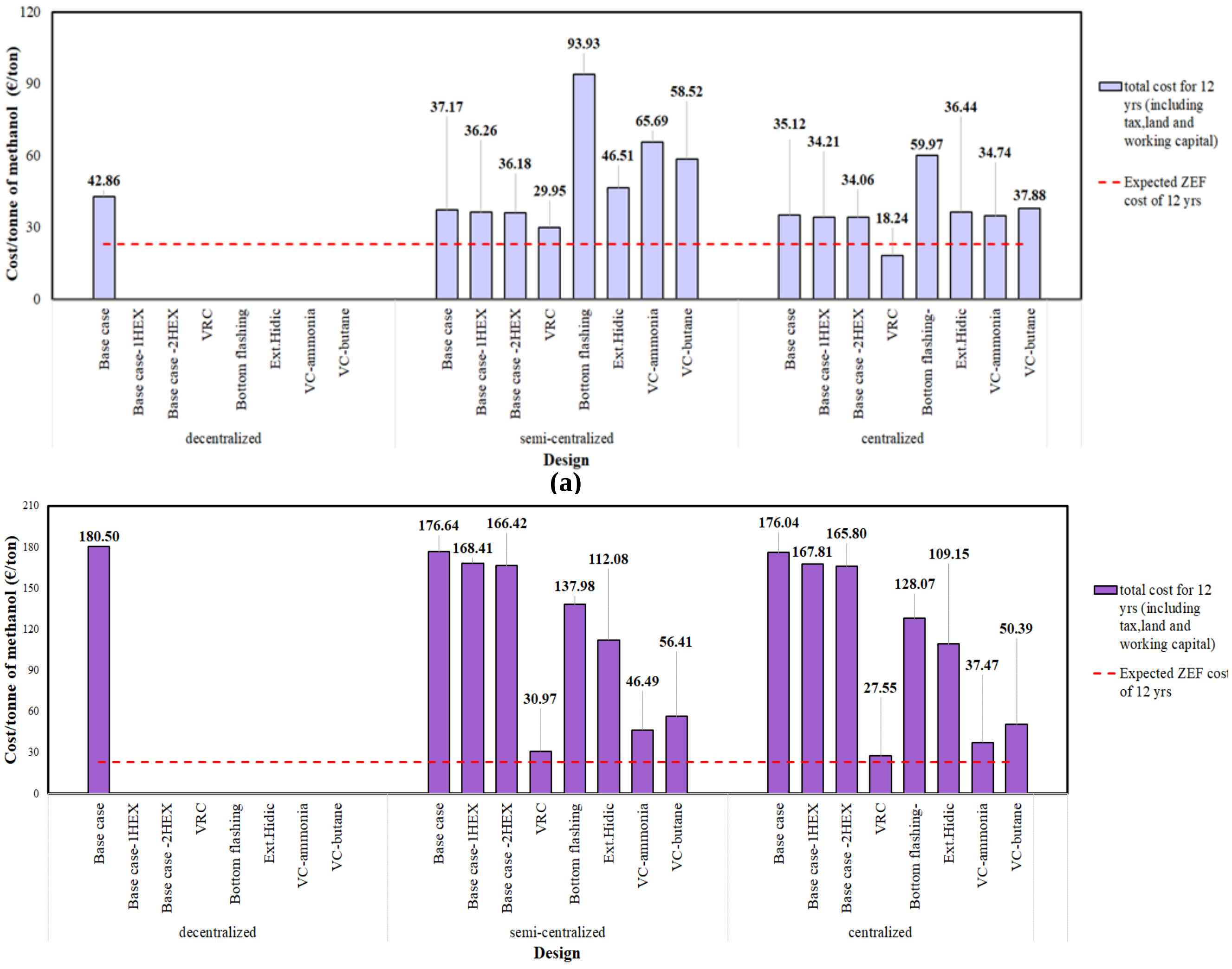


Figure 3.8. Total cost per ton methanol comparison of DS system powered by Solar PV for different designs across 3 schemes operating in Sahara location for two cases: (a) 7-hour operation (b) 24-hour operation

- The conclusions drawn from the above-mentioned plots

[1] From Figure 3.7b, **it can be observed that the CAPEX and OPEX cost of all the systems across different systems has increased drastically for the 24-hour operation**. This was because of the inclusion of expensive batteries. A component-wise breakdown is presented in Fig.C.7c in Appendix C.2 and **it shows that the batteries constitute more than 50% of the total capital cost**.

[2] Another observation from the same plot is that **the total plant cost of VRC and VC systems are very less compared to the other designs**. This eventually resulted in lower cost/ton of methanol for these two designs. And the main reason is the total energy demand of the designs. Fig.3.9 provides an overview of the total duty required considering the energy losses for different designs. It can be observed that the total energy demand of VRC and VC system are less due to lower reboiler and compressor duty and therefore the solar PV systems and batteries required are comparatively less which reduces the total plant cost significantly

- **Storage systems such as batteries are extremely expensive which significantly affects the total plant cost**. Even though the cost per ton of methanol for 24-hour operating Centralized VRC systems was comparable to 7-hour operating Centralized VRC systems, the value was higher. But based on the learning curve of batteries presented in the literature, which mentions that the cost of batteries can reduce to 58€/kWh in 2030, implementing the 24-hour operating DS system for VRC systems can be a possible option.
- Hence **7-hour operation was chosen as the preferred operation period of the DS system** and all the analyses carried in upcoming sections are based on this operation.

3.4.2 Energy analysis

- The main idea of this analysis is to analyse the total demand of different designs across 3 schemes and assess the designs based on the energy savings. For this analysis, the column energy losses were considered and the assumptions and methodology to calculate the energy losses are presented in Appendix C.2[3]and these energy losses are added to the reboiler duty. The analysis was carried for the DS system operating for 7 hours and located in Sahara Location. From the COCO energy results and using equation 3.1, the total duty required for each design can be estimated and the results are presented in.Figure 3.9. Total duty demand of DS system for different designs across 3 schemes

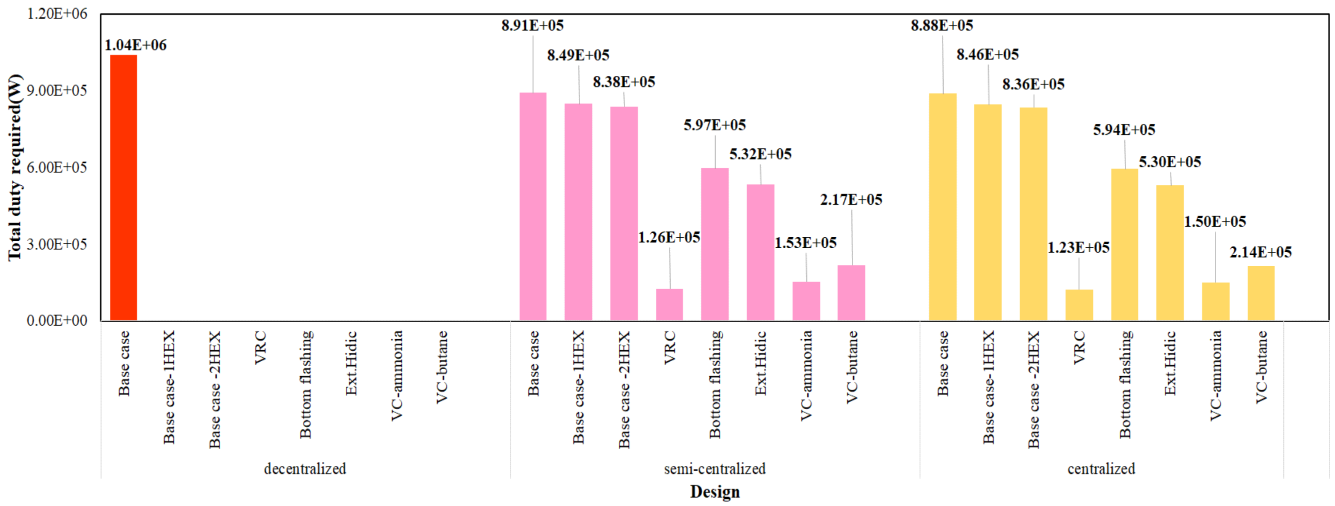


Figure 3.9. Total duty demand of DS system for different designs across 3 schemes

- The conclusions are drawn from Fig.3.9

[1] The **total duty required was higher for decentralized systems, followed by semi-centralized and finally the centralized systems** and **this is because of the higher energy losses** taking place in decentralized systems.
Due to these energy losses, to maintain the temperature in the reboiler, excess energy needs to be supplied to overcome these losses. E.g.: The energy loss per unit of the decentralized base case system is low but when the entire ZEF park with 13500 plants is considered, the energy losses are higher than the Centralized base case system.

[2] **In both semi-centralized and centralized schemes, the VRC system was found to be more energy efficient** which had an energy saving of 87.8 % and 88.2 % respectively when compared with the total duty of decentralized base case.

[3] **This was followed by VC ammonia where centralized systems** had an energy saving of 84.7% and 85% respectively. The other systems showed a significant reduction in the total duty required. The lowest energy-saving designs are the Base case-1hex and base case 2hex systems.

3.5 Final discussion and decision

From the previous section, we observed that VRC systems could be a possible design that is not just energy-efficient but also economically viable. It was also recommended that operating the DS system for 7-hours in a high radiation location where the system is powered by a Solar PV could be a possible solution to reduce the total plant cost. Other heat integrated designs were not considered as the cost per ton of methanol value was higher than the base case. In this section, a quantitative analysis based on the calculated cost has been presented and compared with the base case systems and later a qualitative analysis was also presented.

3.5.1 Quantitative and Qualitative Analysis

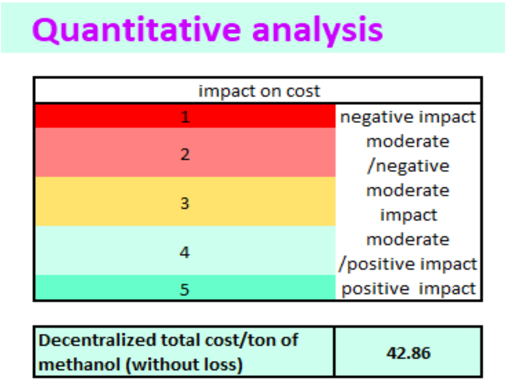
Quantitative Analysis

- **The quantitative analysis presented in** Figure 3.10 **is based on the total cost per ton of methanol that was calculated in the previous section**. The analysis was performed for the DS system powered by solar PV and for 4 main cases which include 2 cases for 7-hour operation (with and without energy losses) and 2 cases for 24-hour operation (with and without energy losses).
- **The comparison was done between the VRC systems and the base case systems for all the 3 schemes**. The severity of impact was indicated by colour codes shown in Figure 3.10. Quantitative cost comparison of VRC and base case systems across 3 schemes
- The colour **code 1**-dark red indicated a negative cost impact and **unacceptable design** and the colour code dark green indicated a positive impact. **Code 4 and code 5** can be considered **acceptable designs**.
- **These codes were assigned to designs based on the cost factor**. **The decentralized base case (without energy losses) was chosen as the reference case.** The cost factor indicates the fraction of cost per ton of methanol of a particular design with a decentralized base case design without energy losses.

$$Cost\ factor = \frac{Cost\ per\ ton\ of\ methanol\ for\ particular\ design}{Cost\ per\ ton\ of\ methanol\ for\ decentralized\ base\ case\ (without\ energy\ losses)} \qquad (3.28)$$

This gives a fraction of the cost required for a particular design when compared with a decentralized base case. **The lowest cost factor indicates the highest cost savings**.

- The design which had the highest cost factor was assigned code 1 and the design which had the lowest cost factor was assigned code 5
- These factors were introduced to quantify the cost results and choose the design based on factors.



Quantitative analysis

impact on cost	
1	negative impact
2	moderate /negative
3	moderate impact
4	moderate /positive impact
5	positive impact

Decentralized total cost/ton of methanol (without loss)	**42.86**

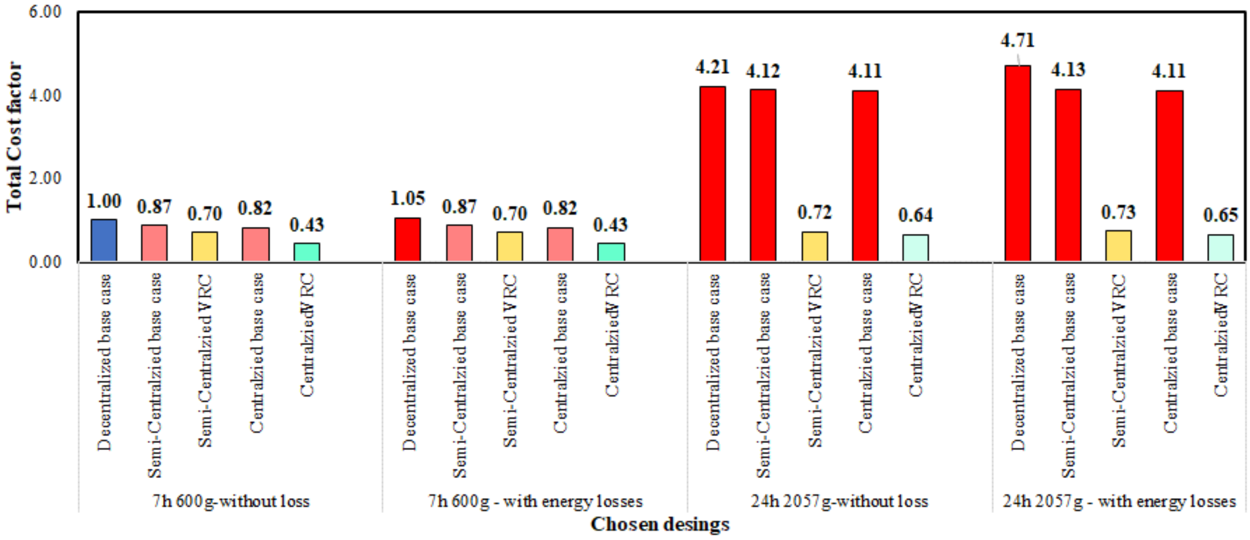
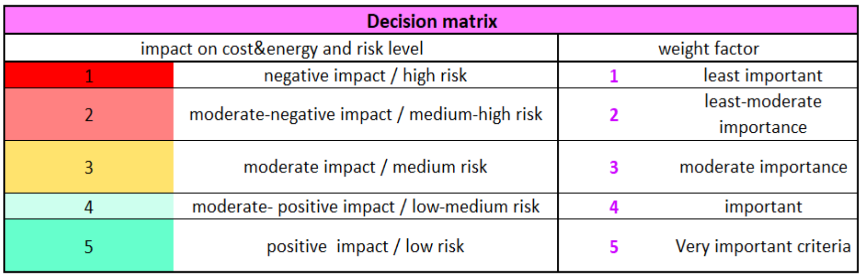


Figure 3.10. Quantitative cost comparison of VRC and base case systems across 3 schemes

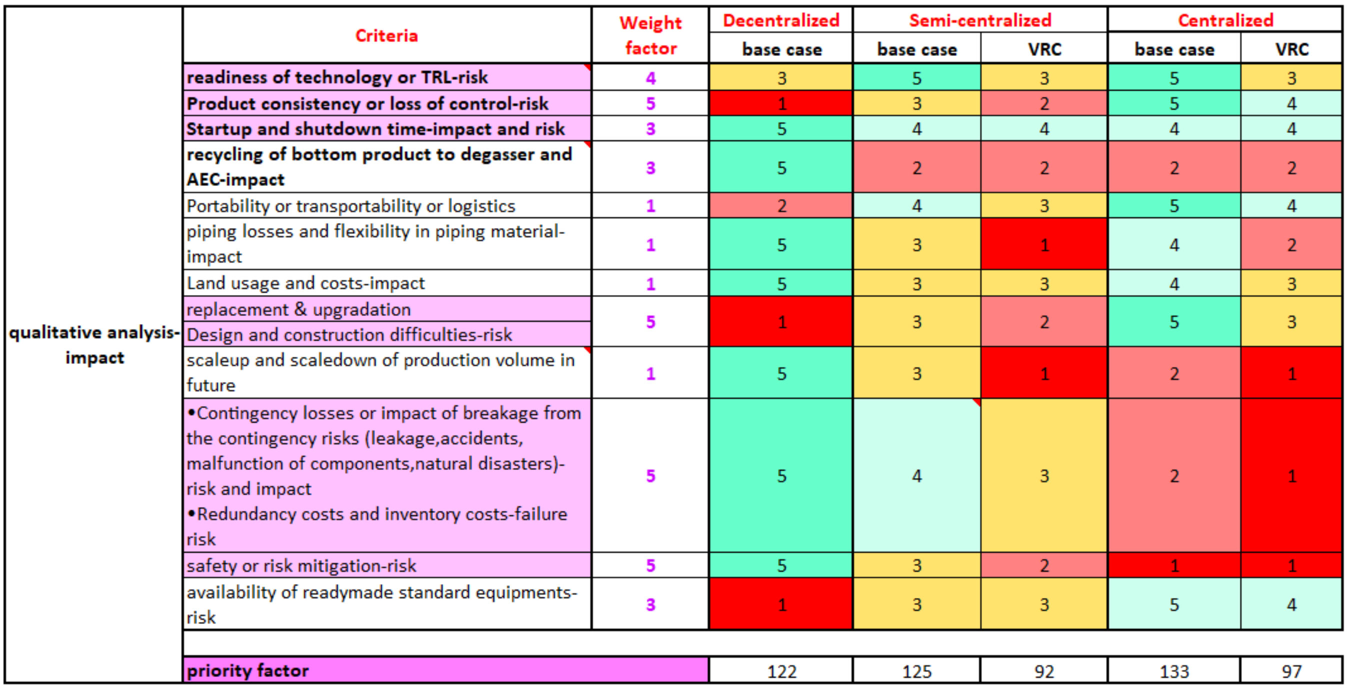
- From the analysis, it can be observed that the **lowest cost factor was for the centralized VRC systems** 7-hour operation without loss case and therefore it was assigned code 5. When energy losses were considered, the cost factor was reduced slightly and therefore it was assigned code 4

Qualitative Analysis

- Even though, the quantitative economic analysis shows that Centralized VRC can be a potential cost-efficient design that can be implemented at ZEF, estimating the impacts of risks which cannot be analyzed theoretically is equally important. Therefore, based on intuition and inputs given by ZEF, a qualitative analysis was performed to analyze their risks and impacts.
- An approach similar to the Pugh matrix was followed where **colour codes were introduced to denote the impacts and risks of each design**. Additionally, weight factors were introduced to denote the criteria which we felt could highly influence the decision of implementing the system at ZEF.
- Each impact factor was multiplied with respective weight factors and the total factors of all the criteria were added to get the total priority factor. **The design which had the highest priority factor was selected as the preferred design for ZEF**.



Decision matrix			
impact on cost&energy and risk level		weight factor	
1	negative impact / high risk	1	least important
2	moderate-negative impact / medium-high risk	2	least-moderate importance
3	moderate impact / medium risk	3	moderate importance
4	moderate- positive impact / low-medium risk	4	important
5	positive impact / low risk	5	Very important criteria



	Criteria	Weight factor	Decentralized	Semi-centralized		Centralized	
			base case	base case	VRC	base case	VRC
qualitative analysis-impact	**readiness of technology or TRL-risk**	4	3	5	3	5	3
	Product consistency or loss of control-risk	5	1	3	2	5	4
	Startup and shutdown time-impact and risk	3	5	4	4	4	4
	recycling of bottom product to degasser and AEC-impact	3	5	2	2	2	2
	Portability or transportability or logistics	1	2	4	3	5	4
	piping losses and flexibility in piping material-impact	1	5	3	1	4	2
	Land usage and costs-impact	1	5	3	3	4	3
	replacement & upgradation Design and construction difficulties-risk	5	1	3	2	5	3
	scaleup and scaledown of production volume in future	1	5	3	1	2	1
	•Contingency losses or impact of breakage from the contingency risks (leakage,accidents, malfunction of components,natural disasters)-risk and impact •Redundancy costs and inventory costs-failure risk	5	5	4	3	2	1
	safety or risk mitigation-risk	5	5	3	2	1	1
	availability of readymade standard equipments-risk	3	1	3	3	5	4
	priority factor		122	125	92	133	97

Figure 3.11. Qualitative comparison of VRC and base case systems across 3 schemes

- Different criteria were considered and each of these criteria is explained below
  - [1] **TRL- The readiness of technology level greatly influences the selection of design**. TRL indicates the maturity of technologies in industries, and it **gives us an idea of whether implementing these systems at ZEF could be a feasible option and also the risk level associated with it**. The base decentralized was given a moderate impact factor as commercialized mini-distillation systems are not being implemented in industries. And therefore, implementing these systems at ZEF would be risky whereas semi-centralized, and centralized base case DS systems are available in industries and therefore they have a low risk. From the literature, we found out that VRC systems are technologies that are still under development and therefore an impact factor of 3 was suggested.
  - [2] **Product consistency-** As the number of plants increases, it becomes increasingly difficult to monitor the quality of products. **It is given the highest weightage as the final product with desired purity decides the revenue.** The risk is higher for VRC systems as it includes compressors and heat exchangers. If the heat exchange is not efficient in heat exchangers or if there are any compressor issues, the product purity decreases significantly.
  - [3] **Startup and Shutdown time-** The startup time for decentralized, centralized and semi-centralized systems were calculated for assumed reboiler dimensions using the equation mentioned in Chapter 4 and it was found that **the startup time was high for centralized systems**.
  - [4] **Recycling of bottom product to degasser and AEC-** For decentralized systems, the bottom water product can be utilized by the AEC subsystem where it can be easily recycled by connecting a plastic pipe. AEC team found out that recycling the water to AEC can reduce the energy demand (estimated 27W per plant-AEc subsystem). On the other hand, recycling bottom products for semi-centralized and centralized increases the piping and transportation cost.
  - [5] **Transportability and logistics-** Transporting large scale units require less manpower and it can be easily transported using trucks and cranes whereas you need a lot of manpower to move decentralized units. As VRC systems include big compressors and heat exchangers, transporting these equipment are comparatively difficult.

[6] **Land usage and scale-up of systems -** It is easier to scale up decentralized units and the area occupied is less. Centralized units occupy a lot of space especially VRC systems as condensers, compressors use a large proportion of land and scaling up is also difficult.

