



**CHALMERS**  
UNIVERSITY OF TECHNOLOGY



# Modelling future refineries on the path to net-zero CO<sub>2</sub> emissions

Master's thesis in Innovative and Sustainable Chemical Engineering

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## Abstract

Refineries are major emitters of carbon dioxide, thus major mitigation measures are required for this industrial sector. In this research, a model was developed to evaluate mitigation options for refineries. The model is able to capture the interplay between multiple mitigation options and their total combined effect when applied to a refinery. The mitigation options investigated include carbon capture and storage and bio-based feedstock co-processing. Furthermore, the model is capable of quantifying the effect of recovering excess heat available in the refinery to cover the heat demand of the carbon capture unit.

The performance indicators calculated by the model include the CO<sub>2</sub> mitigation potential and changes in the refinery's energy demand resulting from application of selected mitigation options. The model was tested through a case study of the Preemraff Lysekil refinery, with a focus on mitigation options for the hydrogen production unit which accounts for 20.6% of the refinery's total on-site emissions. The results indicate that implementing carbon capture and storage could potentially mitigate 53.5% of the total emissions of this unit. Furthermore, recovery and use of excess heat could potentially cover the full energy demand of the carbon capture unit, thereby increasing the CO<sub>2</sub> mitigation potential by 55.7%.

The bio-based feedstock co-processing option considered was hydrotreating of lipid-based feedstocks. The method is able to quantify the amount of on-site biogenic CO<sub>2</sub> emissions generated within the upgrading process of the bio-based feedstock. The analysis was conducted for hydrotreating of a mixture of light gas oil and 17 wt% rapeseed oil. Compared to the effects of carbon capture and storage applied to the hydrogen production unit, the mitigation potential of the co-processing was around 2.5 times higher whereas the energy demand increase was shown to be only 9.6%. The interplay between the two mitigation options was analysed based on a number of test points. The best trade-off was identified as a low share of applying carbon capture (62.2%) coupled with co-processing (17 wt% of rapeseed oil). Additional analysis was conducted to evaluate the effects of capturing the on-site biogenic emissions. It was revealed that the rate of increase of the energy demand is notably higher than that of the CO<sub>2</sub> emissions mitigation potential. This could be moderated if excess heat covers the energy demand of the carbon capture unit.

Keywords: Modelling, MATLAB, CO<sub>2</sub> emissions, Mitigation potential, Carbon capture, Bio-based feedstock co-processing, Petroleum refineries



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*Reyhaneh Yaghchi Saghakhaneh, June 2021*



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# NOMENCLATURE

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## Abbreviations

<b>ATR</b>	Autothermal reforming
<b>CC</b>	Carbon Capture
<b>CCS</b>	Carbon Capture and Storage
<b>CFCs</b>	Chlorofluorocarbons
<b>CHP</b>	Combined Heat and Power
<b>EU</b>	European Union
<b>FCC</b>	Fluid Catalytic Cracking
<b>FFA</b>	Free Fatty Acids
<b>FT</b>	Fischer-Tropsch liquids
<b>GHGs</b>	Greenhouse Gases
<b>HDC</b>	Catalytic hydrocracking
<b>HDT</b>	Catalytic hydrotreating
<b>HHV</b>	Higher Heating Value
<b>HPU</b>	Hydrogen Production Unit
<b>HTL</b>	Hydrothermal Liquefaction
<b>HTLO</b>	Hydrothermal Liquefaction Oil
<b>IPCC</b>	Intergovernmental Panel on Climate Change
<b>LGO</b>	Light Gas Oil
<b>LHV</b>	Lower Heating Value
<b>LLGHGs</b>	Long-Lived Greenhouse Gases
<b>LPG</b>	Liquefied Petroleum Gas
<b>MEA</b>	Monoethanolamine
<b>MHC</b>	Mild Hydro Cracker
<b>PSA</b>	Pressure-Swing Adsorption
<b>SMR</b>	Steam Methane Reforming
<b>Synsat</b>	Synergetic saturation

## Symbols

$AddEm_{HPU}$	Additional on-site emissions to the HPU due to hydrotreating of the bio-based feedstock ( $10^6$ t/year)
$Addmol_{HDT}$	Hydrogen consumption to be supplied by steam reforming of fossil-based methane ( $10^6$ mole/year)
$BiogenicEm_{HPU}$	Biogenic CO <sub>2</sub> emissions formed within the processes involved in upgrading the bio-based feedstock in the refinery ( $10^6$ t/year)
$C_{FA}$	Number of carbon atoms in fatty acid FA
$Cmp$	CO <sub>2</sub> mitigation potential of CC technology ( $10^6$ t/year)
$Cmp_{bio-feedstock}$	CO <sub>2</sub> mitigation potential related to the bio-feedstock co-processing ( $10^6$ t/year)
$CP$	Captured CO <sub>2</sub> emissions using CC technology ( $10^6$ t/year)
$CR$	Captured rate (%)
$DB_{FA}$	Number of double bounds available in 1 mole of the fatty acid FA
$EC_u$	Electricity consumption of each process unit $u$ (GWh/year)
$EF_{bp}$	Emission factor related to by-product $bp$ (tCO <sub>2</sub> /GJ)
$EF_f$	Emission factor related to fossil fuel ( $f$ ) (tCO <sub>2</sub> /GJ)
$EF_{Make-up f}$	Emission factor of make-up fossil fuel ( $f$ ) (tCO <sub>2</sub> /GJ)
$Em_{RE_{bio-feedstock}}$	CO <sub>2</sub> emissions from the resource extraction phase of bio-feedstock ( $10^6$ t/year)
$Em_{RE_{Make-up f}}$	CO <sub>2</sub> emissions from the resource extraction phase of make-up fossil fuel ( $f$ ) ( $10^6$ t/year)
$Em_{RE_{Replaced fossil share}}$	CO <sub>2</sub> emissions from the resource extraction phase of the replaced fossil-based share ( $10^6$ t/year)
$Em_u$	CO <sub>2</sub> emissions associated with each process unit $u$ ( $10^6$ t/year)
$Em_{u,on-site}$	On-site CO <sub>2</sub> emissions from each process unit $u$ ( $10^6$ t/year)
$Em_{UP_{bio-feedstock}}$	CO <sub>2</sub> emissions from the user phase of bio-feedstock ( $10^6$ t/year)
$En_{CCS}$	Addition to the energy demand of the refinery of focus due to the energy consumption of CCS (GJ/year)
$En_{HPU_{bio-feedstock}}$	Energy demand of HPU related to the bio-based feedstock ( $10^6$ GJ/year)
$FC_{u,f}$	Consumption of fuel $f$ in process unit $u$ ( $10^6$ GJ/year)

$FP$	Fuel penalty that is the energy consumption of the applied CC technology (GJ/t CO <sub>2</sub> )
$H_{FA}$	Number of hydrogen atoms in fatty acid FA
$i - 1$	Number of carbon atoms for $C_{i-1}$ n-alkane in the liquid product
$i$	Number of carbon atoms for $C_i$ n-alkane in the liquid product
$LHV_{bp}$	Lower Heating Value of by-product $bp$ (GJ/Sm <sup>3</sup> )
$LHV_{Me}$	Lower Heating Value of fossil-based methane (GJ/mole)
$m_{bio-feedstock}$	Mass flow of bio-based feedstock (10 <sup>6</sup> t/year)
$M_{bio-feedstock}$	Molar mass of lipid-based feedstock (t/mole)
$M_c$	Molar mass of carbon (t/mole)
$M_{C_i}$	Molar mass for $C_i$ n-alkane in the liquid product (t/mole)
$M_{C_{i-1}}$	Molar mass of $C_{i-1}$ n-alkane in the liquid product (t/mole)
$M_{CO}$	Molar mass of CO (carbon monoxide) (t/mole)
$M_{CO_2}$	Molar mass of CO <sub>2</sub> (carbon dioxide) (t/mole)
$m_{Gp}$	Mass flow of gaseous product of hydrotreating the bio-based feedstock (10 <sup>6</sup> t/year)
$M_H$	Molar mass of hydrogen (t/mole)
$m_{H_{HDT}}$	Total hydrogen consumption due to hydrotreating of the lipid-based feedstock (10 <sup>6</sup> t/year)
$m_{Lp}$	Mass flow of liquid product of hydrotreating the bio-based feedstock (10 <sup>6</sup> t/year)
$M_{Me}$	Molar mass of methane (t/mole)
$m_{Me}^{Metn}$	Mass flow for methane formed by methanation (10 <sup>6</sup> t/year)
$M_O$	Molar mass of oxygen (t/mole)
$m_{tot}$	Mass flow of total liquid input to the process unit (10 <sup>6</sup> t/year)
$m_{water}$	Mass flow of water produced through hydrotreating the bio-feedstock (10 <sup>6</sup> t/year)
$mol_{H_{DB}}$	Hydrogen consumption for hydrogenation of double bounds in the lipid-based feedstock (10 <sup>6</sup> mole/year)
$mol_{H_{DC}}$	Hydrogen consumption for decomposition of triglycerides in the lipid-based feedstock into the corresponding fatty acids (10 <sup>6</sup> mole/year)

$mol_{H_{DCn}}$	Hydrogen consumption of decarbonylation ( $10^6$ mole/year)
$mol_{H_{HDO}}$	Hydrogen consumption resulted from hydrodeoxygenation ( $10^6$ mole/year)
$mol_{H_{HDT}}$	Total hydrogen consumption due to hydrotreating of the lipid-based feedstock ( $10^6$ mole/year)
$mol_{H_{Me}}$	Hydrogen consumption to be supplied by steam reforming of methane ( $10^6$ mole/year)
$mol_{H_{Metn}}$	Hydrogen consumption for methanation ( $10^6$ mole/year)
$mol_{H_{Propane}}$	Hydrogen consumption to be supplied by steam reforming of propane ( $10^6$ mole/year)
$n_{CO}$	Molar flow of CO produced by decarbonylation of the lipid-based feedstock ( $10^6$ mole/year)
$n_{CO}^{Gp}$	Molar flow of CO in the gaseous product ( $10^6$ mole/year)
$n_{CO}^{Metn}$	Molar flow of methanized CO ( $10^6$ mole/year)
$n_{CO_2}$	Molar flow of CO <sub>2</sub> produced by decarboxylation of the lipid-based feedstock ( $10^6$ mole/year)
$n_{CO_2}^{Gp}$	Molar flow of CO <sub>2</sub> in the gaseous product ( $10^6$ mole/year)
$N_{DB}$	Number of double bounds available in 1 mole of the lipid-based feedstock
$n_{Me}^{Metn}$	Molar flow of methane in the gaseous product ( $10^6$ mole/year)
$n_{Propane}$	Molar flow for propane in the gaseous product ( $10^6$ mole/year)
$OE_E$	Overall efficiency inclusive of generation, transmission and distribution of electricity supplied from each source of power, $E$ (%)
$OE_{grid}$	Grid overall efficiency inclusive of generation, transmission and distribution of grid electricity (%)
$Sh_{DCn}$	Share of $C_{i-1}$ n-alkanes that are received through decarbonylation (%)
$Sh_E$	Share of electricity supplied from different sources of power $E$ (%)
$Sh_{grid}$	Share of electricity supplied from the grid (%)
$TE$	Total energy consumption ( $10^6$ GJ/year)
$TE_m$	CO <sub>2</sub> emissions associated with all the process units ( $10^6$ t/year)