[7] **Contingency losses, Safety risk and mitigation-** A major advantage with decentralized units is that it is easier to contain the risks during unexpected failures or breakdowns. The faulty systems can be easily isolated while simultaneously running other systems. **The economic losses would be lower when there are multiple systems available**. This is possible even in semi-centralized systems, but the risk is comparatively higher. Centralized systems have the maximum risk. **They were given the highest weight factor** as both risk and economic impact are involved.

[8] **Availability of readymade components and construction difficulties-** Standardized components are available for large scale systems whereas for decentralized systems it is difficult to design and buy components based on our specifications. The replacement and upgradation in decentralized systems are difficult and expensive.

- Based on the priority factors, **a Centralized base case was found to be a safer option** when compared to be VRC systems implemented at ZEF. Qualitative analysis for other designs was not performed as the cost per ton of methanol of other designs were found to be higher than the base case. The Centralized 2hex design could be a possible option but the priority factors were found to be lower than the base case. Therefore, a Centralized base case was selected as a feasible design.
- **VRC systems could be a potential design in near future, and one should not eliminate the VRC designs** as they offer better benefits in terms of cost and energy.

3.5.2 Sensitivity Analysis

- The **sensitivity analysis was carried out** for Centralized base case and VRC systems **to understand the impacts on the total cost per ton of methanol for different uncertainties**. The influence of each parameter was also mentioned. The sensitivity analysis has been summarized in Figure 3.12

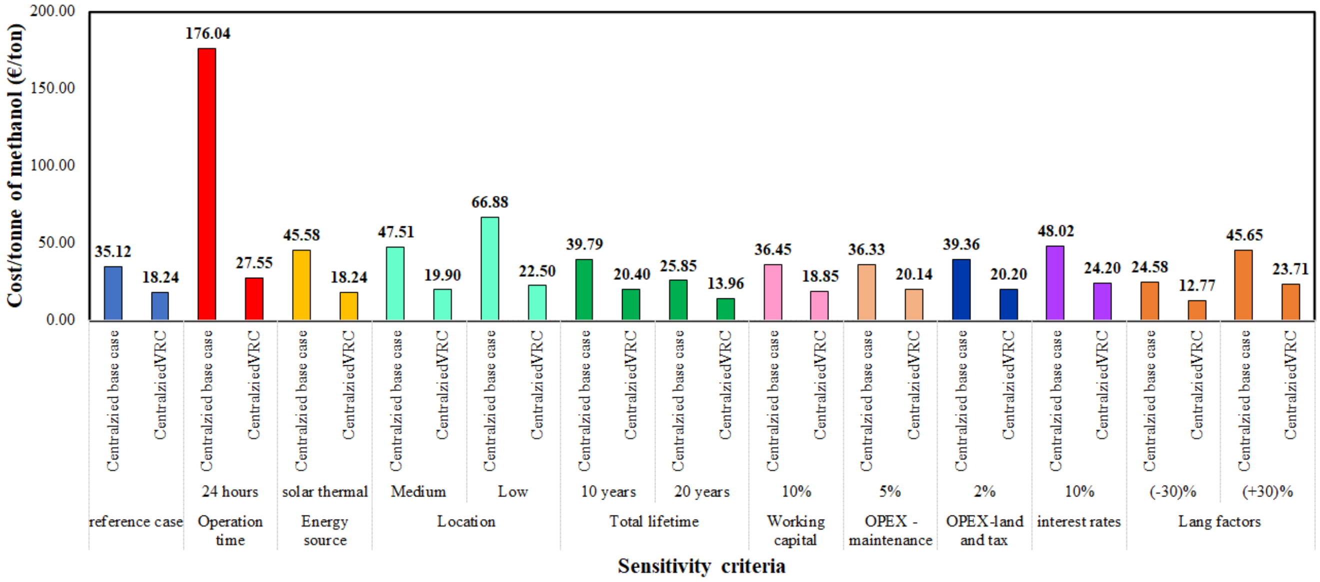


Figure 3.12. Sensitivity analysis

- For sensitivity analysis, a reference case for Centralized VRC and Centralized base case was chosen, and the description of reference case are mentioned below

- **Reference Base and VRC case**: Solar PV(energy source), 7hr operation, Sahara -High radiation (location), Interest rates (3%), Total lifetime (12 years), 5% (CAPEX working capital%), 3%(OPEX- maintenance%), 1%(OPEX-land and tax%).
- The **results of the reference case were already presented in** Figure 3.6**a**. The cost per ton of methanol for reference base case was 35.12 €/ton and for reference, VRC was 18.24 €/ton.
- **Each parameter in the reference case was varied and the total cost per ton value was estimated**. For. eg. in the first sensitivity analysis-Operation time: The operation hour was changed from 7hour to 24 hours for both the reference cases. It was observed that when operation time was changed to 24 hours, the cost of the Centralized base case and VRC was found to be 176.04 and 27.55 €/ton.
- **Operating hours, location, interest rates and lang factors** were found to be sensitive parameters

3.6 Conclusion

- An energy and economic analysis were performed for the selected designs across three different schemes. Different case parameters were presented, and each case parameter was analyzed based on energy and cost performance indicators.
- From economic analysis, it was observed that operating DS system in low radiation location resulted in increased total plant cost. The total plant cost when a solar thermal system is implemented was found to be higher than systems powered by solar PV. The future projection of the solar PV cost curve also suggested that implementing solar PV would be a more feasible option.
- The 24-hour continuous operation was not recommended due to expensive batteries. But the cost of these batteries is also declining and therefore, it could be a possible option in future.
- DS systems powered by solar PV which operates for 7 hours in High radiation regions such as Sahara was recommended as a possible solution to reduce the total plant cost.
- The decentralized and semi- centralized systems can be eliminated as the total cost per ton of methanol and the energy losses were found to be higher than the centralized systems
- For the Centralized systems, the heat integrated designs such as external HiDiC, bottom flashing and VC systems were found to be expensive than the base case systems. VRC design was found to be an efficient system in terms of energy and cost. The difference in cost and energy wasn’t much between the feed heating systems and base case systems.
- VRC systems could be a possible design for the ZEF plant, a quantitative and a qualitative analysis was carried and finally, the Centralized Base case systems were chosen.

Chapter 4

Dynamic Analysis of DS system

This chapter primarily deals with understanding the impacts of the dynamic environment on the DS system. As discussed previously, the DS system will be powered by solar PV. A major drawback with these systems is the fluctuating panel output and these disturbances directly influence the performance and product outputs of the DS system. Therefore, understanding and modelling these disturbances are cardinal. This chapter provides insights into the dynamic modelling of the DS system and also suggests measures to mitigate the impact of disturbances on the DS system. Finally, the start-up and shutdown analysis of the DS system is also explained. The analysis in this chapter was performed using MATLAB and these analyses are based on the Centralized base case distillation system that operates for 7 hours in Sahara Location.

4.1 Effect of external disturbances on the DS system

Varying environmental conditions such as variation in solar radiation, relative humidity and ambient temperature greatly affects the performance of all the ZEF sub-systems. This section highlights the impacts of two major disturbances on the DS system

Incident solar radiation and ambient temperature:

- It is a well-known fact that **large fluctuations in solar radiation can be observed between different hours of the day, between consecutive days or between different seasons which directly affects the solar PV output**.
- Figure 4.1 depicts a weekly variation in incident solar radiation for January in the Sahara location. This incident radiation steadily increases from sunrise and reach the peak at midday and later the radiation gradually starts reducing and therefore, the solar radiation varies over time.
- Varying weather patterns can influence the availability of sunlight, air temperature and humidity Figure 4.1 also shows fluctuations in the solar radiation for a couple of hours which indicates sudden changes in local weather patterns such as dust storms or clouds momentarily covering the sun or thunderstorms. Geographical location can also play an important factor as certain locations receive low solar irradiance and low temperature. **For our analysis Sahara location was chosen** [Chapter 3]. The panel output also shows a profile similar to Figure 4.1 and the panel output has been modelled and presented in Section 4.2

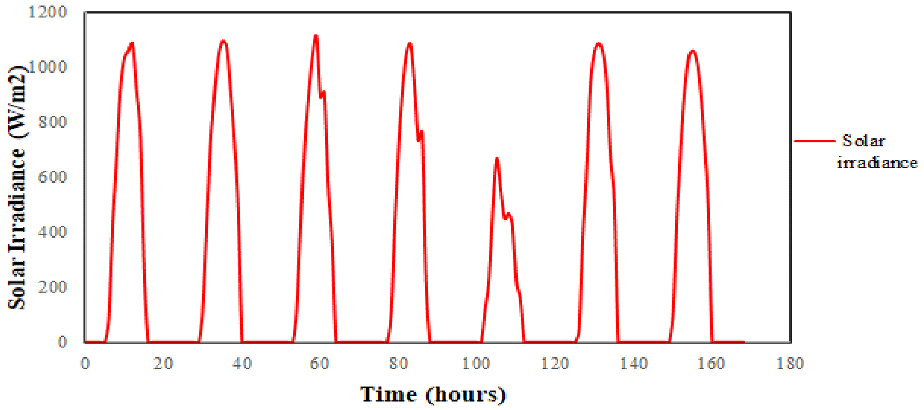


Figure 4.1. Variation in Solar radiation over a week in January month for the year 2016 in Ardar, Algeria (Sahara location) [45]

- **These variations highly influence the panel output and thus affect the reboiler duty**. Due to a change in reboiler duty, **the reboiler temperature changes which in turn affect the top and bottom products purity**. Figure 4.2 shows a schematic of the effect of solar radiation disturbance on the DS system.

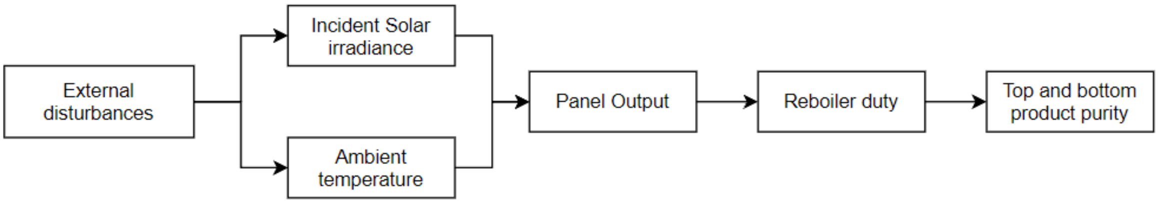


Figure 4.2. Schematic representing the impact of variation in incident solar radiation and ambient temperature on the DS system

Feed flow rate:

- Another disturbance that can affect the DS system will be the feed compositions. Feed composition to distillation system depends on the product produced from the methanol synthesis reactor. An increase or decrease in air temperature or relative humidity affects the performances of the DAC and MS sub-system which in turn influences their end products production. This eventually affects the feed flow conditions of the DS system. Due to these fluctuations, the bottom and top product purity vary.
- Even though these dynamic changes will be addressed by respective systems as each system will have a control scheme, modelling these disturbances are recommended.

Therefore, these perturbations will play a crucial role in the performance of the system. It is important to implement a control scheme in such a way the distillation system can withstand these fluctuations without breaking down and produce the required amount of methanol of specified purity without any interruption. And for this purpose, it is important to model the DS system in MATLAB so that the control scheme can be implemented, and this model should produce the same results as the COCO model presented in Chapter 2. Dynamic simulation in COCO was not possible as it is a steady-state software This analysis will be carried for a Centralized base case distillation system that operates for 7-hour and the modelling methodology is presented in the next section.

4.2 Dynamic Modelling of the DS system

The solar PV model and the DS model are the foundation for the dynamic modelling of the DS system which was developed for the primary purpose of understanding the dynamic behaviour of the distillation system for fluctuating energy source and feed rates. The main outcome of this dynamic model is to provide the variations in flow rates, stage temperatures, duties and mole or phase fractions for fluctuating disturbances. Based on this dynamic modelling an appropriate control structure was proposed to mitigate the impacts from these disturbances. **The model was developed in MATLAB and COCOImport function was used to import the thermodynamic data from COCO**. Figure 4.3 represents a schematic of the input and output structures of the proposed dynamic model.

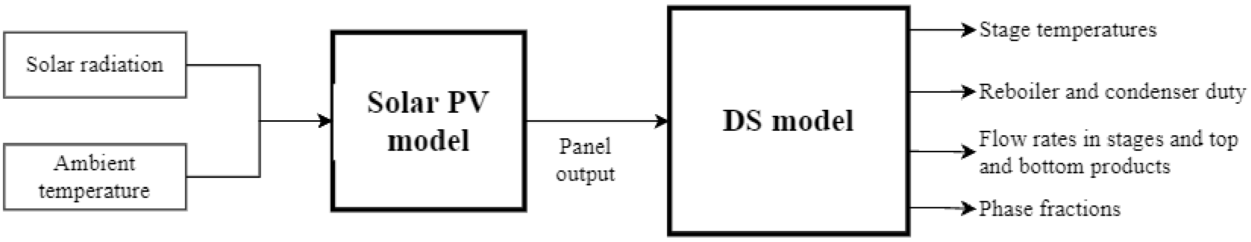


Figure 4.3. Schematic representing the input and output structures of the dynamic model

Solar PV model:

- The main objective of this model is to produce the desired panel output or electrical for fluctuating incident radiation and ambient temperature. Besides these two parameters, the area of the PV panel is also taken into consideration
- Formulas from the literature [46]were used in estimating the panel output and these formulas are presented in equations 4.1-4.5. Panel temperatures were required for determining the panel output and they were calculated using the energy balance equations. Certain assumptions were considered for the calculation of panel output, and they are presented below

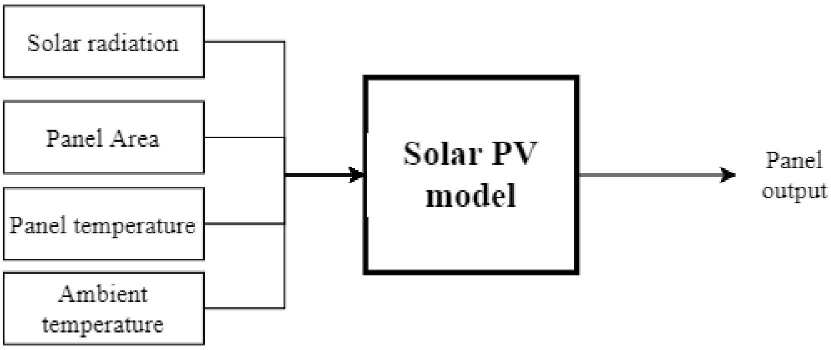


Figure 4.4. Schematic representing the input and output structures of the Solar PV model

Assumptions:

- An ideal circuit was assumed for the panel model where the shunt resistance and line resistance were assumed to be negligible. The losses and thermal storage in the solar panel are also assumed to be negligible [47]The fluctuations in voltage due to temperature variations are neglected and therefore the voltage was assumed to be constant.
- The maximum panel voltage, maximum watt peak, short circuit current, K_{isc} and panel area data were extracted from the panel datasheet and was assumed to be 48V,500W, 10.87A, 0.05% and 1979 x1320 mm respectively. The total panels of 1769 were assumed, and it was calculated based on the watt peak of the panel and steady-state energy demand of the centralized base case distillation system.
- The heat transfer in solar panels is considered to be one dimensional as the thickness of the panel is minimum and the entire panel temperature is assumed to be uniform.
- An average convection heat transfer coefficient and radiation heat transfer coefficient was assumed to be 14 and 6α W/m^2K respectively where α is the absorptivity and it was assumed to be 1 [38]

$$Sky\ temperature, T_{sky} = 0.0552\, T_{\mathrm{ambient}}^{1.5} \tag{4.1}$$

$$Panel\ temperature, T_{panel} = \frac{G\, A_{\mathrm{panel}} + h_{\mathrm{rad}} T_{\mathrm{sky}} + h_{\mathrm{conv}} T_{\mathrm{sky}}}{h_{\mathrm{conv}} + h_{\mathrm{rad}}} \tag{4.2}$$

$$I_{\mathrm{solar}} = \left(\frac{G_{\mathrm{incident}}}{G_{\mathrm{maximum}}}\right) \quad I_{\mathrm{sc}} + K_{\mathrm{isc}}\left(T_{\mathrm{panel}} - T_{ref}\right) \tag{4.3}$$

$$Panel\ output, P = I_{\mathrm{solar}} V \tag{4.4}$$

$$Total\ Panel\ output\ of\ solar\ park, P_{total} = Total\ number\ of\ panels * P \tag{4.5}$$

DS model:

- The DS model was developed in MATLAB, and it replicated the COCO model presented earlier in Chapter 2. This was done to understand how the fluctuating reboiler duty affected the end products of the distillation column. The same column specifications of Centralized Base case systems specified in Chapter 4 was considered. The total number of stages was 19 and a total condenser with a reflux ratio of 1.287 and reboiler with a boil up the ratio of 2.131 was considered. The thermodynamic properties were imported from COCO using the COCOImport and therefore the results were the same as the COCO results.
- Besides the column specifications, the panel output from the Solar PV model was the main input for the DS system. At every time step, the reboiler duty varied based on the panel output. The Rashford-rice approach was used to solve the mass balance and energy balance equations in each stage and the methodology is presented in Appendix D.1. The model predicts the stage temperatures, flow rates, vapour and liquid fractions and the duties of DS systems. Certain assumptions were considered for this model, and they are

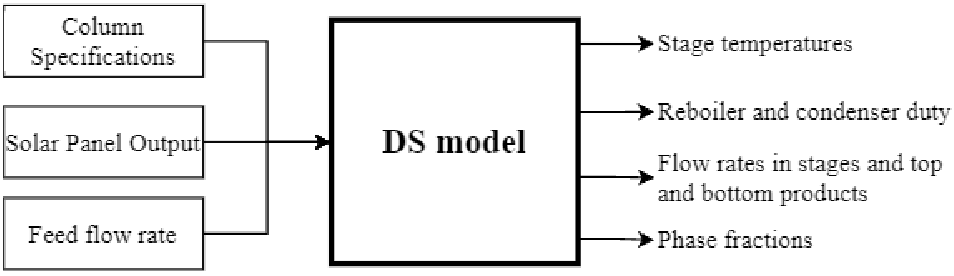


Figure 4.5. Schematic representing the input and output structures of the DS model

Assumptions:

- The heat losses in the DS system are not considered and at every time step the model was assumed to be at equilibrium and therefore the outputs were obtained for steady-state conditions. The vapour and liquid phases are assumed to be homogeneous in all stages.
- The pressure inside the distillation system is assumed to be constant and the assumed column pressure was 1 bar. Even though in reality there will be a pressure gradient between the bottom reboiler and top condenser, these pressure fluctuation effects are assumed to be negligible. A constant liquid hold-up is assumed, and the vapour hold-up is negligible and the effects due to column internals (occlusion, weeping flooding, etc.) are neglected. The reflux ratio and boil up ratio are constant and fixed.
- A major assumption here is that an ideal condenser is assumed. The fluctuating ambient temperature does not influence the condenser and it is assumed that the condenser perfectly cools the overhead vapour to saturated liquid.

4.3 Control Scheme

- From modelling results, it was clear that in order to maintain the **desired water and methanol purities in top products (0.2%water and 99.8% methanol) and bottom products (99.6 %water and 0.4% methanol), it is important to maintain the reboiler at 98.7°C**.
- **For the centralized base case distillation system**, it was assumed that a constant feed flow rate of methanol-water mixture is fed into the distillation system and **the system had a fluctuating reboiler duty as they were powered by solar energy. Due to this reason, a constant temperature of 98.7°C could not be maintained in the reboiler which affected the top and bottom products purity**. Therefore, a control structure was recommended to control the reboiler temperature to the desired level to maintain the product purity.

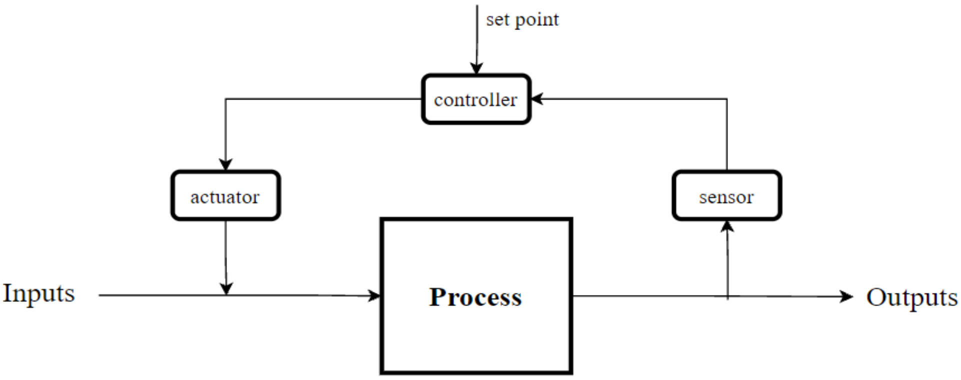


Figure 4.6. Schematic representing the feedback control

- To design the control structure, it is important to understand the possible manipulated variables. The manipulated variables are variables that can be manipulated or adjusted to achieve the desired limit of the control variable and control variables are variables that need to be maintained at desired level or constant throughout the process. Manipulated variables should be chosen in such a way that adjusting these variables should effectively control the impacts of external disturbances.

- Feedback control was chosen, and Figure 4.6 provides a schematic of a feedback control system. All the important variables are presented in Table 4.1. Controlled variable, manipulated variable and external disturbances , and it has been noted that the manipulated variables are limited. Based on these variables the feed flow control structure was developed

Table 4.1. Controlled variable, manipulated variable and external disturbances

Controlled variable	**Manipulated variable**	**External disturbance**
Top and bottom product purity	Reboiler temperature Feed mass flow rate of the DS system	Ambient temperature Solar radiation (reboiler duty)

4.4 Solar Panel Output

- Before analyzing the control system, it is important to obtain data for the fluctuating reboiler duty and this duty was estimated using the solar PV model mentioned in Section 4.2. The solar radiation data for the Sahara location is presented in Figure 4.1. Variation in Solar radiation over a week in January month for the year 2016 in Ardar, Algeria (Sahara location) **[45]**was chosen to calculate the output of all the solar panels in the solar park and the solar park output data are presented in Figure 4.7

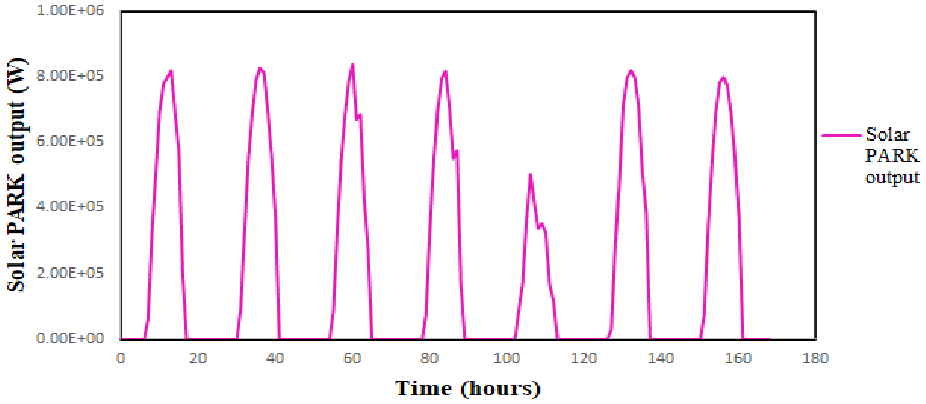


Figure 4.7. Weekly variation in Panel output of entire solar park over a week in January month for the year 2016 at Ardar, Algeria (Sahara location)

- **The panel output follows a profile similar to the solar radiation curve**. The plot presented in Figure 4.7 corresponds to the solar panel output of the entire ZEF park. **The panel output keeps varying depending on the solar radiation (see** Figure 4.1. Variation in Solar radiation over a week in January month for the year 2016 in Ardar, Algeria (Sahara location) **[45]which varies over time**, seasons and the total number of daylight or sunshine hours.