$TEm_{bio-feedstock}$	CO <sub>2</sub> emissions from the value chain regarding bio-feedstock (10 <sup>6</sup> t/year)
$TEm_{on-site}$	Total on-site CO <sub>2</sub> emissions from all process units (10 <sup>6</sup> t/year)
$V_{u,bp}$	Volume of by-product of process unit $u$ (10 <sup>6</sup> GJ/year)
$V_{u,i}$	Input(s) $i$ to unit process $u$ (10 <sup>6</sup> Sm <sup>3</sup> /year)
$V_{u,p}$	Outputs/product(s) $p$ of process unit $u$ (10 <sup>6</sup> Sm <sup>3</sup> /year)
$w_{bio-feedstock}$	Weight fraction the bio-based feedstock in the liquid input to the process unit (%)
$w_{C_{i-1}}^{Lp}$	Weight fraction of n-alkane with $C_{i-1}$ carbons in the liquid product (%)
$w_{C_i}^{Lp}$	Weight fraction for n-alkane with $C_i$ carbons in the liquid product (%)
$w_{CO}$	Weight fraction of CO in the gaseous product (%)
$w_{CO_2}$	Weight fraction of CO <sub>2</sub> in the gaseous product (%)
$w_{Me}$	Weight fraction related to methane in the gaseous product (%)
$x_{FA}$	Molar fraction of fatty acid FA (%)
$Y_{LP}$	Yield related to the liquid product of hydrotreating the bio-based feedstock (%)
$Y_{u,i,p}$	Volume yields corresponding to the production of product $p$ in the process unit $u$ with the input $i$ (%)
$Y_{water}$	Yield related to water produced through hydrotreating the bio-feedstock (%)
$\Delta H_{PR}$	Enthalpy of reaction for propane reforming (GJ/mole)
$\Delta H_R$	Enthalpy of reaction
$\Delta H_{SMR}$	Enthalpy of reaction for SMR (GJ/mole)
<b>Subscripts</b>	
$bp$	By-product
$f$	Fossil fuel



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# 1. INTRODUCTION

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## 1.1. BACKGROUND

Since the trends in the climate change pose an urgent and potentially irreversible threat to man-kind and the planet, the Intergovernmental Panel on Climate Change (IPCC) strongly recommends that the global temperature rise should be limited to 1.5°C above pre-industrial levels to mitigate the potential impacts and associated risks of global warming as a result of human activities [1]. Accordingly, the European Union (EU) has adopted ambitious targets for transition to a sustainable and climate-neutral economy by 2050 [2]. Furthermore, the Swedish climate policy framework has adopted a more stringent approach in this regard, including a number of new climate goals one of which is that Sweden is to have zero net emissions of greenhouse gases (GHGs) to the atmosphere by 2045 followed by negative emissions thereafter. These targets entail that Sweden will contribute to reducing the concentration of GHGs in the atmosphere after 2045 [3].

Among greenhouse gases, carbon dioxide (CO<sub>2</sub>) contributes the most to global warming [4]. This is due to the fact that it is one of the long-lived greenhouse gases (LLGHGs), with a relatively high and steadily rising concentration in the atmosphere, although other LLGHGs such as methane and chlorofluorocarbons (CFCs) have much higher global warming potential [4],[5]. Regarding anthropogenic CO<sub>2</sub> emissions, industry and petroleum refineries contribute the most [6]. In Sweden, the largest liquid fuel producer is Preem that accounts for 80% of the Swedish refinery capacity. Preem has adopted the strategy to have net zero carbon dioxide emissions from their refineries by 2040 and the same to be applied to its entire value chain by 2045 [7]. In this regard, Preem's plans and investments are designed to address the CO<sub>2</sub> emissions throughout the entire value chain (Well-To-Wheel). Scope 1 includes the direct CO<sub>2</sub> emissions from the refinery sites. Scope 2 is related to the indirect CO<sub>2</sub> emissions from purchased electricity and heating and cooling. Scope 3 encompasses indirect CO<sub>2</sub> emissions from resource extraction, transport, filling stations, business travel, as well as emissions from the end-use of refinery products [7].

Preemraff Lysekil is one of Preem's refineries located in Lysekil municipality [8]. In this thesis, the mitigation of CO<sub>2</sub> emissions is evaluated and modelled with the focus on the Preemraff Lysekil refinery as a case study. Among the candidate measures to significantly reduce emissions, Carbon Capture and Storage (CCS) is a promising technology [9]. There are three industrial scale options for CO<sub>2</sub> capture: post-combustion, pre-combustion and oxyfuel combustion [10]. Among those, post-combustion is a particularly appropriate option for retrofitting since there is no requirement for reconstructing the available facilities [5], [11]. Moreover, transition from fossil-based to renewable feedstock and use of fossil-free hydrogen for production of biofuels [7] as well as energy system integration and process intensification [9] are other possible technical measures for achieving large emissions reduction. In the near future crude oil will still be dominantly used for energy purposes especially in the

transport sector, which in turn accounts for 49% of the world's oil demand [12]. In this regard, co-processing of bio-based feedstocks will enable continued use of existing refinery infrastructures and avoiding the need of constructing new plants while reducing emissions [13].

## **1.2. AIM AND SCOPE**

This thesis aims to develop a methodology to assess proposed measures for mitigation of CO<sub>2</sub> emissions along the refinery value chain, including Scope 1, 2, and part of Scope 3 emissions. The method focuses on analyzing the changes in CO<sub>2</sub> emissions and energy consumption associated with the deployment of Carbon Capture (CC) technology and/or the introduction of bio-based feedstock in the refinery. The objective is to develop the methodology and model such that it can be used to evaluate CO<sub>2</sub> mitigation options in complex refineries. The work was conducted using Preemraff Lysekil refinery as a case study. The results constitute a basis for decision makers to evaluate potential measures that can be implemented to reach the goal of zero fossil carbon emissions by 2045.

The model is generic and easily adaptable for future changes regarding factors such as capacities, improved rate of CC, and reduced energy usage due to increased energy efficiencies and/or process integration. The model provides a platform for the user to decide on the choice of mitigation option(s) to be applied. The model is constructed so that it can capture the interplay of mitigation options instead of investigating just one option in isolation, thereby failing to capture the effect of the combination of different options. The model is able to estimate the effect of different mitigation options, in terms of CO<sub>2</sub> mitigation potential and changes in the energy requirement of the focused refinery. The overall purpose of the model is to reduce time, effort, and costs when evaluating the effects of mitigation options and deciding on the potential measures to be taken.

## **1.3. LIMITATIONS**

This study only investigated one type of CC technology i.e. post-combustion. There are various techniques for post-combustion separation of CO<sub>2</sub> such as absorption by different solvents or by membranes. However, in this research only absorption by Monoethanolamine (MEA) solvent is considered. Moreover, it is assumed that the emissions from the energy supply to satisfy the energy requirements of the carbon capture process are not captured.

Another area of limitation is that capital and operating costs are not considered, which could be significantly influential on the choice of technologies and CO<sub>2</sub> mitigation options or combinations thereof.

A further limitation of the study is related to the quality of data used in the model. For a more precise investigation, data inventory for emissions specific to the case study plant is needed. Data collected from the literature such as CO<sub>2</sub> emission factors related to grid electricity or fuels, or energy requirements of CC facilities may be not sufficiently relevant for the studied system. In addition, the data related to Preemraff

Lysekil refinery (e.g. energy demands of unit operations) is associated with uncertainties since some data could be erroneous due to lack of instrumentation, accuracy in instrumentation (flow, temperature), incorrect physical data in terms of unknown composition, phase change, etc. [14].

#### **1.4. RESEARCH QUESTIONS TO BE ADDRESSED**

This project aims to address the following research questions:

- To what extent could CO<sub>2</sub> emissions be reduced along the entire value chain by applying carbon capture technology at the Preemraff Lysekil refinery?
- Is there a reasonable trade-off between the CO<sub>2</sub> mitigation potential and the increased energy consumption resulting from the implementation of the CO<sub>2</sub> capture process?
- How can the introduction of bio-based feedstock contribute to reducing CO<sub>2</sub> emissions along the value chain?
- How is the refinery energy demand affected by co-processing of bio-based feedstock?
- What is the CO<sub>2</sub> mitigation potential of the combination of carbon capture and bio-feedstock co-processing?
- Does the combination of the two mitigation options lead to an increase or decrease of the refinery energy demand? Is there a satisfactory balance between the amount of CO<sub>2</sub> emissions reduced and the energy demand?



## 2. THEORY

In this research, the focus is on evaluating the effect of different CO<sub>2</sub> mitigation options to be applied to refineries in order to move towards zero emissions. This chapter provides an overview of the refinery process units and the concepts of the selected mitigation options.

### 2.1. PREEMRAFF LYSEKIL REFINERY

Preemraff Lysekil is a complex refinery with a crude oil capacity of 11.4 Mt/year [15] and CO<sub>2</sub> emissions of 1.625 Mt/year [7]. A simplified process flow diagram of the refinery, showing the main process units, is shown in Figure 2-1. Crude oil is distilled in the *Crude Distillation* unit (atmospheric distillation column) to produce gas, naphtha, kerosene, light gas oil, heavy gas oil, and the residue [8], [9]. The gas undergoes further separation and purification resulting in fuel gas that can be used within the refinery, and Liquefied Petroleum Gas (LPG), which is sold or used as gasoline components.

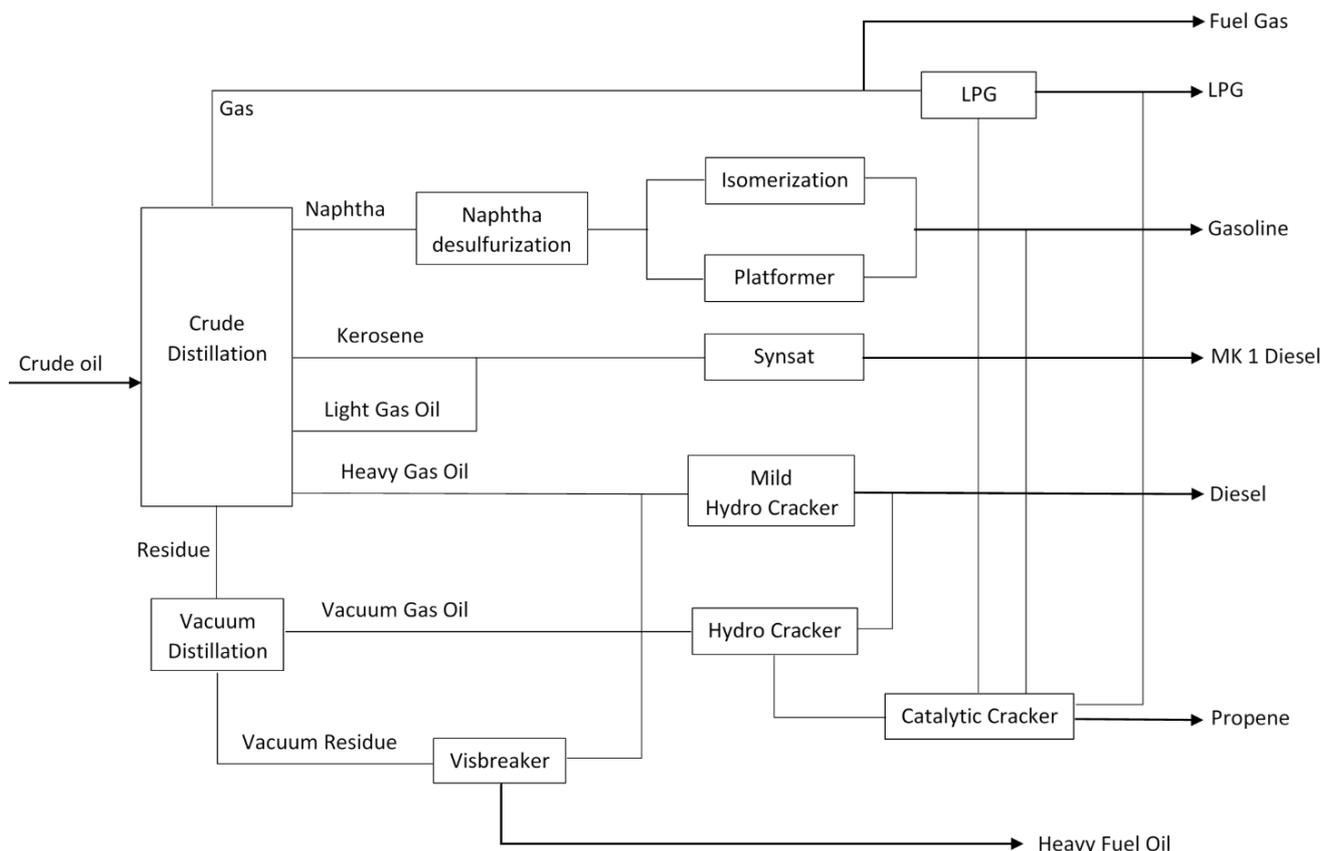


Figure 2-1: Overview of the main process flows at the Preemraff Lysekil refinery (adapted from [8])