- **The panel output depends on the solar radiation, panel temperature and daylight hours**. High panel output is produced when the solar radiation is high and high panel temperature results in reduced panel efficiency and hence panel output decreases.

- For our control system analysis, one particular curve was chosen which was the second curve from Figure 4.8 and this curve represents the solar panel output produced by the solar park on the second day of the selected week. The control analysis including the startup and shutdown analysis was carried for this particular solar output profile.

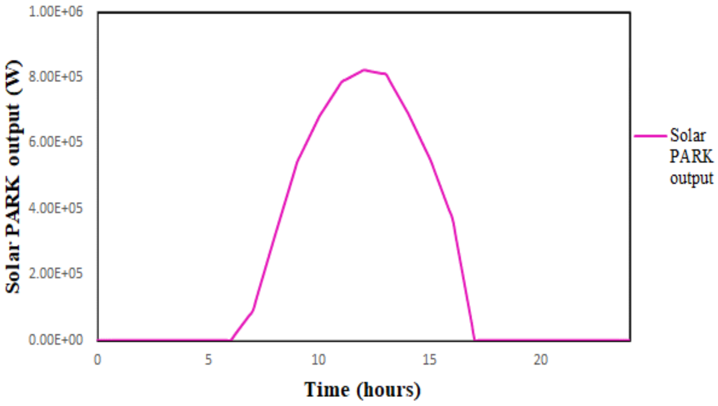


Figure 4.8. Selected solar panel output profile for control system analysis

4.5 Start-up and Shutdown Analysis

- This section provides an analysis of the startup and shutdown process of the column and also describes the conditions for starting up and shutting down the system.

-
- The Startup process is the initial phase of the distillation system operation. **During this process, the feeds and the outlet stream of the distillation column are closed, and the column is allowed to heat up till the system reaches the steady-state temperature.** The **control system does not operate during this phase** and starts functioning only when the system reaches a steady-state temperature. A rough flow chart representing the different operational phases of the distillation system is presented in Figure 4.9

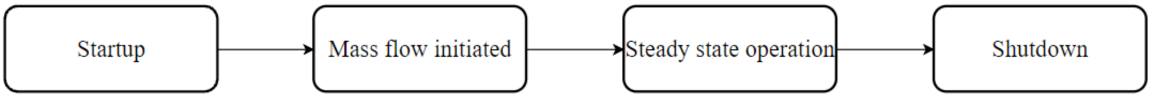


Figure 4.9. Flow chart representing the operational phases of distillation system

- The **Time and energy are the main parameters that need to be considered during the startup process, and they are highly influenced by the column specifications, thermal mass and fluctuating reboiler duty**. These parameters can be estimated by modelling the dynamic behaviour of the distillation system during startup

4.5.1 Startup model for DS system

The model can be developed using the unsteady energy equation mentioned in equation 4.6 and certain assumptions were considered for deriving these equations and they are

Assumptions

[1] The column including the reboiler and its contents were assumed to be lumped mass system and therefore they were at the same and uniform temperature.

[2] A major assumption here is that there are no significant time delays in heating the reboiler and column. The stages instantaneously heat up once the reboiler is heated and the stages follow the temperature-time response of the reboiler.

[3] The pressure inside the system was assumed to be constant. The specific heat capacity and density were assumed to be constant. The ambient temperature was also assumed to be constant

$$accumulated\ heat\ in\ the\ system = Heat\ transfered\ through\ loss + Heat\ genergated\ with\ system \tag{4.6}$$

$$\rho V c_p \frac{dT}{dt} = Q_{conv} + Q_{reboiler}$$

$$\frac{T - T_e + \frac{Q_{reboiler}}{h_c A}}{T_0 - T_e + \frac{Q_{reboiler}}{h_c A}} = e^{-\frac{h_c A}{\rho V c_p} t} \tag{4.7}$$

- The above equation represents the unsteady energy equation where the Q_{conv} denotes the heat losses through the system and $Q_{reboiler}$ indicates the total heat generated within the system and this contributes to the increasing temperature of the system. $Q_{reboiler}$ is a fluctuating energy source that varies for every time step.
- Equation 4.7 is obtained by solving equation 4.6. T represents the final steady-state reboiler temperature whereas T_0 indicates the initial reboiler temperature which is assumed to be equal to ambient temperature and the T_e represents the ambient temperature. The thermal mass specifications are mentioned in table D.1 in Appendix D.2.
- It is clear that the **startup depends on three important factors namely the thermal mass, energy losses and varying power input**. A significant amount of energy is spent for heating the thermal mass and a

certain amount of energy is lost to the environment. The energy losses can be reduced if proper insulation is provided.

4.5.2 Startup Analysis: Energy and Time

- **The final temperature of the system is estimated from equation 4.7 and it is determined for every time step and the total time required for the system to reach a steady-state is also calculated**.
- The reboiler duty was obtained from the solar PV model and for this analysis, the profile mentioned in Figure 4.8 was considered as an input to reboiler duty. The column and thermal mass specifications are mentioned in table D.1 in Appendix D.2. The assumptions necessary to calculate the startup time are mentioned below

Assumptions

[1] The convection heat transfer coefficient range of 3-25 W/m^{2}K was reported by Mills and therefore an average of 14 W/m^{2}K was assumed. The conductivity of stainless steel is assumed to be 15W/mK.

[2] The pressure inside the column was assumed to be constant at 1 bar. The specific heat capacity and density of fluid were assumed to be constant at 4146.J/kgK and 946.3kg/m^3. These values were obtained from COCO steady-state simulation. The ambient temperature was assumed to be 20°C.

[3] A major assumption was the liquid level inside the reboiler which was assumed to be 1m. Constant energy losses were considered and the same column dimensions calculated in economic analysis were used.

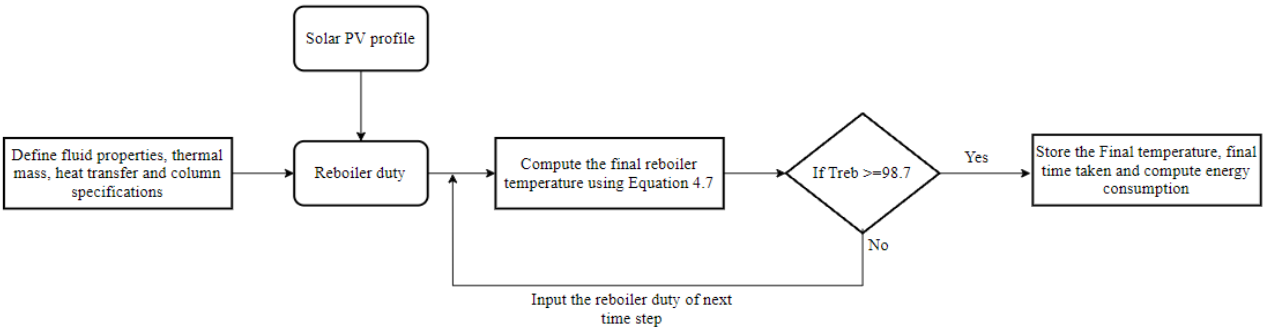


Figure 4.10. Flow chart representing the methodology to compute startup time

- As mentioned earlier, during the start-up process the column is allowed to heat up till it the column reaches the desired steady-state temperature. The temperature inside the column gradually increases with increasing reboiler duty and this trend is presented in Figure 4.11

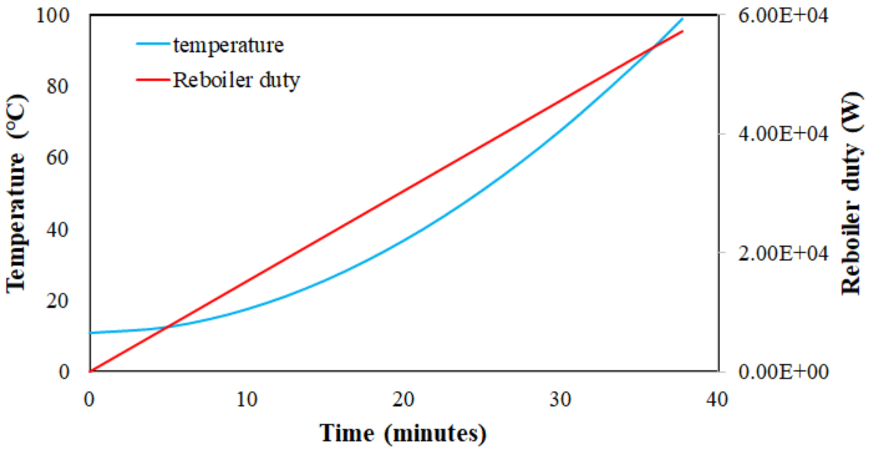


Figure 4.11. Startup time of Centralized base case distillation system for varying reboiler duty

- An important parameter related to start-up time is the time and energy fractions which are presented in Equations 4.8 and 4.9 respectively. The energy and time required for a start-up can be estimated from Figure 4.13

$$Energy\ Fraction\ = \frac{Energy\ consumed\ during\ start-up}{Total\ energy\ available\ for\ entire\ daylight\ hours\ per\ day} \tag{4.8}$$

$$Time\ fraction = \frac{Time\ consumed\ during\ start-up}{Total\ daylight\ hours\ available\ per\ day} \tag{4.9}$$

- From Figure 4.11, **the start-up time for the current model was found to be 35-40 minutes and the energy fraction was estimated to be 0.4-0.5% of total energy available per day and the time fraction was found to be between 5-6% of total daylight hours available**. An average monthly variation of energy and time fractions are presented in Appendix D.2.
- The average monthly variation of time fraction for column start-up was found to be between 4-8% and the average monthly energy fraction was found to be 0.2-0.6%
- The lower time and energy fractions indicate that the time and energy required to startup are small and therefore the steady-state can be easily achieved.

4.6 Minimum flow rate and Buffer sizing

Minimum Flow rate:

- One of the important parameters that need to be considered **is the turndown ratios of the distillation system. Turndown ratio of Distillation system is defined as the ratio of maximum to minimum vapour lo**ad and this turndown ratio varies for different column internals. The highest turndown ratio of 6 is observed in the Bubble cap tray and the lowest turndown ratio of 2 in sieve trays and packed columns [48].
- **If the feed flow rate is lower than the turndown ratio**, the vapour load reduces and hence due to insufficient vapour flow **weeping occurs** where liquid drips through the holes in plates. Therefore, the **turndown ratio is used in estimating the minimum feed flow rate of distillation systems.**
- Turndown ratios are provided for flexible operation of distillation system to cover up for the varying feed flow rates and startup and shutdown conditions. Turndown ratio plays an important role in the ZEF DS system as they highly influence the startup and shutdown of the systems.
- A minimum feed flow rate is necessary to operate the column to avoid weeping. As the temperature of 98.7°C needs to be maintained within the reboiler, a minimum reboiler duty is required for this estimated feed flow rate in order to maintain the temperature. Therefore, the column does not operate until the panel produces the necessary minimum reboiler duty. Until the panel produces the necessary output, the inlet and outlet valves are closed and the column is heated up under total reflux conditions.
- The higher the turndown ratio, the lower the feed flow rate and the lower will be the required minimum duty. Hence, the column can begin to operate at lower duty and therefore, the operating period of the distillation system is higher.
- **For our analysis, an average turndown ratio of 4 was chosen**. The selection and design of column internals are out of the scope of this thesis and therefore an average value was considered. But the selection of column internals could be research that can be carried in future. The column will be designed for steady-state feed flow rate and therefore based on this flow rate and turndown ratio, the minimum feed flow rate and reboiler duty is determined. The minimum reboiler duty is estimated from COCO.

Table 4.2. Turndown ratio of the DS system

Parameters	**Values**	**Units**
Steady-state feed flow rate	1.83E+06	g/hr
Turndown ratio	4	
Minimum feed flow rate	4.58E+05	g/hr
Minimum reboiler duty, Q_{min}	2.21E+05	W

- As mentioned earlier, a certain amount of energy and time is consumed in order to reach the steady-state temperature during the startup process. It has to be noted that apart from this startup energy and time, due to the minimum limit in duty and feed flow, additional energy and time is consumed.

Buffer sizing:

- When a control structure is implemented, the feed flow rate varies depending on the fluctuating reboiler duty and therefore, a buffer tank is necessary to store a sufficient amount of feed mixture produced by the methanol synthesis reactor. This buffer tank also serves the purpose of mitigating the effect of varying feed on the DS system.

Figure 4.12. Schematic representing the buffer tank

- The buffer tank will be placed between the MS sub-system and the control valve of the DS subsystem as shown in Figure 4.13. The high-pressure methanol-water mixture from 13500 MS reactor plants are depressurized and the mixture is stored in the buffer tank at 35°C.
- It should be noted that the buffer tank is sized in such a way that a minimum level or reserve level should be maintained so that during insufficient production, the
- For this analysis, **the feed flow rate of the mixture from the MS subsystem is assumed to be constant** and the composition inside the tank is assumed to be uniform. It is assumed that a sufficient amount of mixture is available. The sizing of the buffer is out of the scope of this thesis and so this could be a future recommendation.

4.7 Feed mass flow-Temperature Control Scheme

- **The major problem with the distillation system was that the feed mass flow rate was constant**, and the value of feed mass flow rate for the Centralized Base case is mentioned in Chapter 2. But on the other hand, **the reboiler duty fluctuated and therefore for lower reboiler duty the mass flow rate into the distillation system was very high which reduced the reboiler temperature.**
- Therefore, controlling the feed mass flow rate was found to be one of the efficient ways to control the reboiler temperature and maintain the desired purity level of top and bottom products. The controller model was developed in MATLAB and the results of this controller are presented in Chapter 5.
- The MATLAB model is a combination of the DS model and the Solar PV model. The fluctuating solar panel power was the main input to the DS model. The panel output was varying for every time step and the DS model estimated the reboiler temperature, flow rates and purities of products using the COCOImport

function. Along with this model, the control structure was also incorporated and therefore, based on the temperature and reboiler duty, the controller varied the flow rate.

- Both the DS model and the Solar PV model mentioned in Section 4.2 were used and along with this model, the control structure was incorporated. For the analysis, it was assumed that enough feed liquid is available in the buffer tank. The dynamic fluctuation of feed liquid in the buffer tank is not considered as they are out of the scope of the current thesis.

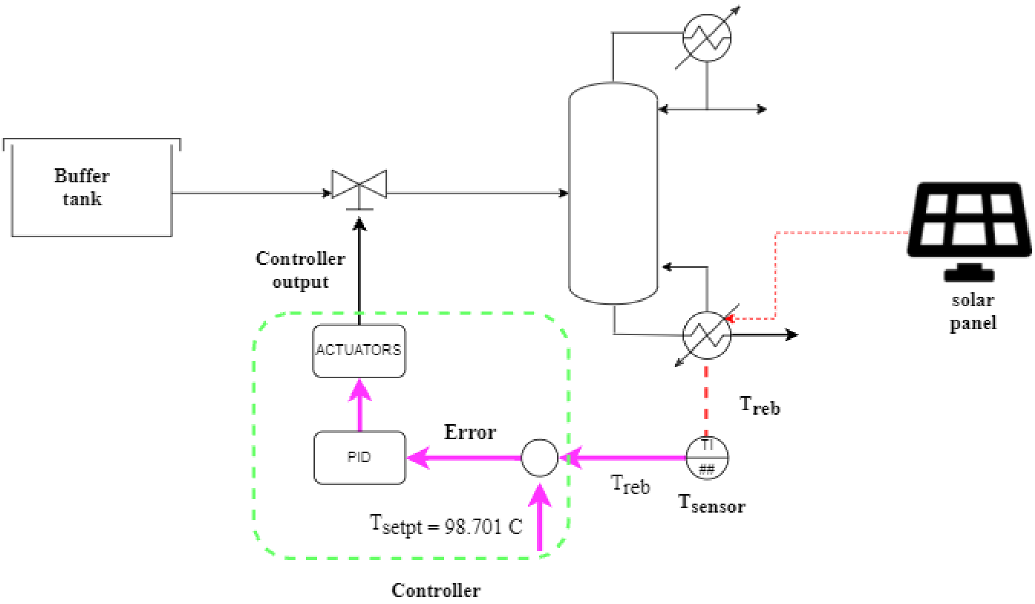


Figure 4.13. Proposed feed mass flow rate-temperature Control scheme

- Figure 4.13 presents the proposed control scheme for the centralized base case DS system. **The sensor senses the temperature of the reboiler and a set point of 98.7°C was provided which was obtained from the modelling results to maintain the purity**. The **PI controller [**Appendix D.2**] was used, and this controller does the necessary correction and adjusts the mass flow rate of the feed**.
- The controller was manually tuned and the gains are chosen in such a way that the controller response quickly to the errors and reached a stable state. The optimized gain was estimated by trial and error method where the controller gains were changed continuously until good stability and quick response was observed.

Table 4.3. PI Controlled specifications

Parameters	**Values**
Controller Action	Direct Acting
Temperature Setpoint	98.7011 °C
Proportional and integral gain	750 and 60

- The **control action of the controller is direct-acting** because if the reboiler duty decreases, the controller should reduce the feed flow rate to maintain the desired reboiler temperature. Similarly, the controller should increase the feed flow rate if the reboiler duty increases. The controller specifications are presented in Table 4.3 and the controller results are presented in Section 5.2

Chapter 5

Case Study: ZEF DS System

This chapter aims to provide the final recommended design based on the insights gathered from Chapter 3 and Chapter 4. It was concluded that a Centralized Base case system powered by Solar PV was preferred and a control scheme was required to mitigate the fluctuating ambient condition and produce products with the desired purity. Firstly, the ZEF's requirements are mentioned and later the operation criteria and the performance of the control system are presented.

.

5.1 The final design of the ZEF DS Sub-system

The following section presents the final process flow diagram of the recommended design and also describes the requirements and operating criteria of the recommended DS sub-system for ZEF. The main objective of the DS sub-system was to produce distillate methanol and bottom water product with a purity of 99.8% and 99.6% and ZEF was aiming to produce 600 g of methanol per day where the system operated for 7 hours. The methanol-water mixture with an equimolar ratio of 1:1 from the MS reactor is stored in buffer tanks at 35℃ and 1 bar. Figure 5.1 represents the process flow diagram of the DS sub-system. As concluded from the previous chapter, a control structure was incorporated with the distillation system as the DS system is powered by a fluctuating energy source which was the Solar PV.

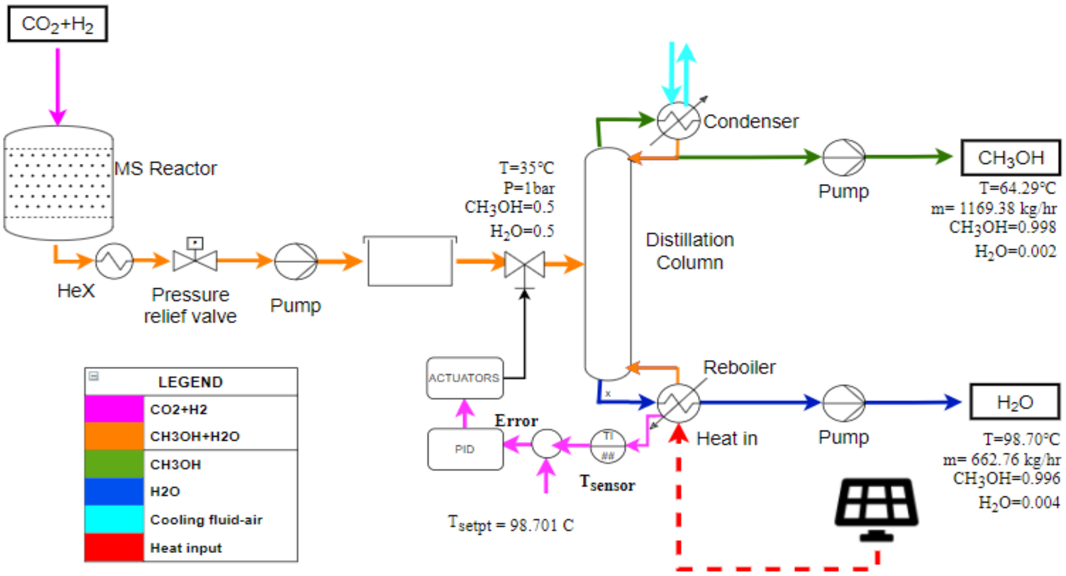


Figure 5.1. Process flow diagram of recommended ZEF system

- Based on the energy and economic analysis **a Centralized Base case system powered by solar PV was preferred** where the methanol-water mixture from 13500 plants was fed into the DS system. Therefore, a feed **flow rate of 1.83E+06 g/hr** was fed into the distillation system. It was also concluded that operating the system for 7 hours and in a high radiation region is preferred.
- In order to achieve the desired product purity, the **column operated at 1 bar and a reboiler temperature of 98.7℃** was necessary.
- The distillation system consisted of **19 stages with a total condenser and a partial reboiler**. Immersion heaters were considered for providing heat to the mixture in the reboiler. Based on the preliminary design analysis (Section 3.2.3), the distillation column with a height of 9.51m and a column diameter of 0.66m and a reboiler height of 2m was assumed.
- The sizing of the buffer tank couldn't be carried out, but this could be a future recommendation. It must be noted that detailed sizing of equipment was not carried out and all the analyses were done for the preliminary designs. An average turndown ratio of 4 was assumed.
- The control structure was implemented to maintain the reboiler temperature at 98.7℃ to mitigate the effect of fluctuating solar panel output on the end products of the DS system. The controller varies the feed mass flow rate based on the reboiler duty or power input.
- From Figure 5.4, it can **be observed that the control structure was able to maintain the desired temperature** at the reboiler. Therefore, the controller is efficient and capable of controlling the reboiler temperature and maintaining the desired purity for most operating conditions.

Operating procedure:

- Figure 5.2, presents the methodology or procedure [49] in operating the proposed Centralized Distillation system

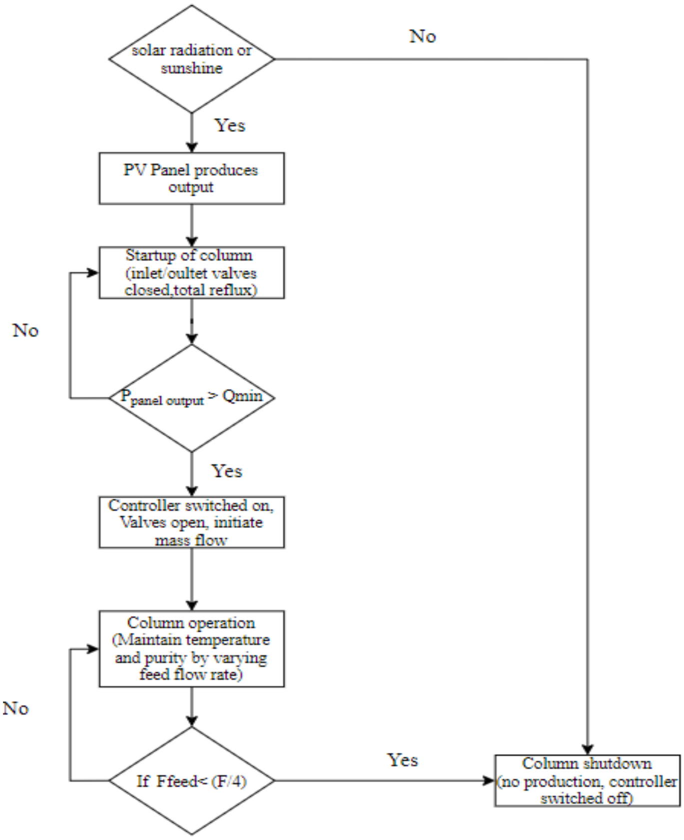


Figure 5.2. Operation procedure of DS system

[1] When solar radiation is available, the PV panel starts producing the power and until the solar radiation is available, the system is in a shutdown state and the column temperature will be equal to ambient temperature.

[2] The power produced by the solar panels are supplied to the column and a startup procedure is initiated where the inlet and outlet valves are closed, and the system is heated up till the system reaches the steady-state temperature.

[3] As mentioned earlier in Chapter 3, the column starts operating only when minimum flow rate and minimum reboiler duty [Section 4.6]is available. Until sufficient power input is available, the system is in the startup mode, and it is allowed to heat up. Total reflux is assumed during this process and therefore, the system temperature is maintained at the same steady-state temperature.

[4] It must be noted that sizing of buffer tanks was not carried out, and so the buffer tanks levels are not checked. If the volume of the mixture is insufficient, then the column does not operate till the volume inside the buffer tank reaches the reserve level. This step is neglected for this analysis.

[5] Once sufficient energy is available, the controller is switched on, and the valves are opened, and the mass flow is initiated. The column starts operating with the mixture being fed into the system at a minimum feed flow rate. It should be noted that, as the system has been total reflux before thee initiating the mass flow, the purity that we obtain after initiating the mass flow is high.

[6] The column is shut down when the feed flow rate is less than the minimum feed flow rate.

5.2 Performance of Final design

- As mentioned earlier in Section 4.7, a control structure was implemented to mitigate the influence of fluctuating solar radiation and temperature on the DS product purity. And this is done by measuring the reboiler temperature and controlling the feed flow rate based on changing reboiler duty.

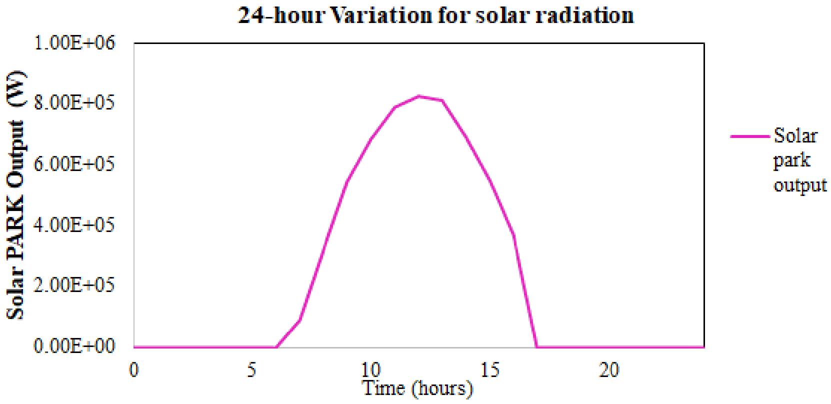


Figure 5.3. 24-hour variation of solar panel output over a day in January month for the year 2016 at Ardar, Algeria (Sahara location)

- For analysing the performance of the control structure, a solar radiation curve for a particular day in January was chosen and the plot (Figure 4.8, Figure 5.3)was already presented in Section 4.4. Based on this solar radiation data, the control structure varies the feed flow rate accordingly to maintain the reboiler temperature. Variation in reboiler temperature, feed flow rate, bottom water purity and distillate methanol purity were plotted and are presented in Figure 5.4

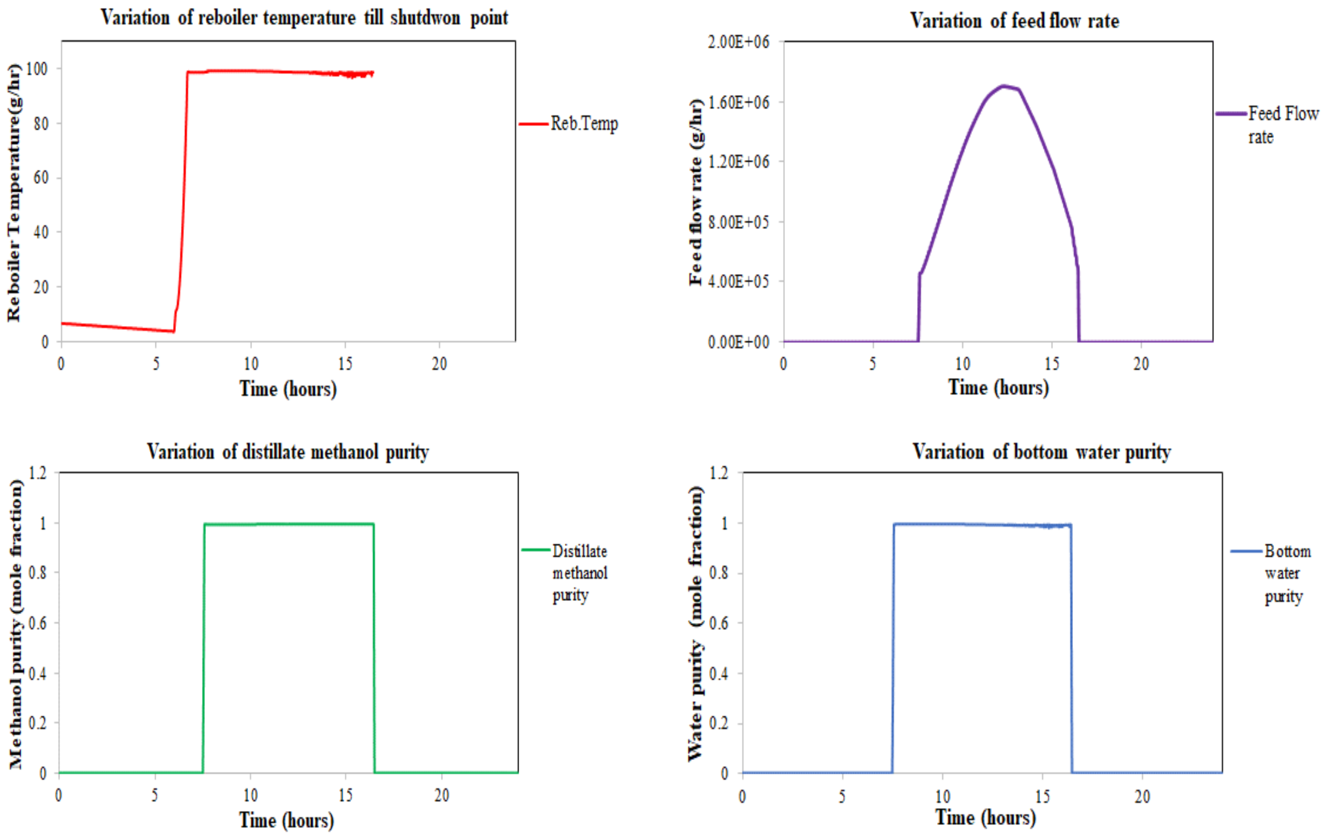


Figure 5.4. Performance of implemented control structure (a) Reboiler temperature measurement (b)Feed flow control (c)Distillate methanol purity measurement (d)Bottom water purity measurement

Reboiler Temperature:

- From Figure 5.4a, it can be observed that the controller was able to maintain the reboiler temperature by varying the feed flow rate.
- Initially, when solar radiation is not available (Figure 5.3), the column temperature is equal to the ambient temperature. When the solar radiation is available, the column is started and is allowed to heat up and reach the steady-state temperature of 98.7°C.
- The controller is started when the panel out is higher than the minimum reboiler duty and at this point, feed flow is also initiated. For E.g. The fluctuations can be observed in Figure 5.4a from time t=6 hours to t=17 hours which shows the region where the controller is operating

Feed flow rate:

- Figure 5.4b represents the feed flow control plot. We can observe that feed flow is initiated only when sufficient minimum reboiler duty is available. The minimum feed flow rate is mentioned in Table 4.2.
- It can also be observed that the feed flow control plot follows a profile similar to the solar PARK output mentioned in Figure 5.3. The feed flow rate is varied depending on the solar panel output. Due to varying reboiler duty, the reboiler temperature varies, and the controller senses this variation and tries to provide the corrected feed flow rate.
- When the flow rate is below the threshold limit which is the minimum feed flow rate, the column is shut down and the valves are closed. This can also be seen in Figure 5.4b. E.g. At time t= 16 hours, it is evident that the feed flow rate suddenly drops to 0.

Product purity:

- Figure 5.4c and Figure 5.4d represents the distillate methanol purity and bottom water purity. It can be observed that initially the purity of methanol and water is 0 and this is because during the start-up process the valves are shut down and there is no product taken out of the distillation system.
- The valves are opened only when feed flow is initiated, and we can observe that controller works efficiently in maintaining the methanol and water purity at 99.8% and 99.6%.

Conclusion:

- The proposed temperature-feed mass controller works efficiently and effectively controls the reboiler temperature at the desired level and maintains the purities of the end products.
- It can be observed that a proportion of energy is wasted during the startup and shutdown of the column and this is because of the threshold limit namely the minimum feed flow rate and minimum reboiler duty. A solution to solve this issue was proposed in the future recommendations.

Chapter 6

Conclusion and Recommendation

The major focus of this thesis work was to investigate and analyse different options (Centralized, Semi-centralized and decentralized) of implementing a fractional distillation system for separation methanol and water and heat integration was introduced as a possible energy saving technique where different models were developed and analysed based on ZEF's requirement. The main objective was to figure out a cost and energy effective design that could be implemented at the DS sub-system of ZEF. Furthermore, the impact of the dynamic environment on the DS system was also studied.

In this Chapter, some important results of the thesis and future recommendations are presented

6.1 Conclusion

Main Results

[1] **Heat integrated configurations:**

- Some of the heat integrated designs proposed based on literature for methanol-water distillation are **Feed heating systems, Vapour Recompression column, external heat integrated columns, bottom flashing, and vapour compression systems** and some of these systems are already implemented in industries.
- These systems were modelled for all three schemes based on ZEF's requirement and compared with the base case model. The energy losses weren't considered. It can be observed (fig.2.8) heat integrated systems reduced the total energy demand and different systems had different energy savings. **VRC system was found to be more efficient with an energy saving of 86.5%**.

[2] **Economic Performance:**

- The cost of the system was found to be influenced by certain factors that were related to the operating conditions of the system. From economic analysis, it was observed that operating DS system in low radiation location resulted in increased total plant cost. The 24-hour continuous operation wasn't recommended as batteries required for storing energy were found to be expensive and solar PV was preferred as an energy source due to development in technologies and reduction in the cost of PV systems.
- It was observed (fig.3.8a) that the designs from decentralized and semi-centralized were found to be more expensive than the centralized systems. For the centralized system, the **VRC design was found to be a cost-effective system**.

[3] **Energy Performance:**

- An important factor that was considered for the energy analysis are the energy losses. It can be observed (Table.C.4) that even though the heat losses per system for decentralized systems are less compared to centralized systems when the entire plant is considered, the energy losses are found to be higher for decentralized systems. Therefore, a centralized system has the least energy demand when compared to respective designs in semi-centralized and decentralized systems.
- The **centralized VRC systems were found to be energy efficient** with the highest energy saving. Both the economic and energy performances suggested the Centralized VRC systems as one of the possible designs but based on qualitative analysis (fig.4.2), a centralized base case was preferred as the risk was more for the VRC systems. VRC systems could be a potential design in near future, and one should not eliminate the VRC designs as they offer better benefits in terms of cost and energy.

[4] **Dynamic Environment:**

- **Fluctuating solar radiation results in varying PV panel output that influences the reboiler duty a**nd hence the **purity of distillate and bottom products is affected**. The panel output depends on total daylight hours, solar radiation, and panel temperature where higher radiation and daylight hours and lower panel temperature result in higher panel output
- **The start-up** of the distillation column depends on the **energy losses, thermal mass and the varying reboiler duty input to the system. The start-up process consumes time and energy.** For the proposed centralized DS system, the energy and time fraction was found to be small and therefore, the steady-state operation can be easily achieved, and a larger operation time frame is available.

[5] **Dynamic Environment:**

- The feed mass flow-temperature control was used to maintain the temperature of the reboiler in order to control the purity of distillate and bottom products at the desired level. The controller was able to maintain the purity by continuously varying the feed flow rate depending on the fluctuating reboiler duty.
- **Operating Criteria:** It should be noted that a minimum reboiler duty and flow rate is necessary to operate the distillation system. During the initial startup, the column is under total reflux condition and the column is shut down when the feed flow rate is below the threshold feed flow rate limit

6.2 Future Recommendations

- **Research the possibility of using feed flow rate as a cooling liquid for the condenser**. The current analysis was carried for the DS system in the Sahara location and air-cooled condensers were considered. Even though air-cooled condensers eliminate the need for cooling water, the cost of air condensers is high. Because of the low cooling capacity and high ambient temperature, these condensers require additional equipment such as fans to cool the overhead vapour. Therefore, the feed stream which is usually at 35℃ can be used to cool the condensers. On the other hand, the feed stream is also preheated, and this preheated stream when fed into the column reduces the sensible heat energy.

- **Investigate the possibility of recycling the bottom water product to the AEC subsystem**. Usually, the water collected at the bottom of the DS system is not utilized and is often considered a waste. As the purity of water produced is high enough, they can be recycled back to the AEC sub-system. Currently, the DAC sub-system produces CO_2 and H_2O in the ratio of 1:3 and therefore recycling the water reduces this ratio and eventually decreases the energy consumption of the DAC sub-system. This can also serve as an alternative source for the AEC subsystem during dry days in Sahara. It is important to analyse the cost of implementing the recycling systems as centralized systems require buffer tanks and larger pipings.

- **Possibility of using batteries to store energy and utilizing the energy for DS sub-system in near future**. Even though the batteries were found to be expensive (approximately 142€/kWh), implementing batteries can increase the production, total operating hours and revenue. The cost of batteries is reducing every year and in near future, it might reduce to 58 €/kWh [44].

- **Investigating the possibility of utilizing the energy lost during the shutdown of DS for other sub-systems**. A considerable amount of energy is not utilized during the shutdown of the DS system even though the solar panel produces the power during this phase. The energy can be stored in batteries or can be diverted to other sub-systems.

- **Selection and designing the column internals is necessary.** The column internal plays an important role in the startup and shutdown of the DS system. The turndown ratio is highly influenced by the type of internal chosen and therefore, selection and designing of the column are important.

- **Incorporating the effect of ambient temperature on the condenser in the DS model.** The current DS model assumes an ideal condenser when the overhead vapours are perfectly cooled to a saturated liquid. Understanding the effect of ambient temperature on condensers is important and a control structure for controlling the fan of air-cooled condensers depending on the reboiler temperature could also be implemented.

- **Sizing of the buffer tank and analysing the dynamic fluctuations in feed flow rate to buffer tank is important.** The buffer sizing could not be carried out in the current thesis and estimating the optimum size of the buffer is important. Reserve days should be taken into account while sizing the buffer as the excess amount of feed stored in the buffer can be utilized later during dry days or during insufficient production. The dynamic behaviour of buffer tanks also plays a role in the startup and shutdown of the DS system

- **Developing a control structure for Vapour Recompression Systems** and analysing the impact of dynamic fluctuations on this system is important. VRC systems are one the most important and complicated systems that involve compressors and other equipments. Therefore, understanding the dynamic behaviour of this design is cardinal.

- **More accurate methodology to estimate the cost of design**. For the current thesis, a factorial method approach that involved lang factors (accuracy: ±40% [34]) were used to estimate the cost of designs. Even though this approach was sufficient for choosing a feasible design, a more accurate method of estimating the cost by including the pump and the piping systems is recommended.

Appendix A

Appendix A: Distillation Theory

A.1 Methanol Production

Methyl Alcohol which is popularly known as Methanol or wood alcohol with a methyl and hydroxy group is a colorless, odorless, volatile, flammable, toxic and water-soluble liquid chemical with a molar mass of 32.042 g/mol and boiling and melting point of 64.7°C and -97.6°C respectively at standard conditions is easy to store and transport in liquid form. Methanol with heating value ranging from 19.66 to 22.22 MJ/kg and energy density 15.9 MJ/L and, it is most preferred fuel for long-range vehicles such as ships, trains, aviation, and heavy good vehicles. Methanex, SABIC, Eastman Chemicals, Mitsubishi Chemical are some of the leading methanol suppliers in world. Olah [50]in his paper, proposed a "Methanol Economy" where methanol is suggested as a bridge to sustainable future and a major alternative to fossil fuels.

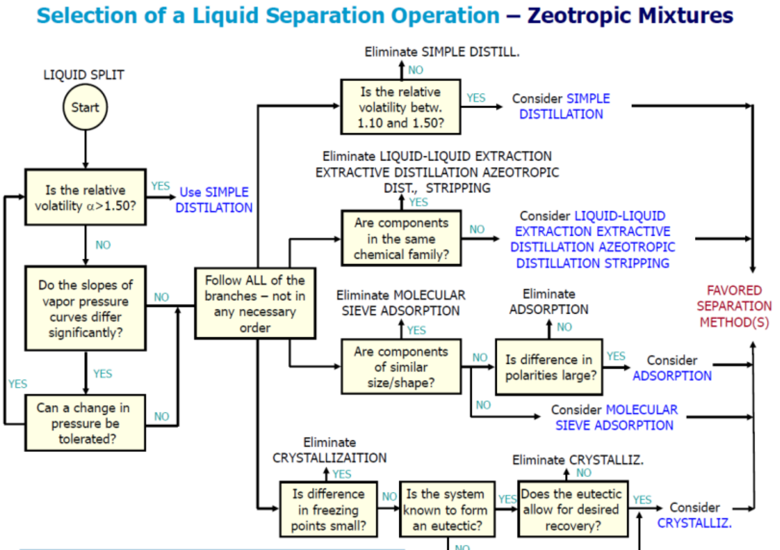
Distillation systems is a very old-fashioned technology introduced during Mesopotamian civilization in production of balms, perfumes, and medicine."Distillation" was derived from "Distillare", a Latin word which means dripping down. Methanol has been in use since the Egyptian Regime where they used a mixture which contained methanol produced from distillation in embalming process. From earlier times, methanol has been produced from non-renewable and carbon-based resources such as coal, wood, natural gas. In 17th Century, Robert Boyle proposed a "wood distillation-pyrolysis" process to produce pure methanol. In 1813, Jean Baptiste Blumenthal from France invented the continuous distillation column which became the starting point for industrial applications of distillation. Later, in 20th Century Sabatier introduced a conventional process which was patented by BASF and this process involves reaction between syngas gas produced from combustion of coal and ZnO/Cr_2O_3 catalyst that took place at very high pressure and temperature ranging between 300-400°C and 250-350 bar. Even though the process was inefficient, this method became the foundation for large-scale industrial methanol production. Numerous research and studies related to catalyst, pressure and temperature was done to make this process efficient which led to developments in the production process. ICI developed the "Low Pressure Methanol" process by reducing the pressure and temperature to 120 bar and 300°C and replaced traditional ZnO/Cr_2O_3 catalyst with chromium, zinc and copper catalyst which resulted in higher production of methanol. Further improvements were made by Lurgi where the design temperature and pressure were further reduced to 230-250°C and 40-50 bar respectively[51]. Lurgi was comparatively expensive than ICI, but the conversion rates and catalyst life was higher. Later, CAMERE process or two methanol synthesis process was developed which was more cost efficient. Presently, catalysts with magnesium, zinc, copper, and aluminum are being used.

In a conventional methanol production process, an important component is the syngas which generated by combustion of fossil fuels such as coal or natural gas. But this contributed to global greenhouse gas emissions and therefore an alternative “green” process which involves production of hydrogen from renewable energy sources and carbon dioxide from Carbon capture technology were developed. Studies from literature [15]shows that there are different methods to produce methanol and out of which the Two-step methanol synthesis method and direct methanol synthesis was predominantly used. Both the methods were almost similar to each other, but the only difference was in former method, Carbon dioxide and hydrogen were used to produce CO through reverse water gas shift. Later this CO was utilized to produce methanol by addition of excess hydrogen into the second reactor. This method gives higher yield of methanol where optimal productivity is achieved at 50-100 bar and 200-300 ^{o}C. In the second method, carbon dioxide and hydrogen were directly injected in ratio of 1:3 to produce methanol and other by-products. The advantage of later method was its comparatively more economical. Mitsui and RITE, CRI, MefCO2 are some of the existing green methanol plants that use CO_2 and H2.