Naphtha is hydrotreated in the *Naphtha Desulfurization* unit, where it undergoes catalytic desulfurization and thereafter fractionation by the addition of hydrogen. The lighter fraction is upgraded in the *Isomerization* unit in which linear molecules are transformed into branched molecules with desired octane number, which constitute the

isomerate [8], [9], [16]. The heavier fraction is sent to the *Platformer* which involves catalytic reforming to produce reformat with a higher octane number. Both isomerate and reformat are applied as components to produce gasoline.

The kerosene fraction is sent to the *Synsat* unit (Synergetic saturation unit) where it is desulfurized in order to be blended into diesel. Light and heavy gas oils undergo catalytic desulfurization and dearomatization using hydrogen in the *Synsat* unit and the *Mild Hydro Cracker* (MHC) unit, respectively. The outcome of the MHC unit is used in diesel, and the product from the *Synsat* unit is an important component in Environmental Class 1 diesel fuel (MK1 Diesel).

The “Residue” (residual oil - bottom products) of the “Crude Distillation” column is sent to the “Vacuum Distillation” unit to be further distilled and separated into vacuum gas oil and vacuum residue. The vacuum gas oil is led to the *Hydro Cracker* where desulfurization and cracking take place using hydrogen, after which around 50% of it is turned into products that are lighter and more valuable including diesel and naphtha. The remainder of the vacuum gas oil, after desulfurization, is led to the *Catalytic Cracker* unit to be mainly broken down into gasoline components and to some extent to propene. The vacuum residue is sent to the *Visbreaker* unit where it is upgraded through thermal cracking to lighter products with lower viscosity and higher values, which are separated into heavy gasoil and heavy fuel oil [8], [9], [16].

## 2.2. HYDROGEN PRODUCTION UNIT

In order to fulfil the hydrogen demand in refineries, hydrogen is usually produced in a Hydrogen Production Unit (HPU) [17],[18]. In this research, the HPU is investigated in more detail since it is a large emission source of CO<sub>2</sub>, which makes it suitable for applying CCS. The introduction of bio-based feedstock is expected to affect the hydrogen balance in the refinery. Furthermore, previous studies of emission mitigation measures have been conducted recently for the HPU at the Preemraff Lysekil refinery, thus, significant amounts of data were available for this refinery unit. A schematic block flow diagram of an HPU is illustrated in Figure 2-2.

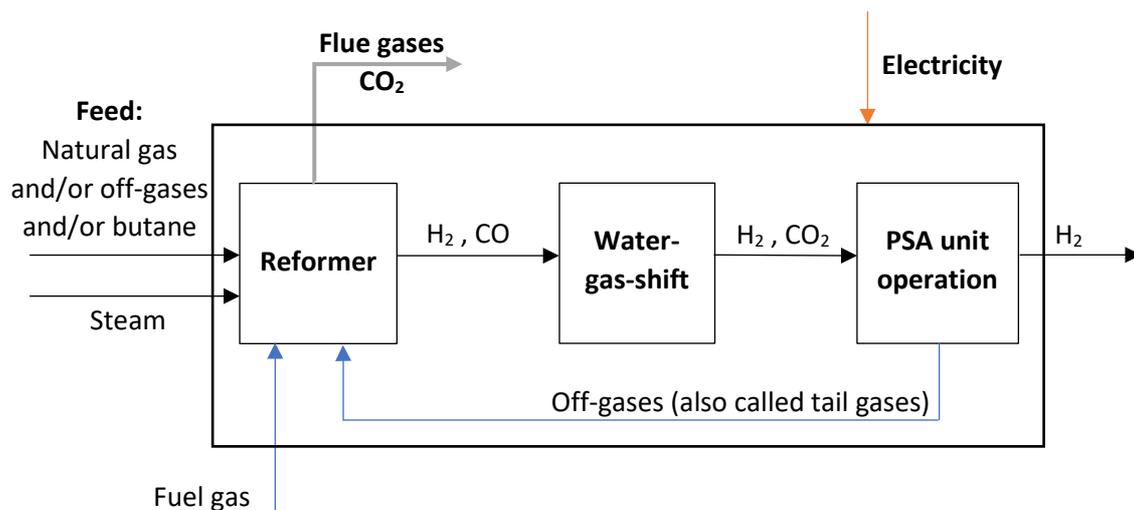
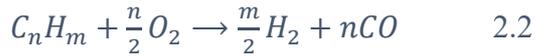
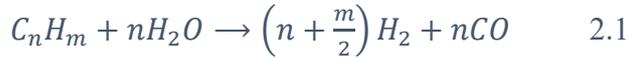
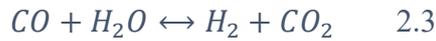


Figure 2-2: Block flow diagram of an HPU based on steam reforming

In the HPU, hydrogen is produced through steam reforming of light hydrocarbons as per Equation 2.1, which is highly endothermic. It could also be produced through partial oxidation based on Equation 2.2, which is an exothermic reaction and can be utilized for heavier hydrocarbons. Hydrogen production can also be achieved by the combination of the two reactions, which is called autothermal reforming (ATR). In ATR, the energy released from the exothermic partial oxidation supplies the energy required by the endothermic steam reforming reaction.



As can be seen in Figure 2-2, fuel gas and tail-gas are typically combusted to supply energy to the reforming process. Reforming is followed by the water-gas-shift reaction based on Equation 2.3, which leads to increased production of hydrogen [17],[18]. Finally, purification of hydrogen is done by separating hydrogen from other gases through pressure-swing adsorption (PSA).



### 2.3. CARBON CAPTURE AND STORAGE

Carbon Capture and Storage (CCS) involves capturing CO<sub>2</sub> from exhaust gases, compressing it to high pressure and transporting it to a certain place for storage [11], [10]. There are three main carbon capture technologies [5], [11], [10]:

**Post-combustion:** After fuel is combusted, CO<sub>2</sub> is separated from the combustion flue gases.

**Pre-combustion:** Before fuel is combusted, it is converted to hydrogen and CO<sub>2</sub>. Thereafter, CO<sub>2</sub> is separated and the obtained hydrogen can be combusted as fuel with no CO<sub>2</sub> emissions.

**Oxyfuel combustion:** Fuel combustion is done with pure oxygen instead of air. Therefore, the generated flue gas is rich in CO<sub>2</sub>, which is then purified.

CO<sub>2</sub> separation can be done through various techniques, which can be categorized under absorption, adsorption, membrane and cryogenics [5], [19]. The proper technique must be selected considering the characteristics of the target flue gas on which carbon capture is supposed to be implemented. For low to medium CO<sub>2</sub> concentrations, as is the case for most refinery flue gases [20], chemical absorption is more suitable. In order to retrofit the existing plants and equip them with CC technology, post-combustion is the prevailing option since no change in the upstream infrastructure is needed. Absorption by MEA is the most mature post-combustion capture technology. MEA absorption has been applied in natural gas refining processes for over half a century. It also has commercialized application for CO<sub>2</sub> removal from combustion flue gases. Therefore, post-combustion based on MEA absorption was selected for carbon capture in this thesis.

## **2.4.CO-PROCESSING OF BIO-BASED FEEDSTOCKS IN EXISTING REFINERIES**

### **2.4.1.Application**

Today, the fulfillment of increasing energy demand relies mostly on fossil-based resources [21]. This results in growing greenhouse gas emissions, depleting fossil sources, and thus, the rise in the price of raw materials [21]. Although there are a number of technologies to decrease CO<sub>2</sub> emissions associated with the oil refining process, user phase is the main contributor to the total emissions within the life cycle of liquid fuels [12]. Use of biomass as an alternative feedstock to crude oil is, therefore, a potential solution in that the released carbon in the use phase of produced biofuels has been consumed in the growth phase of biomass through photosynthesis [12]. On the other hand, renewable nature and extensive availability of biomass makes for huge capabilities worldwide to produce and supply it in a sustainable manner [21].

Petroleum refineries can implement co-processing of bio-based feedstock together with fossil-based feedstock to produce fuels of hybrid origin [21], [22]. This gives the opportunity of utilizing the capacity of well-developed infrastructure of petroleum refineries and avoids the need for high capital investment, at least within the near-term future. In addition, the infrastructure of petroleum refineries is potentially able to process various types of bio-based feedstocks, which makes them flexible with respect to the availability of bio-feedstocks. Moreover, co-processing could result in the production of a variety of biofuels in different ranges such as LPG, gasoline, kerosene, diesel, or fuel oil.

### **2.4.2.Classification of bio-based feedstocks**

Biomass-derived feedstock can be categorized into oleaginous feedstock and carbohydrates [21]. Oleaginous feedstock, also known as lipid-based feedstock [22], mainly consists of triglycerides [21]. Furthermore, hydrolysis of triglycerides releases free fatty acids (FFA), which normally constitute processed and low-grade oleaginous feedstock [21]. Lipids are classified in four groups [21], [22]:

- 1) Edible oils among which the most common are palm oil, rapeseed oil, sunflower oil, and soybean oil
- 2) Non-edible oils such as Jatropha oil, and tall oil
- 3) Residual oils such as waste vegetable oils, waste cooking oils, and animal fats (lard, tallow).
- 4) Algae.

Non-edible oils have the advantage of not competing with food sources. This also applies to algae, which also have the advantage of high lipid content and rate of growth compared to crops used to obtain vegetable oils [23]. While large-scale production of animal fats and vegetable oils are readily achievable, large-scale production of algae is in its infancy [21], [22]. Carbohydrates, as the other category of bio-based feedstock, consist of molecules containing carbon, hydrogen, and oxygen, which have so far found

to be the dominant constituent of biomass [21]. They constitute sources such as sugars, starch mainly derived from crops, and cellulose, hemicellulose and lignin as the main components of lignocellulose. A number of bio-based intermediates can be received from carbohydrates such as pyrolysis bio-oils, hydrothermal liquefaction oils (HTLO), and Fischer-Tropsch (FT) liquids, which are obtained by thermochemical conversion of lignocellulosic feedstocks through pyrolysis, hydrothermal liquefaction (HTL), and gasification respectively [24], [25].

## 2.5.POTENTIAL INSERTION POINTS OF BIO-BASED FEEDSTOCK IN OIL REFINERIES

### 2.5.1.Possible insertion points

Three insertion points are of particular relevance for co-processing bio-based feedstock, as shown in Figure 2-3.

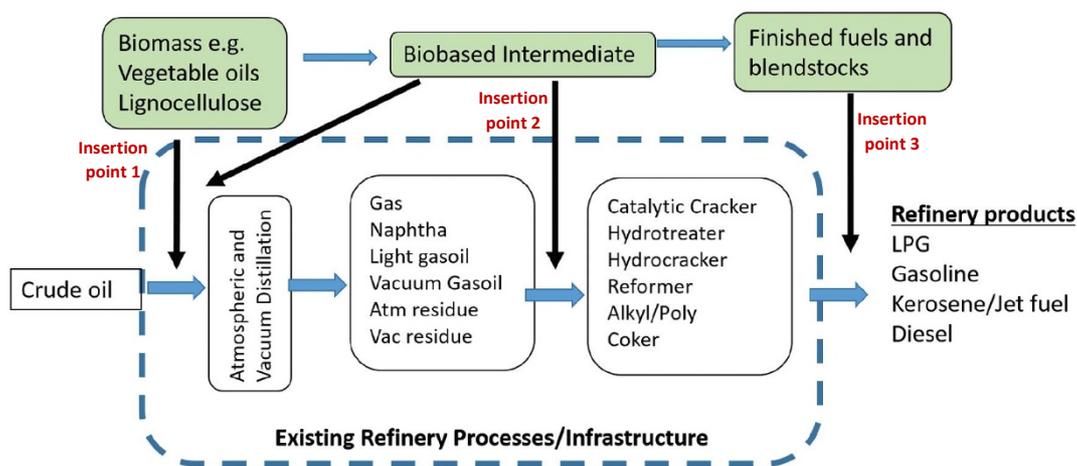


Figure 2-3: Potential insertion points of bio-based feedstock for co-processing in existing refineries (adapted from [26])

These are associated with different levels of risk to the refinery operations [16]. Insertion Point 1 involves feeding bio-derived feedstock to the atmospheric and vacuum distillation units. This is applicable when the characteristics of the bio-feedstock are similar to that of crude oil [26]. Considering that in these units separation is the main operation, and not chemical transformation, bio-feedstock should be almost oxygen-free and with minimal content of reactive species such as olefins, alcohols, carbonyls, and aldehydes [26], [12]. Moreover, this insertion point could lead to spread of contaminants within the whole refinery. Thus, bio-feedstock should not be contaminated. On the other hand, large amounts of non-volatile compounds e.g. sugars and oligomeric phenols are present in many biomass-derived feedstocks, which are problematic for distillation operation. Since bio-feedstocks are not thermally stable, at elevated temperatures polymerization increases resulting in a high level of viscosity and solid residuals. Therefore, blending biomass-derived feedstock with crude oil at Insertion Point 1 poses the highest risk.

Blending biofuels with fossil-based fuels at the Insertion Point 3 is associated with much lower risk since it only affects operations downstream of the main unit operations [16],[26]. Nevertheless, technical challenges as well as high investment costs impede the commercial applicability of the Insertion Point 3 [12]. Insertion Point 2 is applied when bio-based feedstocks are blended with intermediate streams of the refinery in existing unit processes [12]. This could potentially result in lower capital costs and promote upgrading refinery flows to desirable product qualities. This involves medium risk in terms of distribution of oxygenates, impurities and process performance [16].

### **2.5.2.Potential process units**

When considering Insertion point 2, the main possible process units include the fluid catalytic cracking (FCC) and catalytic hydroprocessing which in turn is divided to two categories of catalytic hydrotreating (HDT) and catalytic hydrocracking (HDC) [22]. FCC is usually applied to crack heavy fractions of crude oil i.e. it is typically fed by heavy gas oil, vacuum gas oil or residues. The main products of this process are gasoline and propylene [22], [26].

The HDT process is employed to remove undesirable heteroatoms as well as hydrogenation (saturation) of olefins and limited hydrogenation of aromatic compounds [26], [22]. It includes removal of oxygen, sulfur (hydrodesulfurization, HDS), nitrogen (hydrodenitrogenation, HDN), metals (hydrometalation, HDM), and halide [21], [26]. The feed to HDT includes intermediate flows within the refinery prior to being converted e.g. feed of FCC unit [22]. The catalytic hydrotreating process is exothermic involving high temperatures and pressures using hydrogen [26].

HDC process is utilized to convert heavy fractions to lighter ones with decreased boiling points [16], [22]. Compared with HDT, the feeds to HDC are typically refinery heavier intermediate flows e.g. heavy gas oil and vacuum gas oil. Reactions similar to those in hydrotreater are performed using hydrogen, but under more severe conditions [26]. Normally when there is the need to further decrease the size of bio-feedstock to be upgraded, HDC is applied as a secondary stage. Hydroprocessing has the advantage of being highly flexible in terms of various bio-feedstocks such as lipids and pyrolysis oils [22].



### 3. METHODOLOGY

The purpose of the methodology is to estimate, analyse, and model the changes in CO<sub>2</sub> emissions and energy consumption associated with the two CO<sub>2</sub> mitigation options including CCS and bio-based feedstock. The related procedures are elaborated in this chapter.

#### 3.1. SYSTEM BOUNDARIES

Figure 3-1 shows the system boundary applied in this thesis. The system boundary includes all the refinery operations necessary to convert the feedstock (crude oil or bio-based input) to refined products including the major unit processes as well as CC facilities within the refinery. Since the Preemraff Lysekil refinery is used as a case study in this research, process units are considered as shown in Figure 2-1 as well as the hydrogen production unit (HPU) and utility unit. The boundary is also inclusive of resource extraction for refinery inputs (crude oil, make-up fuel, and bio-feedstock), electricity production and supply to the refinery, CO<sub>2</sub> capture, compression, transport and storage, and the user phase. The analysis accounts for on-site CO<sub>2</sub> emissions and emissions associated with electricity purchased from the grid, the potential of reduction in CO<sub>2</sub> emissions as well as changes in the energy demand in terms of fuel and electricity consumption due to deployment of CCS, bio-based feedstock, or both options as compared to the plant without CCS and using crude oil feedstock. The study focuses on the effects of CO<sub>2</sub> mitigation options in terms of changes in the energy demand of production as well as emissions reduction potential along the value chain, which are aligned with Preem’s Scope 1, 2, and part of Scope 3 as denoted in Figure 3-1. It should be noted that the emissions associated with the processes/activities of CO<sub>2</sub> capture, compression, transport, and storage relate to the CO<sub>2</sub> emissions associated with providing the heat and electricity required by these operations. This choice of system boundary is justified by the fact that the mitigation options are applied in the production stage and that most of the emissions take place in the user phase; approximately 85% of the CO<sub>2</sub> emissions from Preem’s value chain comes from the combustion of fossil fuels in the user phase [7].

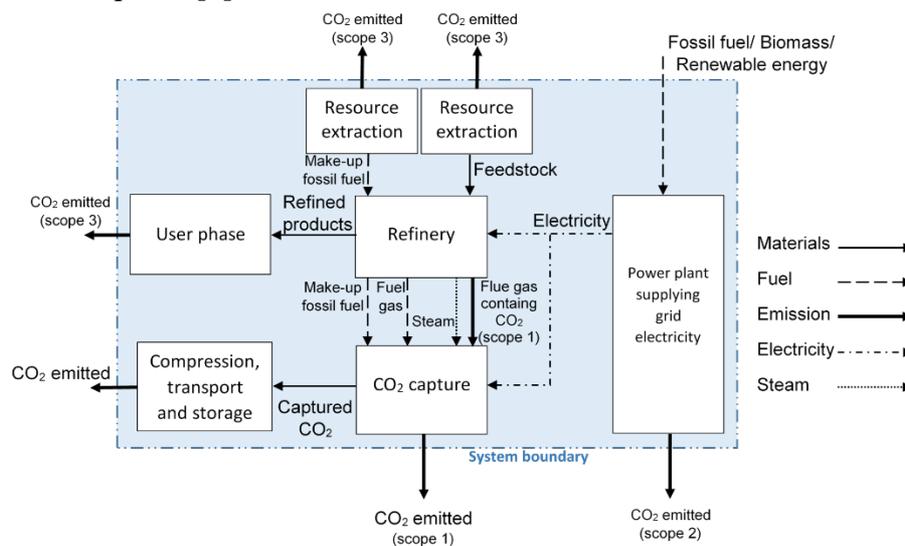


Figure 3-1: System boundary defined in this study

### 3.2. MODELLING

The model to quantify and evaluate different mitigation options was developed in MATLAB. In order to conduct the modelling, first the data required as the input to the model must be collected. Data collection must be adapted to the purpose of its usage [27]. If the precision of required details are not of great importance in the simplified model or they are hard to collect from the case study refinery (e.g. when a mitigation option is not yet applied in practice to have the respective real data), nominal values from literature are sufficient. On the other hand, for specific details of the target refinery real site data needs to be collected. Therefore, since this thesis aims at both a simplified refinery as well as conducting a case study on the Preemraff Lysekil refinery, data was collected from both industry and literature. A bottom-up approach was adopted to build the model so that mass and energy balances were calculated for each process unit of the refinery and used as a basis to build a model of the complete refinery. Within the procedure of modelling, block flow diagrams were applied to depict the structure of aimed units in terms of involved unit operations through representing them by blocks in a simplified input-output diagram; also, to determine the extent of details needed for building the model [27].

The modelling was conducted at several layers (adapted from [27] and [28]). The *micro* layer deals with thermodynamics of reactions and energy balances at a molecular level. The *meso* layer involves mass and energy balances at the level of unit processes. The *macro* layer provides the user interface, which directs the procedure based on the decisions and input from the user side. In this regard, the modelling involves creating several modules (adapted from [28]). The module-based approach provides the possibility to assemble and add different computing procedures and mitigation options to the model. This enables constructing the model in a flexible way so that it can be tuned to the selected mitigation options and any additional mitigation option can be combined with the model in the future. Therefore, the modelling was performed through the following steps:

- Required data was obtained.
- The module for quantifying CO<sub>2</sub> emissions was established on the basis of the method described in Section 3.3.
- The module for CCS was defined following the method under Section 3.4.
- The module for bio-based feedstock mitigation option was created based on the method described in Section 3.5.

Figure 3-2 illustrates the modelling architecture. The algorithm through which the analyses mentioned in Section 3.6 were conducted is depicted in Figure 3-3. Validation of the model was done through comparison of results from modelling with data received from plant and literature.

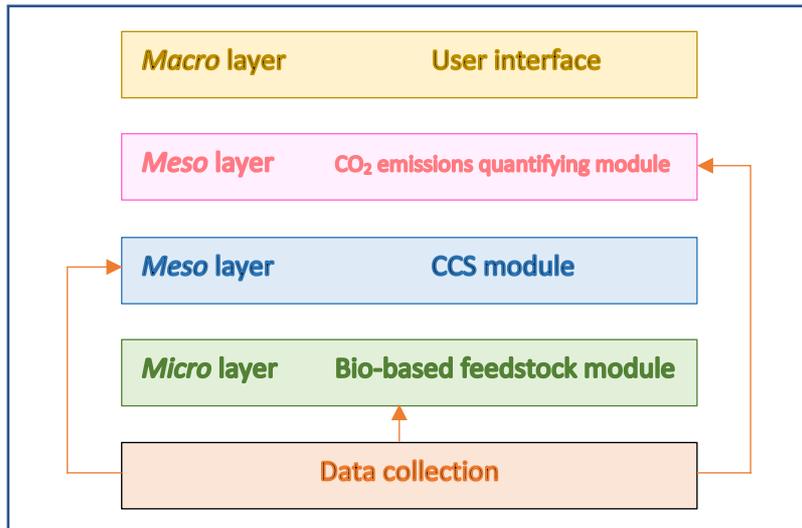


Figure 3-2: Architecture of the modelling.