Table A.1. Advantages and disadvantages of methanol

Pros	Cons
• The major advantage of using methanol in transportation sector is that shifting from diesel engines to methanol engines are economical and has less investment cost when compared to LNG [52]	• Energy consumption in production of green methanol is larger than hydrogen production process as it requires CCS technology and production is expensive due to high investment cost
• It’s a clean burning fuel with lower NOx, SOx and other particulate emissions, , less explosive than gasoline, easier to handle, high specific energy and better flame speed, high octane number and so it is preferred green combustion fuel [3]	• The specific energy is comparatively lower than diesel and gasoline, the flames are undetectable, and less heat is produced [50]
• Easier to store and transport as liquid in standard conditions, easier controllability during leakage and less environmental impact	• Toxic and corrosive with aluminum and mild carbon steels

A.2 Classification of Liquid Separation



Barnicki and Fair, Ind. Eng. Chem. Res. 1990;29:421-432.

Figure A.1. Schematic of selection chart for liquid separation systems

A.3 Distillation Column Basics

This section provides a clear overview of the methanol-water separation process and explains the fundamentals and principles pertinent to Distillation system. Thermodynamics, vapor-liquid equilibrium, and the energy requirements are also described.

The distillation columns are energy intensive technologies where the energy required for vaporization is provided in the form of thermal energy. The separation is usually by vaporization and subsequent condensation where the vapor flows up the column and liquid flows down due to gravity and therefore due to this counter flow, heat and mass transfer takes place in the stages. **Fig. 1.2** represents the conventional multi-stage distillation, and its important characteristics are clearly explained below

Feed: The feed which is a mixture of different components is fed into the distillation column at specific stage and this stage is known as the feed stage. The feed stage divides the distillation column into two sections: Rectifying section and Stripping section. The feed stage location plays an important role in separation of liquid mixture and affects the column specifications and the energy consumption. Optimum feed stage location results in minimum energy consumption, reduced number of stages and high purity products. The feed phase conditions can range from subcooled liquid to superheated vapor. A distillation column can have multiple feed, side and product streams.

Stripping Section: The stripping section corresponds to the stages below the feed stage where more volatile components are stripped from liquid mixture. The liquid mixture is partly heated in the partial reboiler to boiling temperature and due to difference in boiling point temperature, more volatile compounds or light key compounds (LK) vaporizes and these vapors flow to top of the column. Thermosiphon, kettle and forced circulation are three different types of reboiler available.]. The less volatile component or heavy key component (HK) with high boiling point which is always in a liquid state are collected as bottom products. The ratio between flow rate of vapor returned to the column and the liquid flow rate of bottom product is defined as the boil-up ratio.

$$\text{Boil}-\text{up ratio}, V_B = \frac{\text{Vapor flow returned to column}}{\text{Bottom product flow}} = \frac{V}{B} \qquad (A.1)$$

Rectifying Section: This section represents the stages above the feed stage and a reflux drum and total condenser with reflux is available at the top of this section. The vapor which are richer in more volatile components flows through the total condenser where it condenses completely to liquid. A part of the liquid is reflexed back into the column and remaining liquid is extracted as a distillate or top product. The distillate can be liquid, vapor or both. Condensers are of 3 types-total, partial and mixed condensers. The reflux ratio amount of liquid returned to column as reflux to the amount of distillate obtained as top product. Both the reflux and the boil-up ratio necessary to improve the purity of top and bottom products. Purity of products can be increased by increasing the reflux and boil-up ratio or by increasing the number of stages in the column. The minimum number of stages and maximum reflux can be obtained from total reflux condition. Here the top product and feed flow is assumed to be zero whereas the minimum reflux is obtained by assuming infinite number of stages. Therefore, the optimum reflux ratio lies between these ranges and hence the optimum reflux is assumed to be between 1.1 to 1.3 times the minimum reflux ratio.

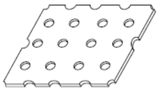
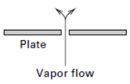
$$\text{Reflux ratio}, R_D = \frac{\text{Liquid flow returned to column}}{\text{Top product flow}} = \frac{L}{D} \qquad (A.2)$$

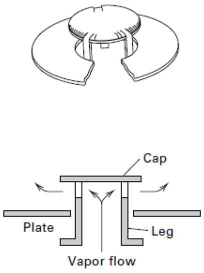
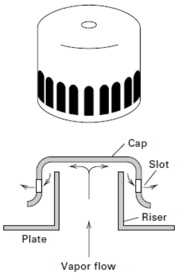
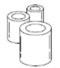
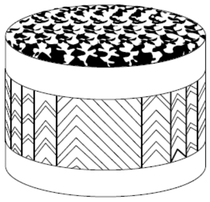
Column internals: Column internals are one of the deciding factors of separation in distillation column and play a very crucial role in heat and mass transfer between liquid and vapor inside the column. Trays or packings, distributors, weirs and downcomers, contactors, baffles, etc. are few parts of internals and these internals are placed inside a cylindrical and vertical pressure vessel. Based on type of internals, column can majorly be classified into Trayed columns, packed columns, spray towers, bubble column and centrifugal contactors

Trayed Column consists series of trays or plates or stages with small openings in order to facilitate the heat and mass transfer between vapor and liquid. Liquid gets accumulated and flows across the plate whereas hot vapor passes through the liquid on plate in counter direction via the small openings thereby transferring heat and mass to cold liquid through convection and diffusion. Due to gravitational force, the liquid flows down the downcomer to the next stage. In trayed columns, three different regimes [4] can be identified and they are Froth, Spray and Bubble regime . In froth regime, vapor passes through the continuous liquid phase in the form of very small bubbles, and this is the most preferred regime. Spray regime occurs when vapor flow rate is high and liquid flow rate is very less whereas bubble regime occurs when the vapor flow rates are low. Large bubbles arising through passive liquid are attributes of bubble regime. Major advantage of trayed columns are the vapor-liquid equilibrium achieved at each stage whereas Occlusion, weeping and entrainment are some of the drawbacks, but they are neglected for ideal cases. The small openings in trays can be of three different types. Sieve or perforated trays are trays with small holes or perforations and the hole size can be varied depending on the requirement. The pressure drop, plate efficiency and cost are minimum, and this reduction of efficiency are mainly due to large vapor flow rates and weeping. Valve trays are like sieve trays, but the hole sizes are larger and are each hole is equipped with liftable flaps. These flaps lifts when vapor flows through the holes and prevents weeping. There is a significant pressure drop, the plate efficiency is higher and can operate at lower vapor flow rates. Bubble-Cap trays are trays with caps and each cap has a rectangular or triangular slot on its sides through which vapor escapes. Even though these trays are expensive, they offer high pressure drop, high vapor flow rate and high efficiency but problems such as fouling, corrosion can occur.

Packed Column: These types of columns consist of packings arranged in random order (random packing) or structured, arranged and stacked (Structured packing) inside the cylindrical pressure vessel. These types of columns are mostly preferred for liquid-liquid extraction, gas absorption and sometimes distillation. The liquid due to gravity flows down between these packings whereas vapor flows upwards. The major advantage of these columns is the contact surface area are larger compared to tray packing and therefore effective mass transfer takes place. A gas injection support plate and hold down place are used for holding these packings and ensures proper and uniform liquid distribution Metal, ceramic and plastic are the commonly used materials for packings and these packings are of different sizes. For structured packing, honeycomb structured extrusions or embossing made from metallic or plastic materials. Packings are quite expensive but the pressure dop ranges from very low to moderate and efficiency is very high for structured packings. **Table A.2** gives different types of internals used for both packed and trayed column

Table A.2. Comparison of between Types of trays and packings

Schematic	Tray/Packed column	Relative cost	Pressure drop	Plate efficiency	Vapor Capacity	Cleaning
  	Sieve tray	Very Low	Low	Low	High	+

	Valve tray	Moderate	Moderate	High	High	-
	Bubble-cap tray	High	High	High	Low	-
 Ceramic Raschig rings  Ceramic Berl saddle  Metal Intalox® IMTP  Metal Pall® ring  Metal Fleximax®  Metal Cascade Mini-ring® (CMR)	Random packing	Moderate	Low	High	High	-
	Structured Packing	Very high	Very Low	Very High	High	-

A.4 Thermodynamics of Distillation System

Importance of thermodynamics in separation process is significant and this is the factor which decides the phase equilibrium, activity, energy, design and sizing of equipment. In this chapter, basic thermodynamic principles and their applications in distillation are briefly discussed below

Phases and its Equilibrium:

Pure substances are substance with fixed and uniform chemical composition that are homogenous throughout, and they can exist in different phases. Phases are defined as distinctive form of matter characterized by uniform chemical and physical properties. Notably there are different phases of matter which are solid, liquid, gases, plasma,etc. and each have their own characteristics. Depending upon variation in external conditions such as pressure, temperature, etc., a qualitative change will be observed in properties of system and system changes from one phase to another which is called phase transition or phase change. For example, the phase transition of liquid to vapor due heating to boiling point. In a system where phase transition occurs, an equilibrium is always reached. A system is said to be at equilibrium if all physical properties remain unchanged with time and the interactions are zero. Equilibrium represents stability. Thermal, mechanical, chemical and phase equilibrium which corresponds to temperature, pressure, chemical potential and phase remaining constant throughout the system and together they form the thermodynamic equilibrium The criterion for equilibrium are presented in Equation 2.1

[53]

Properties of pure substances and mixtures, VLE Gibbs and its behavior can be described by Equation of state which relates pressure, temperature, and volume. Various EOS are available, and the most suited EOS are briefly discussed in later half of this section. Gibbs phase rule helps in determining the total independent intensive properties required to define the state of system. C corresponds to number of components present and P denotes the number of phases .For Binary mixture with two phases and two components, the degree of freedom is 2 and therefore you need 2 properties (Eg: pressure and temperature) to find the state of system.

$$Gibbs\ Phase\ rule\colon F = C - P + 2 \tag{A.3}$$

Distribution coefficient and Relative volatility for Ideal and non-ideal mixtures:

Distribution coefficient: It is defined as the ratio of vapor composition of component i to liquid composition of component I This factor gives details about the phase of component at a particular temperature and pressure. If $K_i > 1$, then i component is in vapor phase and if $K_i < 1$, then i component is in liquid phase

$$K_i = \frac{\text{vapor composition of i component}}{\text{liquid composition of i component}} = \frac{y_i}{x_i} \tag{A.4}$$

Relative Volatility: Volatility means how fast a liquid evaporates into vapor phase. Relative volatility represents the differences in volatilities of two components and for a binary mixture it is defined as the ratio of distribution coefficients of both component i and component j. Relative volatility gives a measure of quality of separationHigher the relative volatility, better and easier will be the separation of components.

$$\alpha_{i,j} = \frac{\left({}^{y_i}/_{x_i}\right)}{{}^{y_j}/_{x_j}} = \frac{K_i}{K_j} \tag{A.5}$$

$For\ binary\ mixtures,\ x_i = x\ ;\ x_j = 1 - x\ ;\ \ y_i = y\ ;\ y_j = 1 - y$, therefore, equation can be rewritten as

$$y = \frac{\alpha_{i,j} x}{1 + \left(\alpha_{i,j} - 1\right) x} \tag{A.6}$$

Vapor pressure: Vapor pressure is the pressure exerted by vapor particles present above the liquid on the surface liquid at any given temperature and pressure. It usually depends on the temperature and composition of components at equilibrium. If vapor pressure is higher than external pressure, then the liquid boils. Saturated pressure of pure or single component can be estimated using the Clausius-Clapeyron relation and Antoine equation

$$Clausius - Clapeyron\ equation,\qquad \frac{dln\ P^{sat}}{dT} = \frac{\Delta\ h_{LV}}{RT^2} \tag{A.7}$$

$$Antoine\ equation,\quad ln\ P^{sat} = A - \frac{B}{T} \tag{A.8}$$

Where A,B are Antoine coefficients of particular component which can be obtained from literature [54]

Raoult’s Law for Ideal and non-ideal mixtures:

Ideal Mixtures:

Dalton's Law: Dalton's law for mixture of ideal gases, states that the total pressure exerted by non-reacting gases are equal to sum of partial vapor pressure of each gas. This law only deals with partial pressure of gases.

$$P_{total} = \sum_{i=1}^{N} P_i^{vap} \quad where\ Partial\ pressure\ of\ component\ i, P_i^{vap} = P_{total}\ y_i \tag{A.9}$$

$$For\ binary\ mixture, N = 2$$

Raoult's Law: Raoult's Law deals with vapor pressure of ideal liquid mixture. It states that the partial pressure of components in vapor phase is directly proportional to mole fraction of particular component in liquid phase. This can be explained with a single component liquid mixture in a system. The pressure exerted by vapor particles of component [23]

$$P_i^{vap} = P_i^{sat} x_i \tag{A.10}$$

It has to be noted that three different pressures are mentioned in above equation. P_i^{vap} represents the partial vapor pressure of component i, P_{total} denotes the total vapor pressure of a system and P_i^{sat} relates to the saturation vapor pressure of pure component. Both the above relations are combined in order to generate the equation for VLE

$$y_i P_{total} = x_i P_i^{sat} \tag{A.11}$$

$$which\ can\ be\ rewritten\ as\ K_i = \frac{y_i}{x_j} = \frac{P_i^{sat}}{P_{total\,j}}$$

Non-Ideal Mixtures:

An important assumption for ideal mixtures is that$\Delta\, H_{mix} = 0\ and\ \Delta\, V_{mix} = 0$. The fluid which is fed into Distillation Column is methanol-water mixture which is a non-electrolyte, miscible and high non-ideal mixture. Both methanol and water are polar compounds and due to this reason, whenever they are mixed together, their total volume will not be equal to sum of individual volume[3]. Methanol, a polar compound with two unpaired electrons on oxygen site , usually forms hydrogen bonding with water and due to this intermolecular forces are weaker than intramolecular forces. Therefore, methanol or water in aqueous mixture will easily escape due this weaker bond whereas in pure mixture it is difficult due to stronger intramolecular bond. This results in increased vapor pressure and causes a positive deviation from ideal Raoult's Law [23] .This can be addressed by introducing fugacity and activity coefficients in ideal Raoult's Law.

Modified Raoult's Law

Fugacity is often referred as the "effective partial pressure or the corrected pressure of real gas". It can also be defined as the "escaping tendency of real gas". It measures the deviation of real gas by taking attraction and repulsion between real gas particles into account.

$$f_i = \varnothing_i P_i^{vap} \tag{A.12}$$

Where $\varnothing\ denotes\ the\ fugacity\ coefficient;\ \varnothing = 1\ for\ ideal\ gas\ and\ \varnothing = \varnothing_i\ for\ real\ gases$

Therefore, for liquid-vapor mixture, the thermodynamic equilibrium will also include the fugacity in liquid and vapor phases which is called the iso-fugacity condition

$$f^L{}_i = f^V{}_i \tag{A.13}$$

$$\varnothing^L{}_i P_i^{vap} = \varnothing^V{}_i P_i^{vap} \tag{A.14}$$

$$x_i \gamma_i P_i = y_i \varnothing^V{}_i P_{total} \tag{A.15}$$

For liquid phases, it is difficult to estimate the escaping tendency and therefore another parameter called the activity and activity coefficient. Activity is a dimensionless quantity which is ratio of fugacity of component at particular condition to fugacity of same component in pure state. It can be defined as an "effective concentration" of component in that mixture. Activity coefficient measures the deviation of solution from ideal solution.

$$\gamma_i = \frac{a_i}{x_i} = \frac{f_i}{x_i f_i{}^o} \tag{A.16}$$

$$Pontying\ Correction\ factor, f_i{}^o = P_{i,vap}^{sat} \varnothing_i exp \int_{P_{i,vap}^{sat}}^{P} \frac{V^L{}_i}{RT} dP$$

For low to moderate pressure, $f_i{}^o = P_{i,vap}^{sat}$ where $P_{i,vap}^{sat}$ $is\ the\ saturated\ vapor\ pressure\ of\ component\ i.$ When this is substituted in equation 2.13, we get the modified Raoult's Law which is VLE relation for non-ideal mixtures

$$y_i P_{total} = \gamma_i\ x_i\ P_{i,vap}^{sat} \tag{A.17}$$

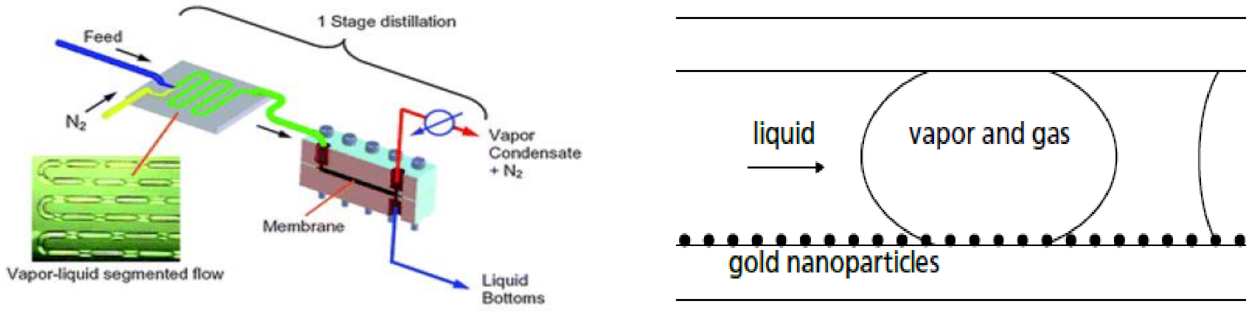
$$which\ can\ be\ rewritten\ as\ K_i\ = \frac{y_i}{x_j} = \frac{\gamma_i\ P_{i,vap}^{sat}}{P_{total\,j}}$$

Activity coefficients depend on the temperature and composition of component i. Activity coefficients are generally evaluated from theoretical formulas provided in numerous literatures and these relations are mentioned in the next section.

A.5 Micro-Distillation Systems and its Classifications

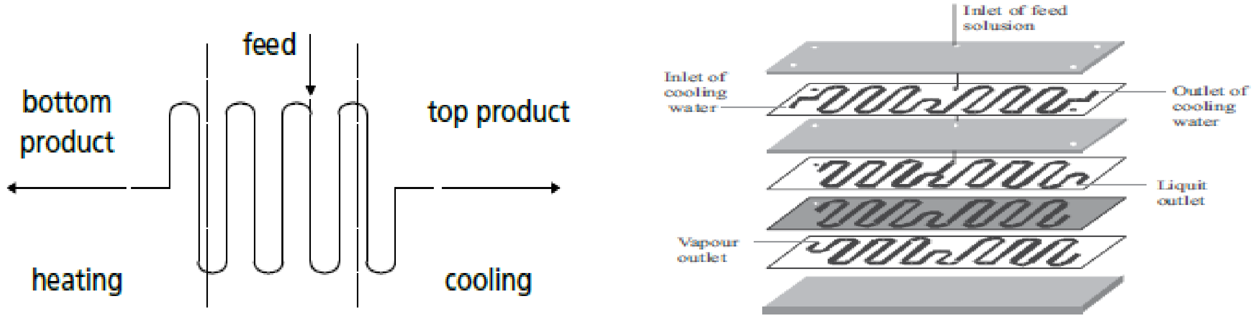
Wootton and DeMello [55] first proposed the microdistillation with segmented flow where a feed mixture along with carrier gases (noble gas-Helium) which acts as a phase contactor, is fed into a microchannel with membrane to separate vapors. Due to differences in partial vapor pressures of components in mixture, vapor and liquid phases are separated at the end of the channel. Hartman et.al used the same principle and selected nitrogen as a gas carrier to separate methanol-toluene and dichloromethane-toluene mixtures at 70°C. Even though high purities were achieved, the cost was higher, and designing was difficult. In bubble assisted distillation column, walls with gold nanoparticles were heated through laser to vaporize the liquid fed on one side and the vapor condenses on other side

Micro-channel distillation introduced by Zheng et.al consists of channels which are heated at one end and cooled on the other end and feed is introduced at the different positions of channel. Due to varying temperature along the channel., more volatile components get collected at cooler end and less volatile at hotter end. Lam et al. introduced reflux system using capillary force principle and changed the shape of micro channel from zigzag to serpentine shape to improve performance. Methanol-toluene and acetone water mixtures were tested. Zhang et.al [25]investigated the membrane distillation which uses PTFE membrane for separation of vapor and liquid phases. The system consists of various layers with micro channels fabricated in it and it has stripping and rectifying zones. Heat is supplied through a hot plate place at the bottom of distillation and cooling water flows through channel in top layer. Due to heating vapor forms and permeates through membrane. Partially condensed vapor is extracted at rectifying section through vacuum pump. Fluid used here was methanol-water mixture. Ziogas et al. [56] replicated industrial rectifying distillation column at a microscale with sieve trays Driving forces were both gravity and capillary forces. Various binary mixtures were experimented and distillates with significant purity was achieved. Rotating spiral microchannel was invented by MacInnes et al. where the separation of phases is due to centrifugal forces. Feed enters the channel at the center with channel rotating at high speed and by increasing temperature and pressure along the channel, vapor and liquid phases gets separated and flows in counter direction. The disadvantage with rotating and membrane distillation is the efficiency and lower throughputs



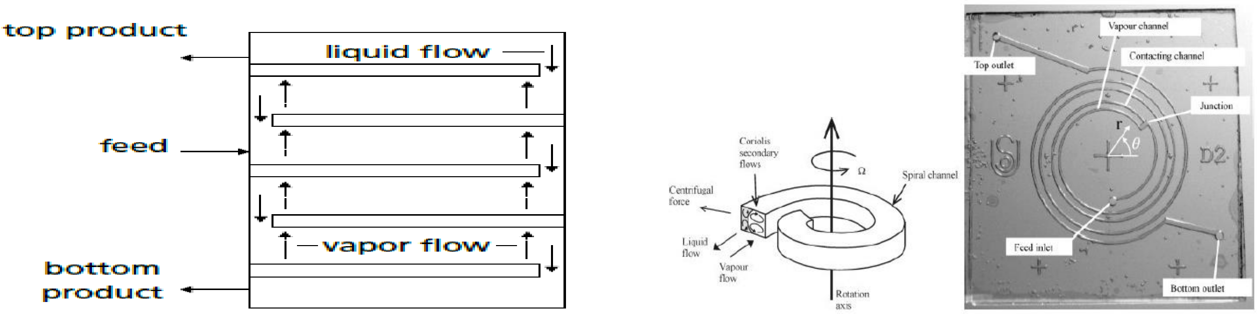
(a) Segmented flow microdistillation

(b) Bubble assisted Distillation



(c) Microchannel distillation

(d) Membrane distillation



(e) Micro-rectification with sieve trays

(f) Rotating spiral distillation

Figure A.2. Micro-Distillation types

A.6 ZEF microdistillation developments

Figure A.3 . (a) ZEF prototype 1[57] (b) ZEF prototype 2-improved version [58]

ZEF’s DS prototype 1: The design by Seok and Hwang became the basis for the first version of the ZEF distillation system. Few design changes were made to ZEF’s distillation system [57]. The feed inlet was positioned directly above the hot end and Sorbo absorber cloth was used as a wick instead of fibreglass material. The adiabatic section was made from polycarbonate due to their high chemical resistance against methanol and good thermal insulation which can be easily machined, and copper joints were used. The separation results were unsatisfactory where the purity of distillate was 77.37% and to improve this the outlet tube length at the hot end was increased. Unfortunately, the system failed due to cracks observed in the polycarbonate tube and distillate was heavily contaminated after long hours of experimentation.