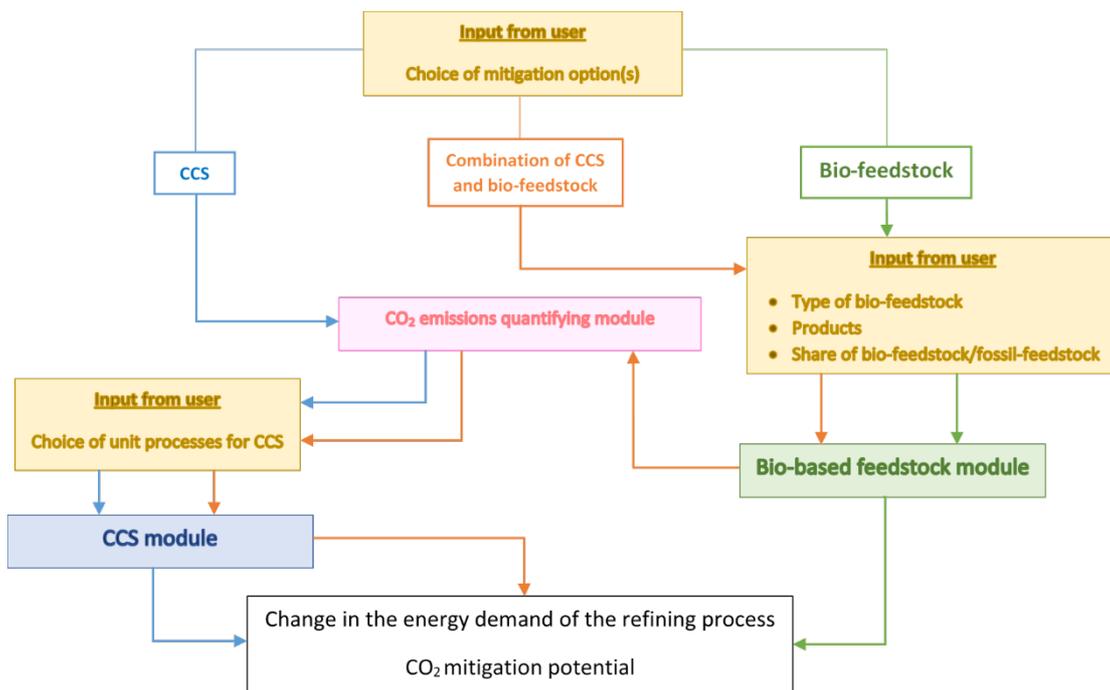


Figure 3-3: Overview of information flow in the model.

### 3.3.METHOD FOR QUANTIFYING CO<sub>2</sub> EMISSIONS

In refineries, CO<sub>2</sub> is emitted from a number of different sources [9]. The emission sources have various flowrates and CO<sub>2</sub> concentrations [9]. The emission points include fired heaters and furnaces available in each process unit, flares, the process units which involve direct emissions of CO<sub>2</sub> (e.g. catalytic cracking unit), and utility systems (e.g. production of steam) [6], [9].

It is assumed that post-combustion CO<sub>2</sub> capture is applied to specific individual CO<sub>2</sub> emission sources, and that the capture facilities are sized to handle the full flue gas streams from these sources. However, the energy supply for CC facilities is associated with generation of emissions, which are accounted for when estimating the mitigation potential of the applied CC technology.

To estimate the amount of CO<sub>2</sub> emitted from different process units within the refinery, a bottom-up model was constructed. In the first step, an Input-Output model was developed for each process unit  $u$  in terms of material, energy, and CO<sub>2</sub> balances. Thereafter, regarding the connected process units within the focused refinery shown in Figure 2-1 as well as the hydrogen production unit (HPU) and utility unit, the model for the whole refinery was built. Finally, the CO<sub>2</sub> reduction potential using CCS was investigated. The details and procedures are elaborated as follows and illustrated in Figure 3-4.

In order to quantify CO<sub>2</sub> emissions in this project and validate the data, among all units within the refinery as described under Section 3.3, hydrogen production unit (HPU) is focused more in detail. This is due to the importance of the unit and the availability of data.

#### Material balances

The material balance for each process unit is modelled based on Equation 3.1 with terms defined in Table 1 [9]:

$$V_{u,p} = \sum_i Y_{u,i,p} \times V_{u,i} \quad 3.1$$

Table 1: Definition of the terms in Equation 3.1

Term	Unit	Denotation	Description
$V_{u,p}$	10 <sup>6</sup> Sm <sup>3</sup> /year <sup>1</sup>	Outputs	Product(s) $p$ of process unit $u$
$V_{u,i}$	10 <sup>6</sup> Sm <sup>3</sup> /year	Inputs	Input(s) $i$ to process unit $u$
$Y_{u,i,p}$	%	Volume yields	Corresponding to the production of product $p$ in the unit process $u$ with the input $i$

<sup>1</sup> Standard cubic meter per year

Regarding Equation 3.1, the material balances require the data related to yield of each product in terms of each input. Since such data is usually not accessible in practice, the data collection was conducted on energy consumption level, which is described hereafter, knowing that the fuel consumptions of units are directly connected to the material balance and any change in the throughput of a unit process would directly affect its fuel consumption. Therefore, the model's ability to handle variable material flows is maintained.

## Energy balances

The energy consumption of each process unit depicted in Figure 2-1 as well as the utility system is estimated on the basis of the material balance and fuel consumption factors, which are thereafter combined to yield the total energy consumption ( $TE$ :  $10^6$  GJ/year) according to Equation 3.2, which is defined in Table 2 [9]. Since electricity consumption is normally reported in GWh/year, to facilitate data collection and input to the model, the same unit is used for the input, but the factor  $3.6/10^3$  is embedded in the equation to convert it to  $10^6$  GJ/year.

$$TE = \sum_u \sum_f FC_{u,f} + \sum_u \sum_E EC_u \times Sh_E / OE_E \times 3.6/10^3 \quad 3.2$$

Table 2: Definition of the terms in Equation 3.2

Term	Unit	Denotation	Description
$FC_{u,f}$	$10^6$ GJ/year	Fuel consumption	Consumption of fuel $f^1$ in process unit $u$
$\sum_u \sum_f FC_{u,f}$	$10^6$ GJ/year	Fuel consumption	Consumption of fuel $f$ in all the process units shown in Figure 2-1, the HPU and utility unit
$EC_u$	GWh/year	Electricity consumption	Electricity consumption of each process unit $u$
$Sh_E$	%	Share of electricity	Supplied from different sources of power, $E^2$
$OE_E$	%	Overall efficiency	Inclusive of generation, transmission and distribution of electricity supplied from each source of power, $E$
$TE$	$10^6$ GJ/year	Total energy consumption	Related to all the process units shown in Figure 2-1, the HPU and utility unit

<sup>1</sup> Fuel  $f$  includes refinery by-products that are potentially used as fuels for different process units (e.g. methane, ethane) and fossil fuels.

<sup>2</sup> This can be electricity purchased from grid or electricity generated on-site.

## CO<sub>2</sub> balances

CO<sub>2</sub> emissions from different process units and the utility system are estimated using the emission factors for the different fuels (fossil fuels and refinery by-products) consumed within the units and the energy consumption obtained from the energy balance(s). Thus, the amount of CO<sub>2</sub> emissions associated with each process unit  $u$  within the scope of this project ( $Em_u$ :  $10^6$  t/year) is calculated based on Equation 3.3 with terms described in Table 3 (adapted from [9]).

$$Em_u = \sum_{bp} EF_{bp} \times LHV_{bp} \times V_{u,bp} + [\sum_f (FC_{u,f} \times EF_f) - \sum_{bp} (V_{u,bp} \times LHV_{bp} \times EF_{bp}) + \sum_f (EC_u \times \frac{Sh_E}{OE_E} \times \frac{3.6}{10^3} \times EF_f)] \quad 3.3$$

The first term in Equation 3.3 is related to the CO<sub>2</sub> emissions from refinery by-products used as fuel, which are part of the on-site emissions framed in Scope 1. The combination of the remaining terms in this equation is related to the CO<sub>2</sub> emissions due to combusting purchased fossil fuels for satisfying the heat demand as well as fossil fuel usage for generation of required power for each unit. The second and third terms account for the CO<sub>2</sub> emissions from purchased fossil fuels that are combusted in the refinery to fulfil the energy demands, which are part of the on-site emissions reflecting

Scope 1. The fourth term is related to the CO<sub>2</sub> emissions from purchased fossil fuels combusted for electricity generation. These emissions are inclusive of the on-site emissions (Scope 1) when the power generation is taking place in the refinery as well as the offsite emissions (Scope 2) for the power generated outside of the refinery and purchased from the grid.

Regarding the scope of this project to account for CO<sub>2</sub> emissions along the value chain of refinery products, CO<sub>2</sub> emissions from resource extraction (Scope 3) and user phase (Scope 3) must be considered as well. The CO<sub>2</sub> emissions from resource extraction ( $Em_{RE}$ : 10<sup>6</sup> t/year) can be calculated from the data available in the literature. The CO<sub>2</sub> emissions from combustion of refinery products (fuels) in the user phase ( $Em_{UP}$ : 10<sup>6</sup> t/year) can be estimated based on Equation 3.4 defined in Table 3.

$$Em_{UP} = \sum_p EF_p \times V_p \quad 3.4$$

Therefore the total emissions of CO<sub>2</sub> ( $TEm$ : 10<sup>6</sup> t/year) within the system boundary of this study is obtained by Equation 3.5, and the terms are also defined in Table 3.

$$TEm = \sum_u(Em_u) + Em_{RE} + Em_{UP} \quad 3.5$$

Table 3: Definition of terms in Equation 3.3, Equation 3.4 and Equation 3.5

Term	Unit	Denotation	Description
$V_{u,bp}$	10 <sup>6</sup> Sm <sup>3</sup> /year	Volume of byproduct <sup>l</sup>	Related to refinery by-product $bp$ of process unit $u$
$LHV_{bp}$	GJ/Sm <sup>3</sup>	Lower Heating Value (LHV)	Related to by-product $bp$
$EF_{bp}$	tCO <sub>2</sub> /GJ	Emission factor	Related to by-product $bp$
$EF_f$	tCO <sub>2</sub> /GJ	Emission factor	Related to fossil fuel ( $f$ )
$Em_u$	10 <sup>6</sup> t/year	CO <sub>2</sub> emissions	Associated with each process unit $u$
$EF_p$	tCO <sub>2</sub> /Sm <sup>3</sup>	Emission factor	Related to product $p$
$V_p$	10 <sup>6</sup> Sm <sup>3</sup> /year	Volume of product	Related to refinery product $p$
$Em_{UP}$	10 <sup>6</sup> t/year	CO <sub>2</sub> emissions	From user phase
$Em_{RE}$	10 <sup>6</sup> t/year	CO <sub>2</sub> emissions	From resource extraction phase
$TEm$	10 <sup>6</sup> t/year	CO <sub>2</sub> emissions	From value chain inclusive of emissions associated with all the unit processes shown in Figure 2-1, the HPU and utility unit

<sup>l</sup> By-product  $bp$ , which is used as a fuel, e.g. methane and ethane

The on-site CO<sub>2</sub> emissions (Scope 1) do not include the emissions associated with electricity purchased from the grid (Scope 2) and other emissions within the value chain of refinery products (Scope 2 and 3). Therefore, on-site CO<sub>2</sub> emissions from each process unit  $u$  ( $Em_{u,on-site}$ : 10<sup>6</sup> t/year) and in total ( $TEm_{on-site}$ : 10<sup>6</sup> t/year) are calculated based on Equation 3.6 and Equation 3.7 according to the definitions presented in Table 4.

$$Em_{u,on-site} = \sum_{bp} EF_{bp} \times LHV_{bp} \times V_{u,bp} + [\sum_f (FC_{u,f} \times EF_f) - \sum_{bp} (V_{u,bp} \times LHV_{bp} \times EF_{bp}) + \sum_f (EC_u \times \frac{Sh_E}{OE_E} \times EF_f - EC_u \times \frac{Sh_{grid}}{OE_{grid}} \times EF_f)] \quad 3.6$$

$$TEm_{on-site} = \sum_u (Em_{u,on-site}) \quad 3.7$$

Table 4: Definition of terms in Equation 3.6 and Equation 3.7

Term	Unit	Denotation	Description
$Sh_{grid}$	%	Share of electricity	Supplied from the grid
$OE_{grid}$	%	Grid overall efficiency	Inclusive of generation, transmission and distribution of grid electricity
$Em_{u,on-site}$	$10^6$ t/year	On-site CO <sub>2</sub> emissions	From each unit process $u$
$TEm_{on-site}$	$10^6$ t/year	Total on-site CO <sub>2</sub> emissions	From all the unit processes shown in Figure 2-1, HPU and utility unit

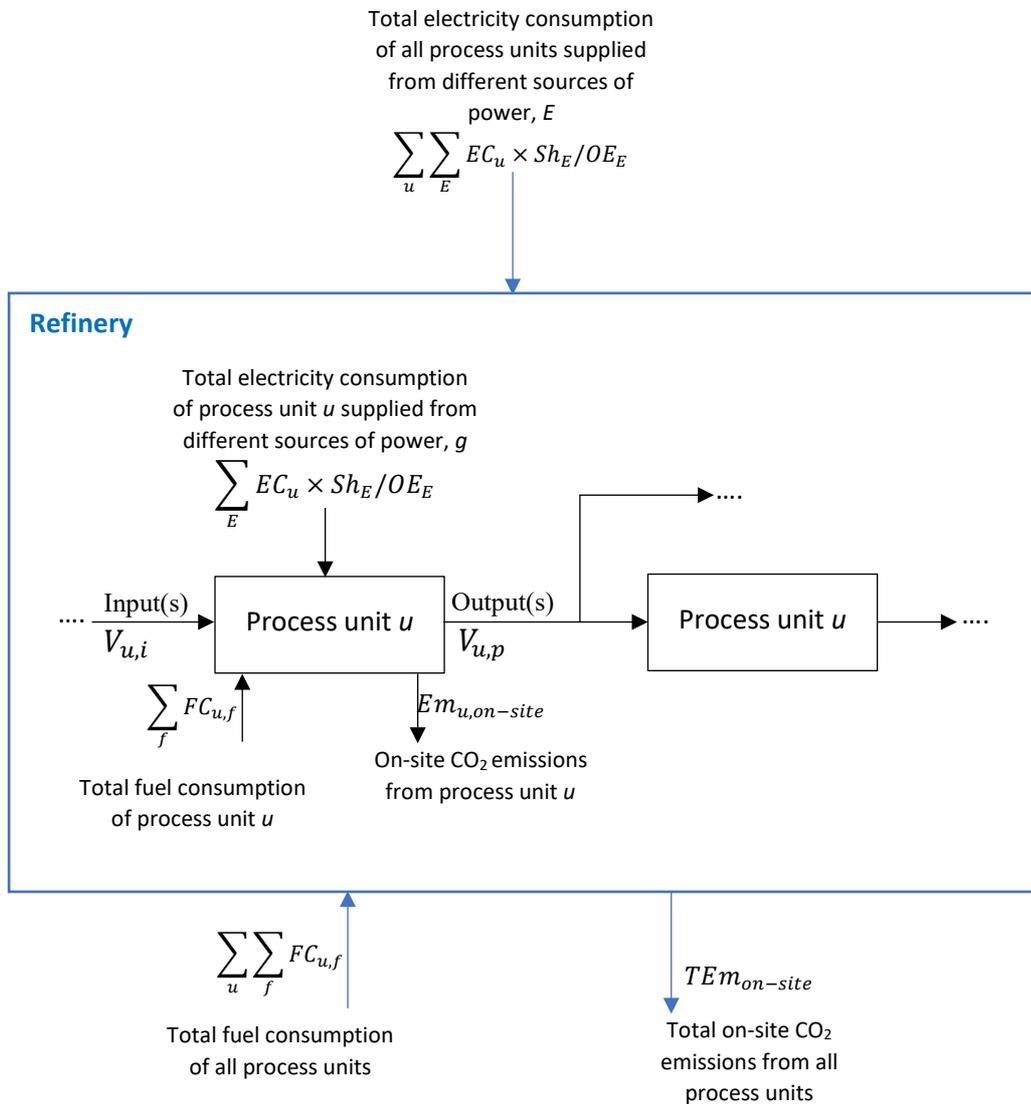


Figure 3-4: Bottom-up model construction based on material, energy and CO<sub>2</sub> balances.

### 3.4. METHOD FOR QUANTIFYING THE CO<sub>2</sub> MITIGATION POTENTIAL OF IMPLEMENTING CARBON CAPTURE AND STORAGE (CCS) TECHNOLOGY

In order to quantify the CO<sub>2</sub> mitigation potential using CCS technology, it is first necessary to quantify the amount of on-site CO<sub>2</sub> emissions through the method described in Section 3.3. Thereafter, it can be decided which process units can be equipped with CCS technology. Then the amount of captured CO<sub>2</sub> can be calculated according to Equation 3.8 with terms defined in Table 5.

$$CP = \sum_u Sel. Em_{u,on-site} \times CR_u \quad 3.8$$

The energy consumption of the CC technology itself leads to CO<sub>2</sub> emissions, which are not captured in this study as mentioned previously. Thus, it is shown as a fuel penalty, which can be estimated based on literature data. In addition, there are CO<sub>2</sub> emissions due to transport and storage of the captured CO<sub>2</sub>, which can be obtained from the literature as well. Therefore, the CO<sub>2</sub> mitigation potential ( $Cmp$ : 10<sup>6</sup> t/year) is estimated by Equation 3.9 described in Table 5.

$$Cmp = CP \times (1 - FP \times EF_f - Em_{CS}) - Em_{REMake-up f} = CP \times (1 - FP \times EF_f - Em_{CS}) - (CP \times FP \times SpecEm_{Make-up f}) \quad 3.9$$

The addition to the energy demand of the refinery in focus is due to the energy consumption of CCS i.e.  $En_{CCS}$  (GJ/year), which can be derived from Equation 3.10, also defined in Table 5.

$$En_{CCS} = CP \times FP \quad 3.10$$

Table 5: Definition of terms in the Equation 3.8, Equation 3.9, and Equation 3.10

Term	Unit	Denotation	Description
$CP$	10 <sup>6</sup> t/year	Captured CO <sub>2</sub> emissions	Using CC technology
$Sel. Em_{u,on-site}$	10 <sup>6</sup> t/year	On-site CO <sub>2</sub> emissions	Related to the selected process unit $u$ for applying CC technology
$CR_u$	%	Capture rate	Related to the applied CC technology to each unit process $u$ , which can be obtained by consulting literature
$Cmp$	10 <sup>6</sup> t/year	CO <sub>2</sub> mitigation potential	Related to the applied CC technology
$FP$	GJ/t CO <sub>2</sub>	Fuel penalty	The energy consumption of the applied CC technology
$Em_{CS}$	t/t CO <sub>2</sub>	CO <sub>2</sub> emissions	Related to transport and storage of the captured CO <sub>2</sub>
$En_{CCS}$	10 <sup>6</sup> GJ/year	Addition to the energy demand of the refinery of focus	Due to the energy consumption of CCS
$Em_{REMake-up f}$	10 <sup>6</sup> t/year	CO <sub>2</sub> emissions	From the resource extraction phase of make-up fossil fuel ( $f$ )
$SpecEm_{Make-up f}$	tCO <sub>2</sub> /GJ	Specific CO <sub>2</sub> emissions	Related to the resource extraction phase of make-up fossil fuel ( $f$ )

### 3.5.METHOD FOR QUANTIFYING THE CO<sub>2</sub> MITIGATION POTENTIAL OF CO-PROCESSING BIO-BASED FEEDSTOCK

The type of bio-feedstock that was considered in this research is lipid-based, as described under Section 2.4. The input data for the calculations relate primarily to rapeseed oil. This is because it is used as one of the common lipids for co-processing [22] as well as being used in the Preemraff Lysekil refinery for this purpose. The hydrotreating unit is a suitable insertion point for vegetable oils [12] such as rapeseed oil. Among all possible insertion points, hydrotreating has been commercialized [12], which is also applied for upgrading rapeseed oil in the Preemraff Lysekil refinery. Therefore, in this study the insertion point of focus is the hydrotreating unit.

#### 3.5.1.Composition

The category of oleaginous/lipid-based feedstock mainly consists of triglycerides [29]. Triglyceride in turn is an ester formed by the combination of glycerol and fatty acids [18]. Thus, the composition of lipids can be defined by fatty acids as model compounds and their representative triglycerides [23]. The typical composition of rapeseed oil is shown in terms of fatty acids in Table 6.

Table 6: Composition of rapeseed oil (wt%) in terms of fatty acids [29], [30]

Fatty acid	Structure <sup>1</sup>	Refined rapeseed oil composition (wt%)
Myristic acid	C14:0	0.06
Myristoleic acid	C14:1	0.00
Palmitic acid	C16:0	4.64
Palmitoleic acid	C16:1	0.24
Stearic acid	C18:0	1.96
Oleic acid	C18:1	63.47
Linoleic acid	C18:2	20.01
Linolenic acid	C18:3	6.97
Arachydic acid	C20:0	0.60
Arachidonic acid	C20:1	1.18
Behenic acid	C22:0	0.15
Erucic acid	C22:1	0.07
Lignoceric acid	C24:0	0.13
Nervonic acid	C24:1	0.14

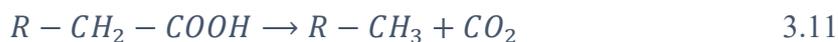
<sup>1</sup> Cx:y is a fatty acid with x carbon atoms and y double bonds

Vegetable oils and animal fats can contain other compounds such as metals, phospholipids, polyphenols, and sterols to a minor extent and thus, need to be pretreated to avoid negative effects on the activity of catalysts [29], [23]. This leads to refined oils rich in triglycerides by more than 99%.

#### 3.5.2.Reaction pathways

The major heteroatom in bio-based feedstock is oxygen [26]. Thus, upgrading mainly involves removing oxygen, which lowers the energy intensity. This is done through

decarboxylation, decarbonylation, and hydrodeoxygenation. The aforementioned reactions for fatty acids in the lipid-based feedstock are shown respectively as follows:



In addition to the aforementioned deoxygenation reactions, methanation is an important side reaction that takes place according to Equation 3.14 [29],[31].



Another side reaction taking place is as per Equation 3.15 [29],[31].



During hydrotreating, hydrogenation and deoxygenation take place [18]. Also, using hydrogen, the model triglycerides are decomposed to fatty acids [23]. Regarding the main fatty acids in rapeseed oil, the corresponding model triglycerides are described in Table 7.