ZEF’s DS prototype 2: A major improvement to the previous version was that the entire system was made from copper thereby replacing the polycarbonate tubes [58] The feed inlet position was shifted to the middle but closer to the hot end which was similar Seok and Hwang’s design. The hot and cold ends were bent slightly mainly to hold more products at the ends and to easily collect samples. To improve the recirculation of vapours and liquids, heaters were placed closer to the outlet valve on the hot side. Methanol purity of 90.58% was achieved. The design was further upgraded by adding buffer storage tanks at hot and cold sides to increase mass transfer. This is done by evaporating a small amount of liquid stored in the tank, before collection of the sample. This increased the methanol purity to 95.77% but the system did not produce enough water after some time. This was because the level of methanol at the hot end was less than the level of water at the cold end and therefore a large amount of water was reflux back to the reboiler

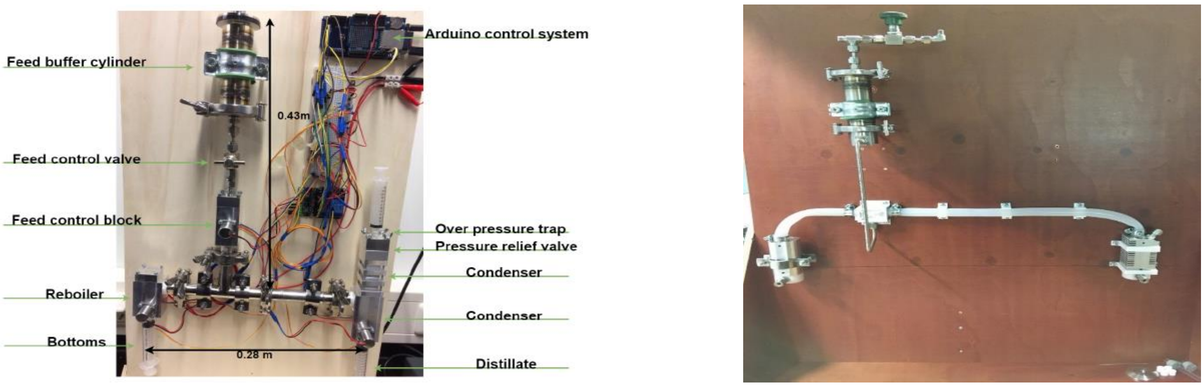


Figure A.4 (a) ZEF prototype 3[11] (b) ZEF prototype 3-improved version [59]

ZEF's DS prototype 3: Some of the problems faced in the previous version were the energy losses, capillary effect of wick was limited, and less yield was produced. The energy losses were due to the copper body which was a good conductor of heat and therefore the condenser and reboiler material were replaced by aluminium which is less conductive than copper. Stainless steel was chosen for the adiabatic section to reduce heat losses. Four different wicks namely Paper wick, Kevlar coated fibreglass wick, synthetic chamois material and microfiber wicks were tested, and Kevlar coated fibreglass wick was chosen as the most suitable material [11, 59]as they offer high capillary flow long lifetime but expensive. The feed was pre-heated and proper insulation was provided to improve efficiency. Continuous experiments were conducted to determine the purity and duty of the DS system. Dylan reported a purity of 93% for distillate and 97% for the bottom product with total production of 200g of methanol per day. The reboiler and condenser temperature were found to be at 95℃ and 65℃ with a feed flow rate of 43.35 g/hr. Even though the reboiler duty was 37.4 W, the heat losses were comparatively less than the previous version. To further improve the purity, he varied different parameters such as feed flow rate, the orientation of the system, heater duty, length of the system. and modelled it in COCO. It was concluded that the purity can be improved by increasing the reboiler temperature, tilting the system, increasing the feed flow rate, proper insulation and optimum length. Nelson and Nick [60] improved the current by making a small of replacing aluminium tubes with silicon tubes which reduced the energy losses. High purity methanol of 99.9% was achieved at a heating temperature of 115℃ and tilting angle of 10º. Information on reboiler duty is not provided but it was expected to be around 50W due to increased reboiler temperature.

Appendix B

Appendix B: Distillation Design and Modelling

B.1 Methanol-Water Feed Flow Rate Calculation

Parameters		CO_2	+	$3H_2$	$\leftrightarrow$	CH_3OH	+	H_2O
ZEF Requirement		600 g/day CH_3OH; 7 hour operation period						
Molecular Weight	[g/mol]	44	+	2		32.04	+	18.02
m	[mol/plant.day]	18.75	+	56.25		18.75	+	18.75
m	[g/plant.day]	825.0	+	112.5		600	+	337.5
m	[g/plant.hour]	117.86	+	16.07		133.93		

From the above hydrogenation equation, we know that 1 mole of CO_2 is required to produce 1 mole of CH_3OH and 1 mole of H_2O. The total methanol production target set by ZEF was approximately around 600g / day and the total operating hours of the plant was 7 hours/day. Therefore, the total number of moles of methanol was around 18.75 moles. Since the molar ratio of methanol and water are 1:1, the total moles of water required was 18.75 moles. The molecular weight for methanol and water was 32.04 g/mol and 18.02 g/mol (NIST)From these data the total mass flow rate for a 7hour period was found to be 937.45 g which corresponds to 133.93 g/hr.

B.2 Modelling of Distillation Systems

Modelling helps us to have a comprehensive understanding of the Distillation system. Vital parameters like flow rate, temperature, number of stages, etc. are required for designing a Distillation system. Mathematical models help in estimating these vital parameters that are difficult to measure and figuring out the failures and performance of DS. Kenig and Blagov classified the modelling of distillation into two methods: Equilibrium based and non-equilibrium based. The distillation column is assumed to be operating at equilibrium conditions and therefore non-equilibrium-based approach will not be further discussed. Fig.B.1 presents the complete classification of modelling methods and each equilibrium-based method are clearly explained below.

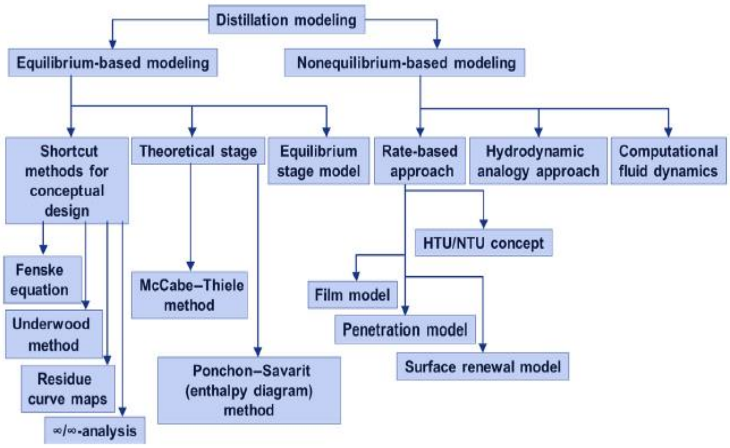
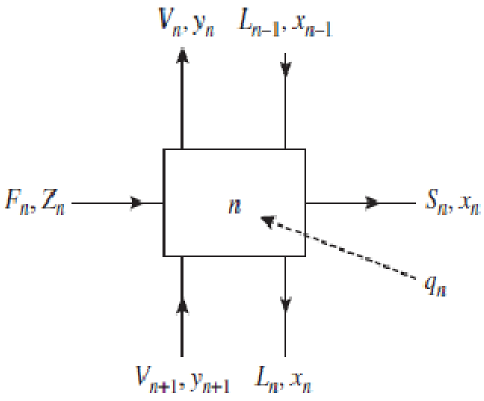


Figure B.1. Distillation Column Modelling classification chart

Equilibrium Based Modelling

This is the most preferred method for binary distillation systems. In this modelling method, a thermodynamic equilibrium between contacting phases is always achieved at each stage of the distillation column and another assumption is that there are no chemical reactions taking place at equilibrium conditions. Occlusion, Entrainment is assumed to be negligible. The temperature and pressure in each stage of distillation are assumed to be constant to stay in equilibrium and mass transfer kinetics and fluid dynamics are not considered in this approach This approach can be further classified into three methods: Equilibrium stage model, Theoretical Stage model and shortcut method.

Equilibrium Stage Model Method: As the name suggests, each stage of the column are at equilibrium. Vapour-liquid equilibrium is achieved between the liquid that flows to the below stage and the vapour that flows to the above stage. The flows are assumed to be completely mixed, in steady-state and there is no accumulation in trays. In this method, modelling of the distillation column is done by using mass and energy balance equations called “MESH equations”. A schematic of an equilibrium stage with inlet and outlet flows from stage n is presented in below figure.



n = Any stage from top of column
$n\text{-}1$ = stage above "n^{th}" stage
$n+1$ = stage below "n^{th}" stage

L_{n-1} = Liquid flow rate into stage n from stage $n\text{-}1$
L_n = Liquid flow rate into stage $n+1$ from stage n
V_{n+1} = Liquid flow rate into stage n from stage $n+1$
V_n = Liquid flow rate into stage $n\text{-}1$ from stage n
F_n = Feed flow rate at "n^{th}" stage
S_n = Side stream flow rate from "n^{th}" stage

x = Liquid mole fraction of component i from $n, n+1, n$-1 stage
y = Vapor mole fraction of component i from $n, n+1, n$-1 stage
z = mole fraction (mixed) of component i feed

q_n = Heat transfer in or out of stage n
H = Specific enthalpy in vapor phase
h = Specific enthalpy in Liquid phase
h_f = Specific enthalpy in Feed

Mass or material balance (M):

Inlet Flow =Outlet Flow

$$(F_n z_n) + (L_{n-1} x_{n-1}) + (V_{n+1} y_{n+1}) = (S_n x_n) + (L_n x_n) + (V_n y_n) \qquad \text{(B.1)}$$

Vapour-Liquid Equilibrium (E):

$$Distribution\ coefficient: \quad y_{i,n} = K\, x_{i,n} \rightarrow y_{i,n} - K\, x_{i,n} = 0 \qquad \text{(B.2)}$$

Summation Equation (S):

$$\sum y_{i,n} = \sum K x_{i,n} = 1 \qquad \text{(B.3)}$$
$$\sum x_{i,n} = \sum \frac{y_{i,n}}{K} = 1$$

Energy balance or Enthalpy balance (H):

The energy of inlet flow-stream = Energy of outlet flow-stream

$$(F_n h_f) + (L_{n-1} h_{n-1}) + (V_{n+1} H) \pm (q_n) = (S_n h_n) + (L_n h_n) + (V_n H) \qquad \text{(B.4)}$$

The above mentioned" MESH equations" are for a specific stage and these equations can be replicated for other stages including total condenser and partial reboiler. These equations help us in determining the stage flow rates, temperature, enthalpy, stage composition, bubble point, dew point, etc at each stage of a column. These equations serve as the foundation for rigorous methods in simulation software such as ASPEN and COCO where many equations are solved simultaneously and iteratively. Initial estimates such as the number of stages, feed compositions, location and temperature or final product purity should be known for solving equations and these estimates can be obtained from the shortcut and theoretical method.

McCabe Thiele Method: This is a simple graphical method for binary distillation systems which are primarily used for determining parameters such as feed location, number of stages, reflux, and boil-up ratio. The method depends completely on two equations: Total column mass balance and VLE-equilibrium curve (Refer Section 2.3.3) Some basic assumptions for McCabe Thiele method are the mixture should be binary, constant column pressure, both liquid and vapour entering and leaving the trays are at equilibrium, an equal heat of vaporization where for every mole of liquid vaporized, one mole of the vapour condenses, and heat effects are assumed to be negligible. VLE Equilibrium curve, Feed compositions, location and temperature and final product purity are initial information necessary to plot the graph. An example is presented below in Fig.2.11

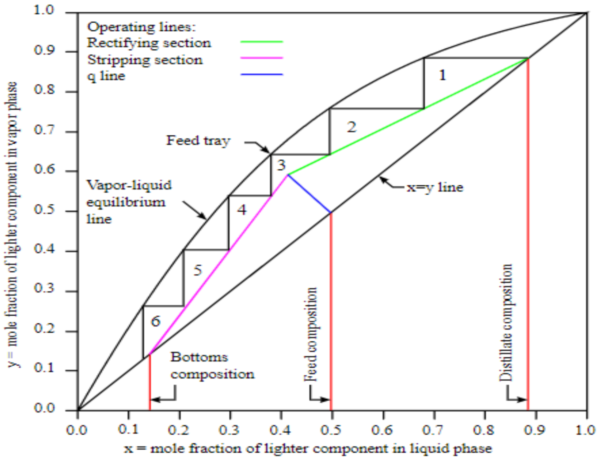


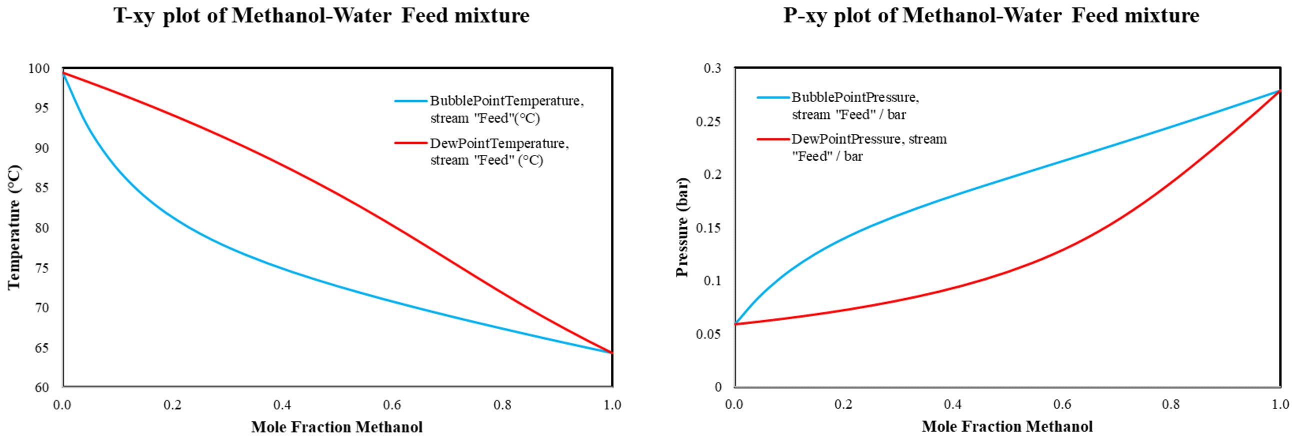
Figure B.2. McCabe Thiele method example with
6 stages

The column is divided into rectifying and stripping sections and four equations that are defined below represents column mass balances, rectification operating line, feed operating line and stripping operating line and they are necessary for determining the number of stages, reflux ratio and feed location. Procedure for plotting this graph and important equations are mentioned in Process book [17]for detailed derivations, definitions and equations. Ponchon-Savarit is another graphical method that includes heat balances that are time-consuming and more rigorous than McCabe and therefore they are not considered for our case.

Fenske-Underwood-Gilliland Method: Graphical method such as McCabe Thiele for binary distillation system requires VLE curve to determine the initial estimates. This method on the other hand uses mathematical formulas to calculate the initial estimate of the design. FUG is the most commonly used method and give an approximate value for binary and multicomponent mixtures. Equations are presented in appendix C2. The equation proposed by Fenske is used to determine the minimum number of stages theoretically and Underwood's equation predicts the minimum reflux ratio. Gilliland provides a correlation between the number of trays and the corresponding reflux ratio if the minimum reflux ratio and the minimum number of stages are known. Kirkbride's equations is an alternative approach to determine the number of stages in the rectifier and stripping section.

B.3 Vapour Liquid Equilibrium for Methanol-Water

An important step in designing a distillation column is determining the vapour-liquid equilibrium curve for the given methanol-water feed mixture. The feed contains 50-50% of methanol and water and is liquid mixture is at 35°C and 1 bar. Two different curves: Temperature-mole fraction and Pressure-mole fraction were plotted in COCO software and the plots are presented in **Fig. B.3**. the red line represents the dewpoint which is the point where saturated vapour changes to droplets and condenses, whereas the blue line represents the bubble-point where liquid starts to boil. The region between these two lines denotes the liquid-vapour region and region above the red line is superheated vapour and the region below the blue line is subcooled liquid. In the T-XY plot, the boiling point of both components can be observed. With this data, the equilibrium curve can be plotted which will be used in modelling the distillation systems.


T-xy plot of Methanol-Water Feed mixture

P-xy plot of Methanol-Water Feed mixture

Figure B.3. Methanol-Water mixture VLE plot at 1 bar (a) T-xy plot (b) P-xy plot

B.4 Heat Integrated Systems

[1] Feed heating system

Table B.1. Feed Pre-heating Model Results

Parameters	Unit	Decentralized		Semi-Centralized		Centralized	
		1hex	2hex	1hex	2hex	1hex	2hex
Feed flow rate	g/hr	135.71	135.71	1.35E+05	1.35E+05	1.83E+06	1.83E+06
Column Pressure	bar	1					
No. of rectifying stages		15 (excl.cond)					
No. of Stripping stages		4(excl.reb)					
Feed stage		16th					
Distillate flow rate	g/hr	86.62	86.62	8.66E+04	8.66E+04	1.17E+06	1.17E+06
Bottom Flow rate	g/hr	49.09	49.09	4.91E+04	4.91E+04	6.62E+05	6.62E+05
Reflux Ratio		1.293	1.294	1.293	1.294	1.293	1.294
Boil-up ratio		2.02	2.003	2.02	2.003	2.02	2.003
Distillate temperature	℃	64.29					
Bottom temperature	℃	98.70					
Reboiler Duty	W	62.34	61.57	6.23E+04	6.16E+04	8.42E+05	8.31E+05
Condenser Duty	W	-63.11	-63.15	-6.31E+04	-6.32E+04	-8.52E+05	-8.53E+05
Heat exchanger results							
Heat exchanger duty	W	3.32	1.59/2.54	3.32E+03	1.59E+03/ 2.54E+03	4.48E+04	2.16E+04/ 3.43E+04
Hot fluid inlet/outlet temperature-hex 1	℃/℃	98.7/40	64.2/40	98.7/40	64.2/40	98.7/40	64.2/40
Cold fluid inlet/outlet temperature-hex 1	℃/℃	35/62.9	35/48.6	35/62.9	35/48.6	35/62.9	35/48.6
Hot fluid inlet/outlet temperature-hex 2	℃/℃	-	98.7/53.6		98.7/53.6	-	98.7/53.6
Cold fluid inlet/outlet temperature-hex 2	℃/℃	-	48.6/69.6		48.6/69.6	-	48.6/69.6

[2] Vapour Reompression system

Table B.2 VRC Model Results

Parameters	Unit	Decentralized	Semi-Centralized	Centralized
Feed flow rate	(g/hr)	**135.71**	**1.35E+05**	**1.83E+06**
Column Pressure	(bar)	1		
No. of rectifying stages		15 (excl.cond)		
No. of Stripping stages		4(excl.reb)		
Feed stage		16th		
Distillate flow rate	(g/hr)	86.62	8.66E+04	1.17E+06
Bottom Flow rate	(g/hr)	49.09	4.91E+04	6.62E+05
Reflux Ratio		1.29		
Boil-up ratio		2.13		
Distillate temperature	(℃)	64.29		
Bottom temperature	(℃)	98.70		
Reboiler Duty	(W)	0	0	0
Condenser Duty	(W)	-6.20	-6.20E+03	-8.38+04
Heat exchanger results				
Heat exchanger duty	(W)	65.49	6.55E+04	8.84E+05

Hot fluid inlet/outlet temperature	(°C/°C)	169.58/100.98	169.58/100.98	169.58/100.98
Cold fluid inlet/outlet temperature	(°C/°C)	95.98/98.70	95.98/98.70	95.98/98.70
Compressor results				
Compressor Duty	(W)	8.78	8.78E+03	1.19E+05
Pressure ratio		4.38	4.38	4.38

[3] Bottom Flashing System

Table B.3 . Bottom Flashing Model Results

Parameters	**Units**	**Decentralized**	**Semi-Centralized**	**Centralized**
Feed flow rate	(g/hr)	**135.71**	**1.35E+05**	**1.83E+06**
Column Pressure	(bar)	1		
No. of rectifying stages		15 (excl.cond)		
No. of Stripping stages		4(excl.reb)		
Feed stage		16th		
Distillate flow rate	(g/hr)	86.62	8.66E+04	1.17E+06
Bottom Flow rate	(g/hr)	49.09	4.91E+04	6.62E+05
Reflux Ratio		1.29		
Boil-up ratio		2.13		
Distillate temperature	(°C)	64.29		
Bottom temperature	(°C)	98.70		
Reboiler Duty	(W)	0	0	0
Condenser Duty	(W)	0	0	0
Heat exchanger results				
Heat exchanger duty	(W)	62.93	6.29E+04	8.49+05
Hot fluid inlet/outlet temperature	(°C/°C)	64.33/64.29		
Cold fluid inlet/outlet temperature	(°C/°C)	59.29/61.18		
Compressor results				
Compressor Duty	(W)	13.19	1.32E+04	1.79E+05
Pressure ratio		4.49	4.49	4.49
Other results				
Heater Duty	(W)	30.49	3.05E+04	4.12E+05
Cooler Duty	(W)	-41.12	-4.11E+04	-5.55E+05
Outlet Pressure- expansion valve	(bar)	0.22	0.22	0.22

[4] External HiDiC system

Table B.4 . Ext.HiDiC Model Results

Parameters	**Units**	**Decentralized**	**Semi-Centralized**	**Centralized**
Feed flow rate	(g/hr)	**135.71**	**1.35E+05**	**1.83E+06**
Column Pressure	(bar)	1(stripper) 2.13(rectifier)		

No. of rectifier stages		15 (excl.cond)		
No. of Stripper stages		4(excl.reb)		
Feed stage-Stripper/Rectifier		16th		
Distillate flow rate	(g/hr)	86.62	8.66E+04	1.17E+06
Bottom Flow rate	(g/hr)	49.09	4.91E+04	6.62E+05
Reflux Ratio		0.32		
Boil-up ratio		1.11		
Distillate temperature	(°C)	84.78		
Bottom temperature	(°C)	98.70		
Reboiler Duty	(W)	34.06	3.41E+04	4.59E+05
Condenser Duty	(W)	-35.26	-3.53E+04	-4.76+05
Heat exchanger results				
Heat exchanger duty	(W)	35.72	3.57E+04	8.84E+05
Hot fluid inlet/ outlet temperature	(°C/°C)	84.82/ 80.07	84.82/ 80.07	84.82/ 80.07
Cold fluid inlet/ outlet temperature	(°C/°C)	75.06/ 84.65	75.06/ 84.65	75.06/ 84.65
Compressor results				
Compressor Duty	(W)	4.85	4.85E+03	6.55E+04
Pressure ratio		2.13	2.13	2.13

[5] Vapour Compression System

Table B.5 . Properties of selected refrigerants

type	Refrigerant	Molecular Weight g/mol	Boiling Point (°C)	Freezing point (°C)	Critical temp/Critical Pressure (°C)/(bar)	ODP/GWP	Safety	Refrigerant cost €/kg
Inorganic compound	Ammonia	58.12	-0.49	-138.49	151.98/37.96	0/0	A3	0.8403-2.86
Hydro-carbon	Butane	17.03	-33.327	-79.71	132.25/1113.33	0/0	B2L	6.73-8.41

The biggest challenge in implementing the VC Distillation system at ZEF is the proper selection of refrigerants. The refrigerants need to be eco-friendly, have zero ODP and GWP and should have excellent thermodynamic properties and it should be safer. Another important characteristic of the refrigerant is the Critical temperature and pressure. The refrigerant will be working at high pressure and temperature and therefore the condenser temperature and reboiler temperature should not be greater than the critical temperature. Venkatarathnam et.al [37]has presented a list of eco-friendly refrigerants that are used in industries and has classified the refrigerants based on Boiling point, freezing point, critical temperature, and pressure, ODP and GWP. For our ZEF case, hydrocarbons and inorganic compounds were selected as their ODP and GWP value was zero. In hydrocarbons, butane was selected and in inorganic compounds, ammonia was selected as refrigerants. Most of the other components in the list were neglected as their critical pressure and temperature were higher than our condenser and reboiler temperature. Ammonia and butane belonged to a ASHRAE safety group of B2L and A3. Fig. B.4 give an overview of ASHRAE refrigerant safety standards.