Table 7: The main fatty acids and corresponding triglycerides constituting rapeseed oil

Fatty acid	Structure	Formula	Corresponding triglycerides	Formula
Oleic acid	C18:1	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	Triolein	C <sub>57</sub> H <sub>104</sub> O <sub>6</sub>
Linoleic acid	C18:2	C <sub>18</sub> H <sub>32</sub> O <sub>2</sub>	Trilinolein	C <sub>57</sub> H <sub>98</sub> O <sub>6</sub>
Linolenic acid	C18:3	C <sub>18</sub> H <sub>30</sub> O <sub>2</sub>	Trilinolein	C <sub>57</sub> H <sub>92</sub> O <sub>6</sub>
Palmitic acid	C16:0	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	Tripalmitin	C <sub>51</sub> H <sub>98</sub> O <sub>6</sub>

The decomposition of model triglycerides to the associated fatty acids is assumed to follow the general reaction as below [23]:



The reaction pathways regarding the main triglyceride constituting rapeseed oil, triolein, are shown in Table 8.

Table 8: The reaction pathways of the main model compound constituting rapeseed oil (adapted from [23],[18])

Reaction	Description
$C_{57}H_{104}O_6 + 3H_2 \rightarrow C_{57}H_{110}O_6$	Hydrogenation
$C_{57}H_{110}O_6 + 3H_2 \rightarrow 3C_{18}H_{36}O_2 + C_3H_8$	Decomposition of triglycerides to fatty acids
$C_{18}H_{36}O_2 \rightarrow n - C17 + CO_2$	Decarboxylation
$C_{18}H_{36}O_2 + H_2 \rightarrow n - C17 + CO + H_2O$	Decarbonylation
$C_{18}H_{36}O_2 + 3H_2 \rightarrow n - C18 + 2H_2O$	Hydrodeoxygenation

## Material balances

A simplified schematic block flow diagram of a hydrotreating unit is illustrated in Figure 3-5. The method accounts for the changes made by the bio-feedstock when added to the fossil-based feedstock for co-processing. Thus, the calculations focus on the bio-share of the system.

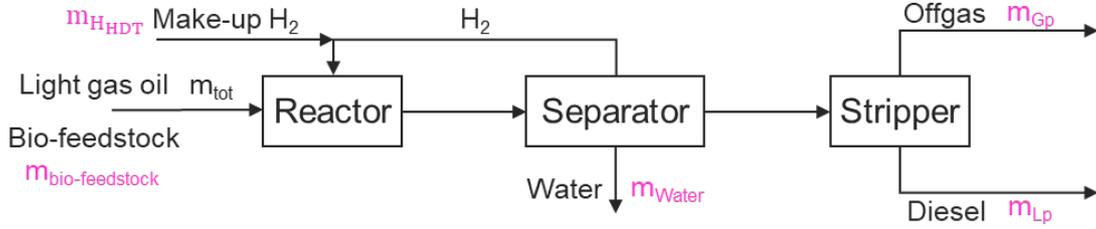


Figure 3-5: Simplified schematic block flow diagram of a hydrotreating unit

Regarding the ratio of bio-based feedstock to fossil-based feedstock ( $w_{\text{bio-feedstock}}$ ), the mass flow of the former is obtained by Equation 3.17. The description of the terms in Equation 3.17 to Equation 3.22 is provided in Table 9.

$$m_{\text{bio-feedstock}} = w_{\text{bio-feedstock}} \cdot m_{\text{tot}} \quad 3.17$$

The lipid-based feedstock to the hydrotreating unit is converted to liquid and gaseous mixtures of compounds [29]. The mass flow of liquid product is obtained based on Equation 3.18. In addition, water generated due to hydrotreating is separated and its mass flow can be estimated based on Equation 3.19. The yields of liquid product and water generation can be obtained by consulting the experimental results in the literature for similar process conditions. Since the mass flow of hydrogen required for hydrotreating of lipid-based feedstock in these equations is unknown and is supposed to be calculated by the proposed method, the method is based on an iterative calculation in which first an estimate is considered for the aforementioned hydrogen consumption. The calculated hydrogen consumption for hydrotreating of lipid-based feedstock is then compared with the estimate and if they are not in agreement, a revised estimate is used until a common value for the hydrogen consumption is received.

$$m_{Lp} = (m_{\text{bio-feedstock}} + m_{H_{HDT}}) \cdot Y_{LP} \quad 3.18$$

$$m_{\text{water}} = (m_{\text{bio-feedstock}} + m_{H_{HDT}}) \cdot Y_{\text{water}} \quad 3.19$$

Using the mass balance regarding the input lipid-based feedstock and hydrogen as well as products as shown in Equation 3.20, the mass flow of gaseous product can be calculated.

$$m_{\text{bio-feedstock}} + m_{H_{HDT}} = m_{\text{water}} + m_{Lp} + m_{Gp} \quad 3.20$$

The amount of hydrogen required for hydrogenation of double bounds in the lipid-based feedstock is calculated by Equation 3.21 (adapted from [31]).

$$mol_{H_{DB}} = \frac{m_{\text{bio-feedstock}}}{M_{\text{bio-feedstock}}} \cdot N_{DB} \quad 3.21$$

Table 9: Definition of terms in Equation 3.17 to Equation Equation 3.22

Term	Unit	Denotation	Description
$m_{bio-feedstock}$	$10^6$ t/year	Mass flow	Related to the bio-based feedstock
$w_{bio-feedstock}$	%	Weight fraction	Related to the bio-based feedstock in the liquid input to the process unit
$m_{tot}$	$10^6$ t/year	Mass flow	Total liquid input to the unit process
$m_{LP}$	$10^6$ t/year	Mass flow	Liquid product of hydrotreating the bio-based feedstock
$Y_{LP}$	%	Yield	Related to the liquid product of hydrotreating the bio-based feedstock
$m_{H_{HDT}}$	$10^6$ t/year	Total hydrogen consumption	Due to hydrotreating of the lipid-based feedstock
$m_{water}$	$10^6$ t/year	Mass flow	Water produced through hydrotreating the bio-feedstock
$Y_{water}$	%	Yield	Related to water produced through hydrotreating the bio-feedstock
$m_{GP}$	$10^6$ t/year	Mass flow	Gaseous product of hydrotreating the bio-based feedstock
$mol_{H_{DB}}$	$10^6$ mole/year	Hydrogen consumption	For hydrogenation of double bounds in the lipid-based feedstock
$M_{bio-feedstock}$	t/mole	Molar mass	For lipid-based feedstock
$N_{DB}$	-	Number of double bounds	Available in 1 mole of the lipid-based feedstock
$DB_{FA}$	-	Number of double bounds	Available in 1 mole of the fatty acid $FA$
$x_{FA}$	%	Molar fraction	Related to fatty acid $FA$
$M_C$	t/mole	Molar mass	Carbon
$M_H$	t/mole	Molar mass	Hydrogen
$M_O$	t/mole	Molar mass	Oxygen
$C_{FA}$	-	Number of carbon atoms	In fatty acid $FA$
$H_{FA}$	-	Number of hydrogen atoms	In fatty acid $FA$

The number of double bounds available in 1 mole of the lipid-based feedstock is derived by Equation 3.22.

$$N_{DB} = \sum_{FA} DB_{FA} \cdot x_{FA} \quad 3.22$$

The molar mass of the lipid-based feedstock is estimated by Equation 3.23 (adapted from [31]).

$$M_{bio-feedstock} = \sum_{FA} (3M_C + 5M_H) \cdot \frac{x_{FA}}{3} + \sum_{FA} x_{FA} (C_{FA} \cdot M_C + H_{FA} \cdot M_H + 2 \cdot M_O) \quad 3.23$$

In addition, the hydrogen consumption for decomposition of the triglycerides in the lipid-based feedstock into the corresponding fatty acids is derived by Equation 3.24. The equation is defined considering that based on Equation 3.16, the number of moles of hydrogen consumed for decomposition of a triglyceride equals the number of moles of fatty acids formed. The terms in Equation 3.23 to Equation 3.35 are defined in Table 10.

$$mol_{H_{DC}} = \sum_{FA} x_{FA} \cdot \frac{m_{bio-feedstock}}{M_{bio-feedstock}} \quad 3.24$$

Similarly, the number of moles of propane that are formed due to the decomposition of triglycerides can be accounted according to Equation 3.25.

$$n_{Propane} = \sum_{FA} \frac{x_{FA}}{3} \cdot \frac{m_{bio-feedstock}}{M_{bio-feedstock}} \quad 3.25$$

Based on Equation 3.13, each mole of fatty acid is deoxygenated through hydrodeoxygenation using 3 moles of hydrogen. Therefore, the hydrogen consumption by hydrodeoxygenation is estimated by Equation 3.26.

$$mol_{H_{HDO}} = 3 \cdot \sum_{C_i} w_{C_i}^{Lp} \cdot \frac{m_{Lp}}{M_{C_i}} \quad 3.26$$

The mass flow of methane resulted from methanation is obtained by Equation 3.27.

$$m_{Me}^{Metn} = w_{Me} \cdot m_{Gp} \quad 3.27$$

Considering Equation 3.14, the hydrogen consumption related to methanation reaction is estimated by Equation 3.28 (adapted from [31]).

$$mol_{H_{Metn}} = 3 \cdot \frac{m_{Me}^{Metn}}{M_{Me}} \quad 3.28$$

The share of  $C_{i-1}$  n-alkanes that are received through decarbonylation is accounted as per Equation 3.29 (adapted from [31]).

$$Sh_{DCn} = \frac{n_{CO}}{n_{CO_2} + n_{CO}} \quad 3.29$$

The CO that is formed through decarbonylation reaction is partly converted to methane by the methanation reaction. Thus, the molar flow of CO due to deoxygenation of the lipid-based feedstock is calculated as per Equation 3.30 [31].

$$n_{CO} = n_{CO}^{Gp} + n_{CO}^{Metn} \quad 3.30$$

The molar flow of CO in the gaseous product is received by Equation 3.31.

$$n_{CO}^{Gp} = w_{CO} \cdot \frac{m_{Gp}}{M_{CO}} \quad 3.31$$

The molar flow of the methanized CO is equal to the molar flow of methane that is received according to Equation 3.32 [31].

$$n_{CO}^{Metn} = n_{Me}^{Metn} = \frac{m_{Me}^{Metn}}{M_{Me}} \quad 3.32$$

In addition, to decarbonylation, CO can be formed by the side reaction as per Equation 3.15. Based on Equation 3.11 each mole of fatty acid is deoxygenated through decarboxylation without using hydrogen. Thus, for each mole of  $CO_2$  formed by decarboxylation that is converted to CO according to Equation 3.15, 1 mole of hydrogen is consumed. Since generation of 1 mole of CO by decarbonylation also consumes 1 mole of hydrogen, in order to calculate the corresponding hydrogen consumption all the generated CO is attributed to decarbonylation. Therefore, total  $CO_2$  formed by decarboxylation based on Equation 3.11 is assumed to be the amount of  $CO_2$  available in the gaseous product. The molar flow of  $CO_2$  can be estimated by Equation 3.33.

$$n_{CO_2} = n_{CO_2}^{Gp} = w_{CO_2} \cdot \frac{m_{Gp}}{M_{CO_2}} \quad 3.33$$

Based on Equation 3.12, each mole of fatty acid is deoxygenated through decarbonylation using 1 mole of hydrogen. Therefore, the hydrogen consumption by decarbonylation is estimated by Equation 3.34.

$$mol_{H_{DCn}} = \sum_{C_{i-1}} w_{C_{i-1}}^{Lp} \cdot \frac{m_{Lp}}{M_{C_{i-1}}} \cdot Sh_{DCn} \quad 3.34$$

The total hydrogen consumption due to hydrotreating of the lipid-based feedstock is estimated by Equation 3.35.