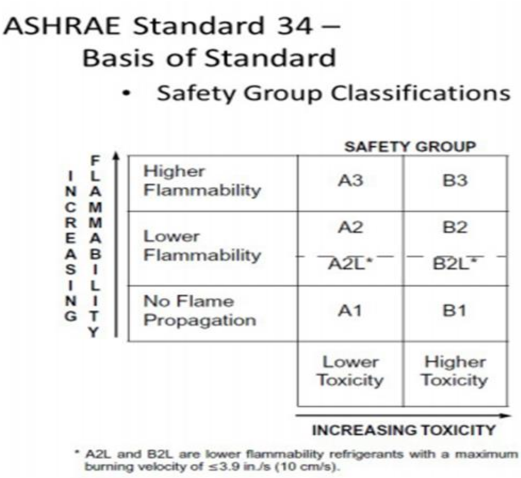


Figure B.4. ASHRAE safety standard specification of refrigerants

From the base case model, it was observed that the liquid from the bottom stage of the distillation column will be at 95.98℃ and this liquid is heated in the reboiler to 98.7℃. To implement VC systems to reduce the reboiler duty, a heat exchanger will be incorporated with the reboiler system. Therefore, the hot refrigerant coming from the compressor provides the necessary heat required to increase the temperature of the liquid mixture in the reboiler. A 5℃ minimum temperature approach was assumed. Therefore, the temperature difference between cold liquid inlet stream and hot refrigerant outlet stream will be 5℃ and hence the refrigerant in the outlet of the heat exchanger will be 100.98℃ and it was assumed to be saturated vapour. Refrigerants need to be chosen in such a way that at this temperature it remains saturated vapour and hence the refrigerants were narrowed down to ammonia and butane. Safety, maximum critical temperature and pressure, chemical stability at high temperatures and thermodynamic properties were considered for selection of working fluid. The COP of the cycle was calculated using the formulas mentioned below and the required data such as enthalpies, compressor duties and heat exchanger duties were extracted from COCO

Table B.6. VC Model Results

Parameters	**Unit**	**Decentralized**		**Semi-Centralized**		**Centralized**	
		Ammonia	**butane**	**Ammonia**	**butane**	**Ammonia**	**butane**
Feed flow rate	(g/hr)	**135.71**	**135.71**	**1.35E+05**	**1.35E+05**	**1.83E+06**	**1.83E+06**
Column Pressure	(bar)	1					
No. of rectifying stages		15 (excl.cond)					
No. of Stripping stages		4(excl.reb)					
Feed stage		16th					
Distillate flow rate	(g/hr)	86.62	86.62	8.66E+04	8.66E+04	1.17E+06	1.17E+06
Bottom Flow rate	(g/hr)	49.09	49.09	4.91E+04	4.91E+04	6.62E+05	6.62E+05
Reflux Ratio		1.29	1.29	1.29	1.29	1.29	1.29
Boil-up ratio		2.13	2.13	2.13	2.13	2.13	2.13
Distillate temperature	(℃)	64.29					

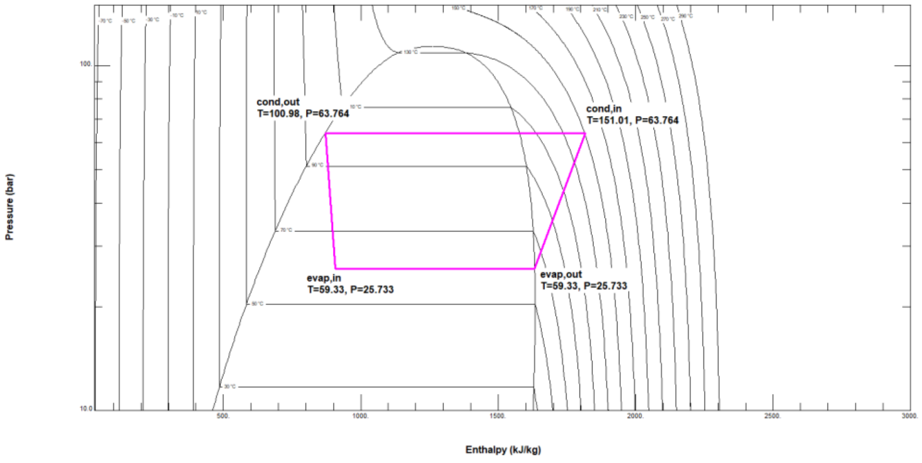
Bottom temperature	(°C)	98.70					
Reboiler Duty	(W)	0	0	0	0	0	0
Condenser Duty	(W)	-8.24	-12.98	-8.24E+03	-1.29E+04	-1.12E+05	-1.75E+05
Heat exchanger results							
Heat exchanger duty	(W)	65.49/ 54.69	65.49/ 49.95	6.55E+04/ 5.47E+04	6.55E+04/ 4.99E+04	8.84E+05/ 7.38E+05	8.84E+05/ 6.74E+05
Hot fluid inlet/outlet temperature-hex 1	(°C/°C)	151.01/ 100.98	103.64/ 100.98	151.01/ 100.98	103.64/ 100.98	151.01/ 100.98	103.64/ 100.98
Cold fluid inlet/outlet temperature-hex 1	(°C/°C)	95.98/ 98.70	95.98/ 98.70	95.98/ 98.70	95.98/ 98.70	95.98/ 98.70	95.98/ 98.70
Hot fluid inlet/outlet temperature-hex 2	(°C/°C)	64.33/ 64.29	64.33/ 64.29	64.33/ 64.29	64.33/64.29	64.33/ 64.29	64.33/ 64.29
Cold fluid inlet/outlet temperature-hex 2	(°C/°C)	59.31/ 59.33	59.20/ 59.33	59.31/ 59.33	59.20/ 59.33	59.31/ 59.33	59.20/ 59.33
Compressor results							
Compressor Duty	(W)	10.79	15.54	1.07E+04	1.55E+04	1.46E+05	2.09E+05
Pressure ratio		2.477	2.476	2.477	2.476	2.477	2.476

COP of ammonia cycle (refrigerant cycle)

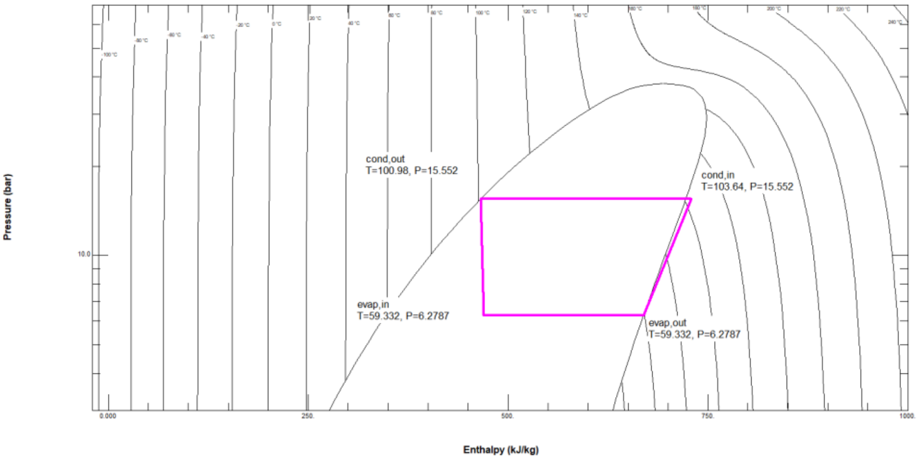
$$COP_{ammonia} = \frac{h_{evap,out} - h_{evap,in}}{h_{cond,in} - h_{evap,out}} = \frac{Evaporator\ duty}{Compressor\ duty} = 5.07 \qquad \text{(B.5)}$$

COP of butane cycle (refrigerant cycle)

$$COP_{ammonia} = \frac{h_{evap,out} - h_{evap,in}}{h_{cond,in} - h_{evap,out}} = \frac{Evaporator\ duty}{Compressor\ duty} = 3.21 \qquad \text{(B.6)}$$



(a) Ammonia Refrigerant -VC cycle



(b) Butane Refrigerant-VC cycle

Figure B.5. Vapor Compression P-h plot for Ammonia and Butane

Appendix C

Appendix C: Energy and Economic analysis

C.1 Cost estimation data

[1] Condenser cost data

The cost per surface area range (€/m^2) were obtained from Alibaba and the cost per surface area of specific condenser design was estimated by interpolation. Later the total cost per unit was calculated by multiplying the cost per surface area with the estimated condenser area. To determine the total cost of condenser for the decentralized system, the calculated cost per unit was multiplied with 13500 units whereas for semi-centralized it was multiplied with 14 units and finally for centralized it was multiplied with 1

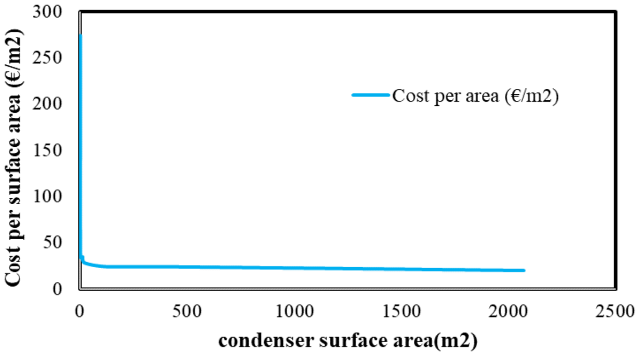


Figure C.1. Stainless-steel Condenser Cost Estimation data [Alibaba]

[2] Immersion heater cost data

Immersion heaters are inexpensive, and they can be easily customized. The cost per surface area range (€/W) were obtained from Alibaba and the cost per wattage of specific immersion heater design was estimated by interpolation. Later the total cost per unit was calculated by multiplying the cost per wattage with the estimated reboiler duty. To determine the total cost of immersion heater for the decentralized system, the calculated euros per unit was multiplied with 13500 units whereas for semi-centralized it was multiplied with 14 units and finally for centralized it was multiplied with 1

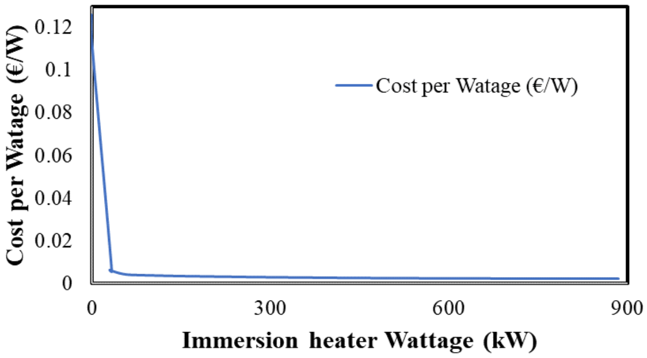


Figure C.2. Stainless-steel immersion heater cost estimation data[Alibaba]

[3] Distillation column cost data

The maximum vapour velocity can be calculated using

$$u_{vapour\ max}(m/s) = K_1 \sqrt{\frac{\rho_L - \rho_V}{\rho_V}} \tag{C.1}$$

The density of liquid and vapour can be obtained from COCO results

K_1 can be calculated using liquid vapour flow factor F_{LV} and plot mentioned in Sinnott and Towler Chapter 17 Figure.17.34

The maximum vapour flow rate can be calculated using

$$V_{vapour}\left(m^3/s\right) = \frac{maximum\ vapour\ mass\ flow\ rate\ in\ column}{density\ of\ vapour} \tag{C.2}$$

The thickness of the column vessel can be calculated using the equation obtained from Sinnott and Towler

$$t(m) = \frac{P_i * D_c}{2S - P_i} \tag{C.3}$$

P_i – pressure inside a column ; D_c – diameter of the column;

S – maximum allowable stress of stainless steel

The mass of the column can be estimated using

$$Mass\ of\ column = \pi\ (\rho_{ss} t\ D_c L_c) \tag{C.4}$$

$$where\ L_c\ -\ height\ of\ column\ and\ \rho_{ss}\ -\ density\ of\ stainless\ steel\ =\ 8000\ kg/m^3$$

The cost per mass range (€/W) of stainless-steel plate was obtained from Alibaba and the main idea here was to convert the flat plate into the cylindrical vessel. For decentralized system, the existing distillation column dimension was chosen

Table C.1. Stainless-steel Distillation column Cost Estimation [Alibaba]

Stainless steel	Cost per mass (€/kg)
SS304 0.2-0.8mm plate	1.922
SS304 0.6mm sanitary tube	2.242

[4] Heat exchanger data

The heat transfer coefficient of shell and tube heat exchangers were obtained from the literature. This was a rough estimation considered for preliminary analysis.

Table C.2. Shell and tube heat exchanger Overall heat transfer coefficients ranges

Design	type	$U_{overall}$ range W/m^2K	$U_{average}$ W/m^2K	Reference
1hex	Liquid-liquid heat exchange	150-1200	675	[39]
2hex	Liquid-liquid heat exchange	150-1200	675	
	Liquid-liquid heat exchange	150-1200	675	
VRC	Condensing vapour-evaporating liquid heat exchange	600-1700	1150	
BF	Condensing vapour-evaporating liquid heat exchange	600-1700	1150	
Ext.HiDiC	Condensing vapour-evaporating liquid heat exchange	600-1700	1150	
VC ammonia	Condensing vapour -evaporating refrigerant mixture	550-850	700	[17]
	Evaporating liquid-condensing refrigerant vapour	800-1050	925	
VC butane	Condensing vapour -evaporating refrigerant mixture	550-850	700	
	Evaporating liquid-condensing refrigerant vapour	800-1050	925	

The total surface area of the heat exchanger was calculated using equation 3.12. The cost per surface area range (€/m^2) were obtained from Alibaba and the cost per area of specific designs was estimated by interpolation. The cost per unit was calculated by multiplying the estimated cost per area with the calculated area.

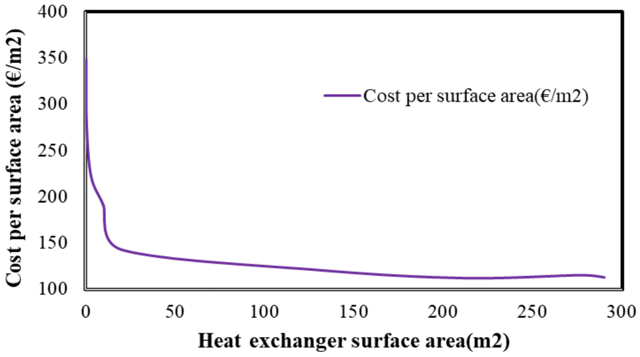


Figure C.3. Stainless-steel heat exchanger Cost Estimation [Alibaba]

[5] Compressor cost data

The cost of compressors was directly obtained from vendors by sending them a quotation with duty, volume flow rate, suction and discharge temperature and maximum pressure ratio and all these data were obtained from COCO results.

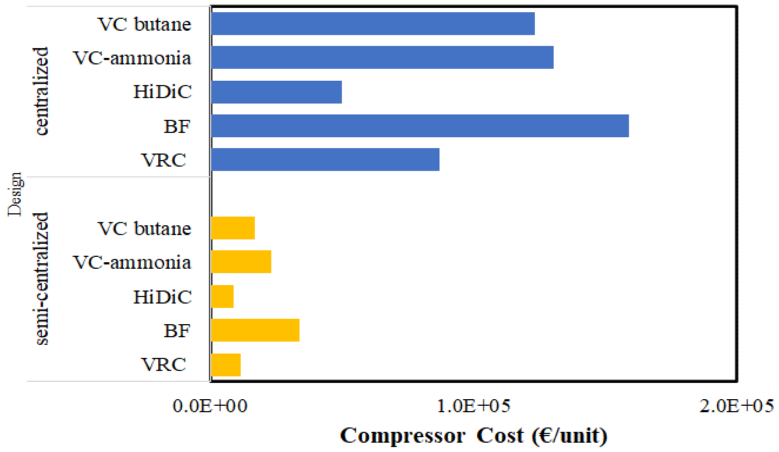
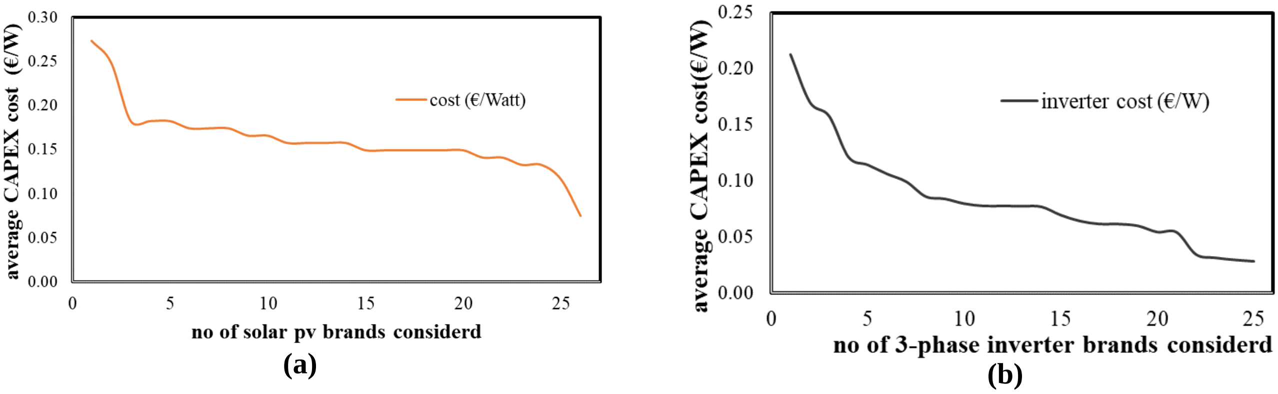


Figure C.4. Compressor cost estimation data [Alibaba]

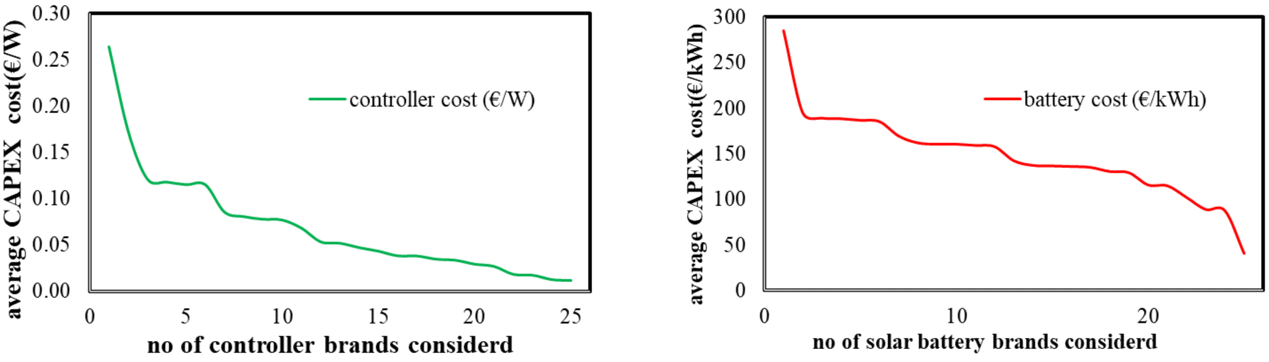
[6] Solar panel, inverter and controller cost data

- **Equivalent Sunshine duration:** It is the duration of total sunshine in a particular location the solar irradiation received in that same location is maximum at 1000W/m^{2}K. PV modules are often designed based on this Equivalent Sunshine duration of peak sun hours and the output of solar panel during this condition is often referred to as Watt peak which denotes the maximum power produced by the solar panel. The Equivalent sunshine duration varies for different locations and to analyze the effect of location on the cost of solar panels, 3 different locations namely Sahara (ESH-7.063 hours)-a high radiation region, Portugal (ESH-4.766 hours)-a medium radiation region and India (ESH-3.16 hours)-a low radiation region were chosen. The ESH data can be extracted from Solar Atlas. For estimating the cost of solar panels, the euros per wattage of solar panels of 25 different brands were considered which are presented in Fig.C.5[a] and the median of this solar panel cost was 0.16 €/W was chosen. The total solar module cost which includes the solar panel frame, and the land cost was assumed to be 2 times the cost per unit wattage of the solar panel. [Appendix C.1[6] - Vendor data and ZEF previous team data sheet]. Therefore, the total cost of a solar module of 0.31 €/W. Similarly, the cost per wattage of inverters and controllers are presented in Fig.C.5[b,c].

- **Battery:** Batteries are usually represented in terms of energy storage and therefore to estimate the cost per energy of batteries, an approach similar to solar PV was followed. The cost/kWh of batteries of 25 brands were obtained from Alibaba and the median of this range which was approximately 142.7 €/kWh was chosen.



(a) (b)



(c) **(d)**

Figure C. 5. Cost Estimation data (a)Solar PV (b) Solar inverter (c) Solar controller (d) Solar battery [Alibaba**]**

[7] The solar thermal system, buffer tanks and glycol cost

- In order to design the solar thermal systems, a few assumptions were to be considered. The mixture in the reboiler was heated using a thermal fluid where hot fluids from solar thermal panels passed through a heat exchanger and transferred the necessary heat. The bottom product was at 98.7°C which was extracted from COCO results and a 5°C-temperature approach was assumed and therefore the exit temperature of the thermal fluid was at 103.7°C.

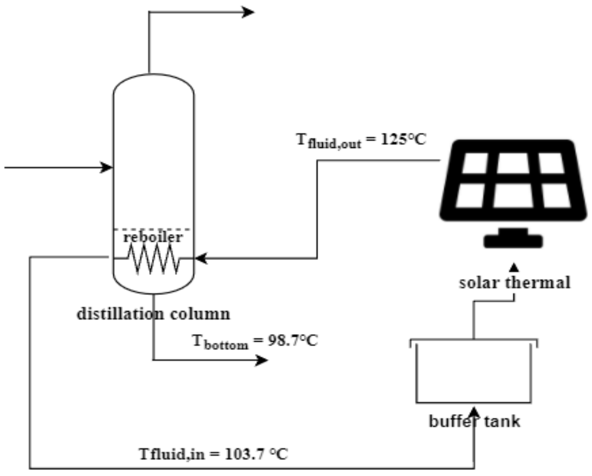


Figure C.6. Design of proposed solar thermal system

- The thermal fluid temperature decided the number of solar thermal panes and the cost of these panels. The higher temperature approach resulted in increased the temperature of the thermal fluid exiting the reboiler and eventually increased the panel temperature. The efficiency of panels usually decreases for increased pane temperature and therefore a large number of panels was required which also increased the cost. On the other hand, an increase in approach temperature increased the flow rate of glycol but the heat exchanger area decreased. Therefore, choosing the appropriate approach temperature was important.
- The mass flow rate of ethylene glycol was determined using equation C.5 where the specific heat capacity was calculated based on the average temperature of inlet and outlet streams of thermal fluids in reboiler and the volume of buffer tank was estimated based on residence time which was assumed as 5minutes [Fannes]. The volume of glycol required was assumed to be 2 times the value of the buffer vessel

The mass flow rate of glycol can be determined using

$$m_{glycol}(kg/s) = \frac{Q_{reboiler}}{c_p * \left(T_{fluid,out} - T_{fluid,in}\right)} \quad \text{(C.5)}$$

The volume of buffer vessel can be estimated using

$$V\left(m^3\right) = Residence\ time * Volume\ for\ the\ rate\ of\ glycol \quad \text{(C.6)}$$

C.2 Energy and Cost Comparative analysis

[1] Lang factors of different process equipment used in Analysis

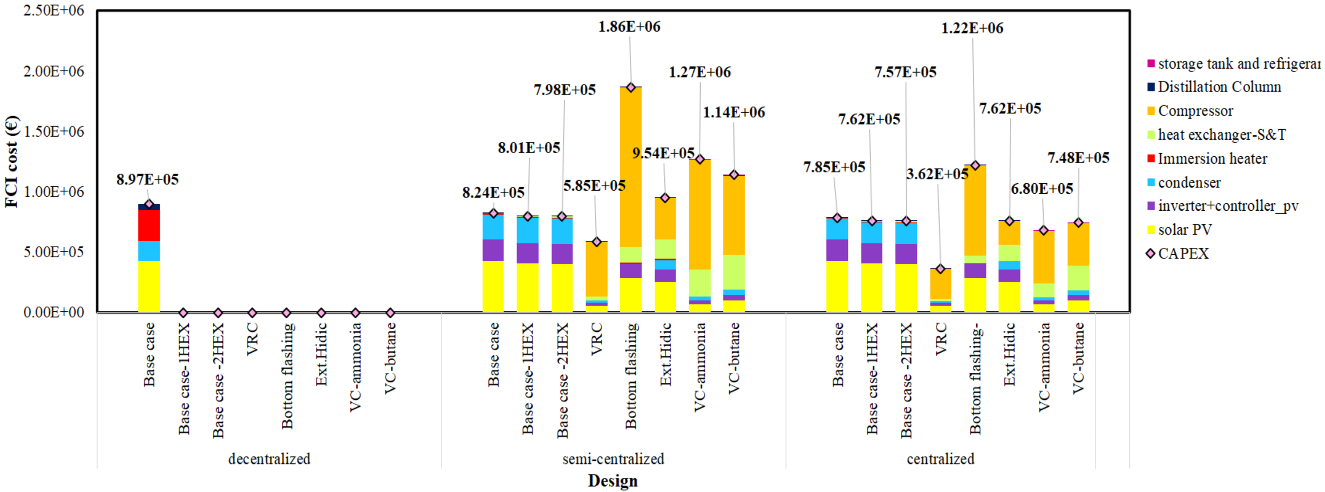
The lang factors of the process equipment are obtained from literature [34]. It must be noted that these lang factors are for large scale systems. For decentralized units, a low range of 2 was chosen.

Table C.3. Lang factors of process equipment

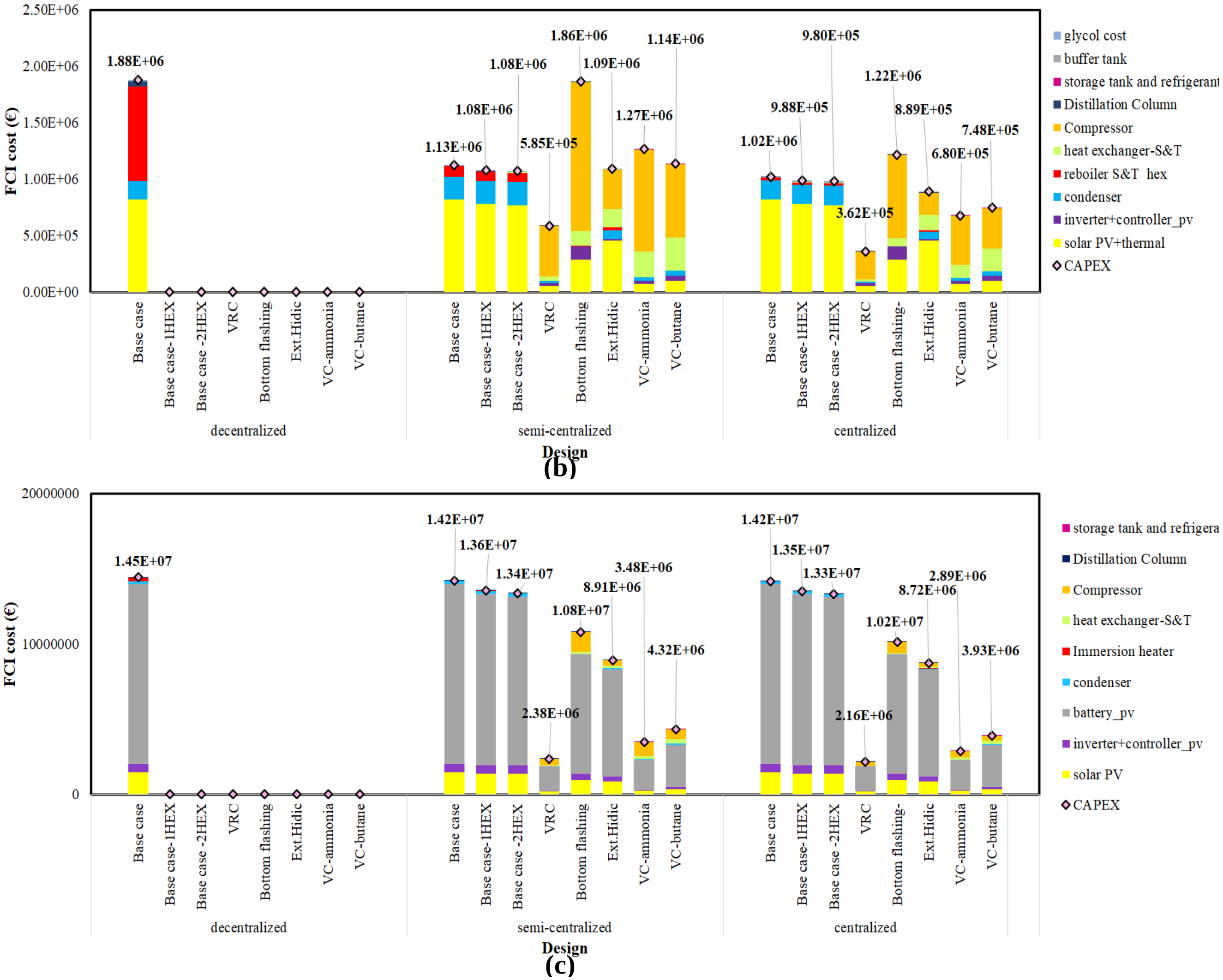
Equipments	Decentralized	Centralized
Electrical components (PV, inverter, battery)	1.26	1.26
Heat exchangers	-	3.5
Compressors	-	2.5
Distillation Column	2	4
Miscellaneous	2	2.5

[2] Fixed capital investment cost of different designs

The fixed capital investment includes the equipment cost, construction, installation, and other essential costs. Factorial method approach was followed to calculate FCI where lang factors are multiplied with equipment cost. These lang factors includes the miscellaneous cost such as equipment, installation, piping, foundation, etc.



(a)



(b)

(c)

Figure C.7. Total fixed capital investment comparison of different DS designs across 3 schemes operating for in Sahara location for 3 cases: (a) Solar PV case-7 hour operation (b) Solar Thermal case-7 hour operation (c)Solar PV case-24 hour operation

[3] Distillation Column Energy losses

Heat losses are a major concern in distillation column and higher heat losses leads to increased reboiler duty. This is because when losses are higher, due to reduced energy the temperature inside the reboiler reduces and therefore to overcome the losses, excess energy is supplied to maintain the reboiler temperature. Therefore, energy losses influences both energy and cost of distillation systems. It also influences the startup and shutdown time of DS system. The energy losses of DS system for all the three schemes were **calculated using heat transfer networks** and certain assumptions were considered.

Assumptions:

- The distillation system was assumed to be vertical cylinder and Rockwell insulation was used to limit the heat losses. The ambient temperature was assumed to be 35℃ (Sahara location). The insulation surface temperature was assumed to be at 40℃ and the insulation thickness was chosen based on this insulation surface temperature. The heat losses are assumed to be constant throughout the column but, in reality the losses are higher at bottom reboiler compared to top stages.
- The convection heat transfer coefficient range of 3-25 W/m^{2}K was report by Mills and therefore an average of 14 W/m^{2}K was assumed. The conductivity of stainless steel and Rockwell insulation are

assumed to 15W/mK and 0.04W/mK. The column including reboiler and its contents were assumed to be lumped mass system and therefore they were at same temperature. The column surface temperature was assumed to be 98.7℃. The same column dimensions used in economic analysis were considered. The design parameters along with column heat losses after insulation are mentioned in Table C.4

Table C.4. Column heat losses for 3 different schemes

Equipments	Units	Decentralized	Semi-Centralized	Centralized
Convection heat transfer coefficient	W/m^2K	14	14	14
Ambient temperature	℃	35	35	35
Column Temperature	m	98.7	98.7	98.7
Column Diameter	m	0.04	0.23	0.66
Column Height	m	1	7.71	11.51
Insulation thickness	m	0.06	0.13	0.17
Stainless steel conductivity	W/mK	25	25	25
Rockwell insulation conductivity	W/mK	0.04	0.04	0.04
Heat loss per plant	W	19.1	494.5	1835.6
Total Heat loss of n plants	kW	257.6	6.92	1.84

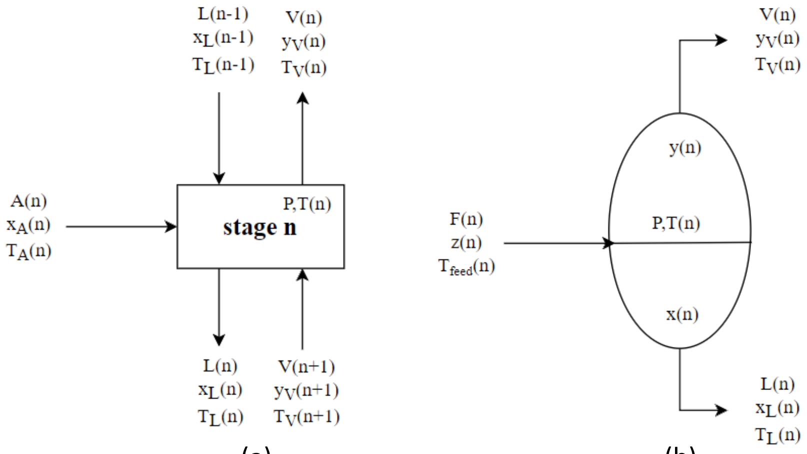
Appendix D

Appendix D: Control Philosophy

D.1 DS modelling

[1] Single stage model

The multi-stage distillation column is solved by solving the mass and energy balances equations for each individual stage. The inputs to the stages are clubbed and assumed to be single feed stream and the compositions and the feed flow rates are given by equation D.1-D.2



(a) (b)

Figure D.1. Simplification of (a) single stage n to (b) a flash tank n at P and T(n) including the relevant mass flows, compositions, and temperatures

$$F_n = A_n + L_{n-1} + V_{n+1} \tag{D.1}$$

$$(F_n z_{n,j}) = (A_n z_{n,j}) + (L_{n-1} x_{n-1,j}) + (V_{n+1} y_{n+1,j}) \tag{D.2}$$

$$z_{n,j} = \frac{(A_n z_{n,j}) + (L_{n-1} x_{n-1,j}) + (V_{n+1} y_{n+1,j})}{F_n}$$

$$h_{n,F} = \frac{(A_n h_{n,A}) + (L_{n-1,L}) + (V_{n+1} y_{n+1,V}) \pm Q}{F_n} \tag{D.3}$$

[2] Mass and Energy balance

In order to estimate the phase fractions in each stage, the mass and component balance are solved for the inlet and outlet streams of flash tank. The mass and component balance equations for the are presented below.

Mass balance: $$F_n - L_n - V_n = 0 \tag{D.4}$$

Component balance: $$(F_n z_{n,j}) - (L_n x_{n,j}) - (V_n y_{n,j}) = 0 \tag{D.5}$$

Energy balance: $$(F_n h_F) - (L_n h_L) - (V_n h_v) \pm Q = 0 \tag{D.6}$$

From these equations the $x_{n,j}$ and $y_{n,j}$ are determined in terms of K_j and β where β represents the fraction of feed that is vapourized and its value lies between 0 and 1 and K_j represents the equilibrium constant. Equation D.7 denotes the Rashford rice Equation.

$$x_{n,j} = \frac{z_{n,j}}{1 + \beta(K_j - 1)} \qquad y_{n,j} = \frac{z_{n,j} K_j}{1 + \beta(K_j - 1)} \tag{D.7}$$

$$\sum \frac{z_{n,j}(1 - K_j)}{1 + \beta(K_j - 1)} = 0 \tag{D.8}$$

$$V_n = F_n \beta \qquad L_n = F_n (1 - \beta) \tag{D.9}$$

Usually, the feed flow rates, feed compositions, feed temperature and pressure and the assumed stage pressure are specified. An initial guess for stage temperature is assumed and based on this the initial K_j is calculated. A value of 0.5 is chosen for β initially. The phase fractions are determined by solving the Rashford Rice equation mentioned in D.7 through trial-and-error iterative process where the β is changed for every time step and simultaneously determining the distribution coefficient. The iteration terminates when the condition in equation D.7 is satisfied. For our case, the same procedure from equation D.3 to D.8 were followed but instead of estimating the phase fractions and β through iterative process they were directly obtained from COCO using the COCOImport function. The input to COCO function are the pressure of the column, feed enthalpy and compositions. With this input the stage temperature and phase fractions can be determined Using these values the flow rates are estimated using equation D.8

[3] Multistage model

The single stage model approach is repeated for all the stages in distillation column. The numbering of stages starts from 1 which represents the top stage and ends at the reboiler stage which is denoted by ‘N’. For the reboiler stage, there are no vapour entering the stage and therefore V_{n+1}. The liquid entering the top stage is estimated using the defined reflux ratio.

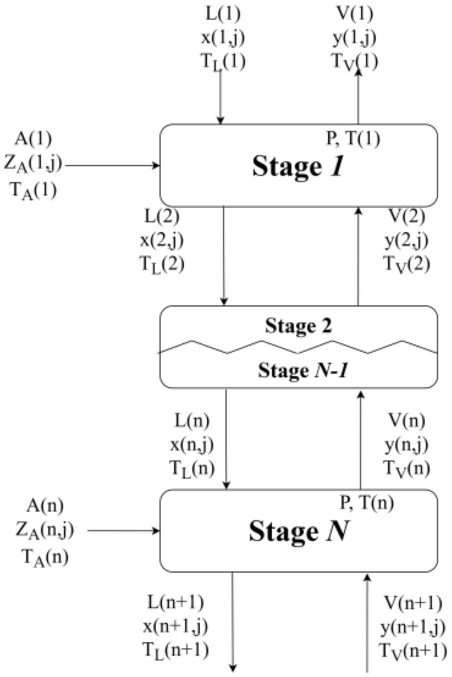


Figure D.2. A multistage model of distillation column

D.2 Control Philosophy

[1] Startup time

The startup time and the final steady state reboiler temperature are estimated using Equation 5.7. The reboiler duty was obtained from the solar PV model and for this analysis the profile mentioned in Fig.5.9 was considered as an input to reboiler duty. The same column specifications for Centralized base case systems used in Chapter 4 were used and all the necessary heat transfer assumptions are already mentioned in Section 5.5.2

Table D.1. Base case column specifications for startup analysis

Parameters	Values
Ambient temperature	20℃
Final steady state temperature	98.7℃
Height of stages	9.51 m
Height of reboiler	2 m
Liquid level inside the reboiler(assumption)	1 m
Diameter of column	0.66 m
Convection heat transfer coefficient	14 W/m^{2}K
Stainless steel Column thermal mass	9.46 kJ/K
Fluid thermal mass	1324.7 kJ/K
Volume of reboiler	0.338 m^3
Steady state bottom volume flow rate	0.7 m^3/hr
Residence time (assuming steady state bottom flow rate)	29 minutes

[2] Energy and Time fractions

Based on the proposed start-up model, the average monthly energy and time fractions can be estimated. It was observed that the average monthly time fraction ranged between 4-8% of the total daylight hours available per day and the energy fractions were between 0.2-0.6% of total energy available per day

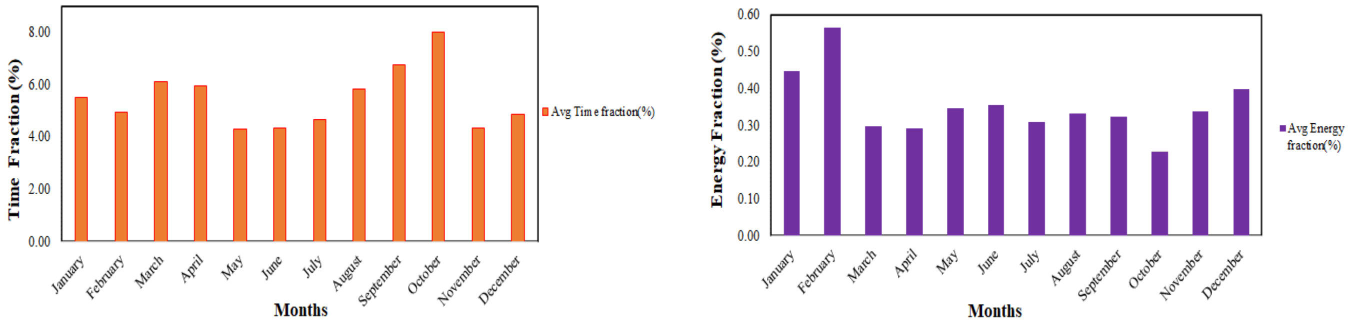


Figure D.3. (a)Average monthly time fractions for given model at Sahara location (b) Average monthly energy fraction for given model at Sahara location

[3] PID controller

Proportional controller: It is a type of feedback control, where the corrections applied to the manipulated variable is directly proportional to the error. Larger the error, higher will the correction. The P term adds a correction to get nearer to the setpoint and how quickly it reaches the setpoint depends on the proportional gain of the controller. Higher gains cause instability in the system and leads to overshoot. Another disadvantage is its inability to achieve the zero steady state error. Therefore, an integral term was introduced to rectify this problem

Integral controller: The integral produces a correction which is proportional to the integral of the error with respect to time. The integral term removes the steady state error, but the response is slower and hence the integral controller is always used with a proportional controller. The I term sums up the errors till the present time step and makes the correction accordingly. PI controller is the most commonly used controller.

Derivative controller: The derivative term is introduced to rectify the slower response of the integral controller. It generates a correction that is proportional to the time derivative of the error. It tries to estimate the rate at which error changes and provides the necessary correction based on the rate of change of error.

$$\textit{Controller output} \qquad MV = Bias \pm K_c(SP - PV) \tag{D.10}$$

Where MV is the manipulated variable (in our case- Feed flow rate valve control) ; Bias is the feed flow rate from previous time step; SP is the set point ,i.e T_{sp}=98.7°C; PV is the process variable which is the measured reboiler temperature.

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Master of Science Thesis

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