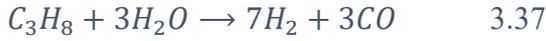
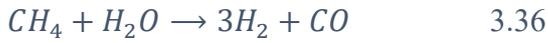
$$mol_{H_{HDT}} = mol_{H_{DB}} + mol_{H_{DC}} + mol_{H_{HDO}} + mol_{H_{DCn}} + mol_{H_{Metn}} \quad 3.35$$

Table 10: Definition of terms in Equation 3.23 to Equation 3.35

Term	Unit	Denotation	Description
$mol_{H_{DC}}$	$10^6$ mole/year	Hydrogen consumption	For decomposition of triglycerides in the lipid-based feedstock into the corresponding fatty acids
$n_{Propane}$	$10^6$ mole/year	Molar flow	For propane in the gaseous product
$mol_{H_{HDO}}$	$10^6$ mole/year	Hydrogen consumption	Resulted from hydrodeoxygenation
$w_{C_i}^{Lp}$	%	Weight fraction	For n-alkane with $C_i$ carbons in the liquid product
$M_{C_i}$	t/mole	Molar mass	For $C_i$ n-alkane in the liquid product
$m_{Me}^{Metn}$	$10^6$ t/year	Mass flow	For methane formed by methanation
$w_{Me}$	%	Weight fraction	Related to methane in the gaseous product
$mol_{H_{Metn}}$	$10^6$ mole/year	Hydrogen consumption	For methanation
$M_{Me}$	t/mole	Molar mass	Methane
$Sh_{DCn}$	%	Share of decarbonylation	Share of $C_{i-1}$ n-alkanes that are received through decarbonylation
$n_{CO}$	$10^6$ mole/year	Molar flow	For CO produced by decarbonylation of the lipid-based feedstock
$n_{CO_2}$	$10^6$ mole/year	Molar flow	For CO <sub>2</sub> produced by decarboxylation of the lipid-based feedstock
$n_{CO_2}^{Gp}$	$10^6$ mole/year	Molar flow	For CO <sub>2</sub> in the gaseous product
$w_{CO_2}$	%	Weight fraction	For CO <sub>2</sub> in the gaseous product
$M_{CO_2}$	t/mole	Molar mass	CO <sub>2</sub> (carbon dioxide)
$n_{CO}^{Gp}$	$10^6$ mole/year	Molar flow	For CO in the gaseous product
$w_{CO}$	%	Weight fraction	For CO in the gaseous product
$M_{CO}$	t/mole	Molar mass	CO (carbon monoxide)
$n_{CO}^{Metn}$	$10^6$ mole/year	Molar flow	Related to the methanized CO
$n_{Me}^{Metn}$	$10^6$ mole/year	Molar flow	For methane in the gaseous product
$mol_{H_{DCn}}$	$10^6$ mole/year	Hydrogen consumption	For decarbonylation
$w_{C_{i-1}}^{Lp}$	%	Weight fraction	For n-alkane with $C_{i-1}$ carbons in the liquid product
$M_{C_{i-1}}$	t/mole	Molar mass	For $C_{i-1}$ n-alkane in the liquid product
$mol_{H_{HDT}}$	$10^6$ mole/year	Total hydrogen consumption	Due to hydrotreating of the lipid-based feedstock

## Energy balances

The changes in the energy demand of the refining process is mainly caused by the additional hydrogen consumption due to hydrotreating the bio-share of the feedstock, which must be supplied by the HPU. The hydrogen consumption for hydrotreating lipid-based feedstock is much higher than that of fossil-based feedstock [31], [32]. On the other hand, for the common ranges of co-processing, the major part of the liquid feed to a hydrotreating unit is fossil-based. Therefore, the major change in hydrogen consumption is due to hydrotreating of bio-share. Hence, the change in the hydrogen consumption of fossil-based feedstock is neglected. The gaseous product of lipid-based feedstock contains methane and propane that can be used for hydrogen production through steam reforming. The corresponding reactions are considered as per Equation 3.36 and Equation 3.37



As was mentioned under Section 2.2, reforming is followed by water-gas-shift based on Equation 2.3. Thus, steam reforming and water-gas-shift will lead to 4 moles of hydrogen for each mole of methane, and 10 moles of hydrogen for each mole of propane. Therefore, the moles of hydrogen required for hydrotreating of bio-feedstock that can be obtained by reforming the methane and propane in the gaseous product of the hydrotreating are calculated according to Equation 3.38 and Equation 3.39 described in Table 11.

$$mol_{H_{Me}} = n_{Me}^{Metn} \times 4 \quad 3.38$$

$$mol_{H_{Propane}} = n_{Propane} \times 10 \quad 3.39$$

The additional hydrogen that must be produced using fossil-based feedstock to the HPU is calculated according to Equation 3.40 (terms are defined in Table 11). Since natural gas is normally fed to the HPU, which mainly consists of methane [17], the additional hydrogen is considered to be produced by steam methane reforming (SMR) as per Equation 3.36.

$$Addmol_{H_{HDT}} = mol_{H_{HDT}} - mol_{H_{Me}} - mol_{H_{Propane}} \quad 3.40$$

Table 11: Definition of terms in Equation 3.38 to Equation 3.41

Term	Unit	Denotation	Description
$Addmol_{H_{HDT}}$	$10^6$ mole/year	Hydrogen consumption	To be supplied by steam reforming of fossil-based methane
$mol_{H_{Me}}$	$10^6$ mole/year	Hydrogen consumption	To be supplied by steam reforming of methane
$mol_{H_{Propane}}$	$10^6$ mole/year	Hydrogen consumption	To be supplied by steam reforming of propane
$En_{HPU_{bio-feedstock}}$	$10^6$ GJ/year	Energy demand of HPU	Related to the bio-based feedstock
$\Delta H_{SMR}$	GJ/mole	Enthalpy of reaction	For SMR
$\Delta H_{PR}$	GJ/mole	Enthalpy of reaction	For propane reforming
$LHV_{Me}$	GJ/mole	Lower Heating Value	Related to fossil-based methane

The required energy to supply the additional hydrogen due to co-processing bio-based feedstock is calculated according to Equation 3.41 with terms defined in Table 11. This is regarding the point that the reforming reactions are endothermic and must be supplied by energy. The third term is related to the energy content of fossil-based methane that is converted to hydrogen.

$$En_{HPU_{bio-feedstock}} = (\Delta H_{SMR}) \cdot \frac{(Add_{mol_{H_{HDT}}} + mol_{H_{Me}})}{4} + (\Delta H_{PR}) \cdot \frac{mol_{H_{Propane}}}{10} + LHV_{Me} \times \frac{Add_{mol_{H_{HDT}}}}{4} \quad 3.41$$

## CO<sub>2</sub> balances

The additional on-site CO<sub>2</sub> emissions due to hydrotreating of bio-based feedstock is obtained by Equation 3.42. It is related to the emissions that arise from the additional energy requirement of the HPU. The terms in Equation 3.42 to Equation 3.46 are described in Table 12.

$$AddEm_{HPU} = En_{HPU_{bio-feedstock}} \cdot EF_{Make-up f} \quad 3.42$$

To account for the CO<sub>2</sub> mitigation potential of the bio-based feedstock, the associated CO<sub>2</sub> emissions throughout the value chain are considered. From a cradle-to-grave perspective, the biogenic CO<sub>2</sub> emissions result from uptake of CO<sub>2</sub> from the atmosphere through photosynthesis during the growth step of the biogenic feedstock, which makes this cycle carbon neutral. The biogenic CO<sub>2</sub> emissions formed within the processes involved in upgrading the bio-based feedstock in the refinery are, therefore, considered as neutral. The corresponding biogenic CO<sub>2</sub> emissions, which all end up in the HPU, are quantified according to Equation 3.43.

$$BiogenicEm_{HPU} = (n_{CO_2} + n_{Me}^{Metn} + 3 \times n_{Propane}) \times M_{CO_2} \quad 3.43$$

Table 12: Definition of terms in Equation 3.42 to Equation 3.46

Term	Unit	Denotation	Description
$AddEm_{HPU}$	10 <sup>6</sup> t/year	Additional on-site emissions	Related to HPU due to hydrotreating of the bio-based feedstock
$EF_{Make-up f}$	tCO <sub>2</sub> /GJ	Emission factor	Related to make-up fossil fuel ( <i>f</i> )
$Em_{UP_{bio-feedstock}}$	10 <sup>6</sup> t/year	CO <sub>2</sub> emissions	From the user phase of bio-feedstock
$i$	-	Number of carbon atoms	For $C_i$ n-alkane in the liquid product
$i - 1$	-	Number of carbon atoms	For $C_{i-1}$ n-alkane in the liquid product
$BiogenicEm_{HPU}$	10 <sup>6</sup> t/year	Biogenic CO <sub>2</sub> emissions	Formed within the processes involved in upgrading the bio-based feedstock in the refinery
$Em_{RE_{bio-feedstock}}$	10 <sup>6</sup> t/year	CO <sub>2</sub> emissions	From the resource extraction phase of bio-feedstock
$Em_{RE_{Make-up f}}$	10 <sup>6</sup> t/year	CO <sub>2</sub> emissions	From the resource extraction phase of make-up fossil fuel ( <i>f</i> )
$Em_{RE_{Replaced fossil share}}$	10 <sup>6</sup> t/year	CO <sub>2</sub> emissions	From the resource extraction phase of the replaced fossil-based share
$TEm_{bio-feedstock}$	10 <sup>6</sup> t/year	CO <sub>2</sub> emissions	From the value chain regarding bio-feedstock
$Cmp_{bio-feedstock}$	10 <sup>6</sup> t/year	CO <sub>2</sub> mitigation potential	Related to the bio-feedstock co-processing

The amount of CO<sub>2</sub> emissions arising from bio-share of the produced fuels in the user phase can be considered as CO<sub>2</sub> reduction in this case. This is because the biogenic share of the final fuel produced through co-processing replaces the same amount of fossil-based fuel, which means the corresponding fossil-based CO<sub>2</sub> emissions are replaced by neutral biogenic CO<sub>2</sub> emissions. Considering each mole of  $C_i$  and  $C_{i-1}$  n-alkanes are converted to CO<sub>2</sub> when the bio-share of the produced fuel is combusted in the user phase, the amount of associated CO<sub>2</sub> emissions related to the user phase ( $Em_{UP_{bio-feedstock}}$ : 10<sup>6</sup> t/year) is derived by Equation 3.44.

$$Em_{UP_{bio-feedstock}} = \left( \sum_i i \cdot w_{C_i}^{Lp} \cdot \frac{m_{Lp}}{M_{C_i}} + \sum_i (i-1) \cdot w_{C_{i-1}}^{Lp} \cdot \frac{m_{Lp}}{M_{C_{i-1}}} \right) \cdot M_{CO_2} \quad 3.44$$

Therefore, the total value chain CO<sub>2</sub> emissions associated with the bio-feedstock being co-processed ( $TEm_{bio-feedstock}$ : 10<sup>6</sup> t/year) within the system boundary of this study is obtained by Equation 3.45.

$$TEm_{bio-feedstock} = AddEm_{HPU} + Em_{RE_{bio-feedstock}} + Em_{RE_{Make-up f}} \quad 3.45$$

The CO<sub>2</sub> mitigation potential due to applying bio-based co-processing as the mitigation option ( $Cmp_{bio-feedstock}$ : 10<sup>6</sup> t/year) is estimated by Equation 3.46.

$$Cmp_{bio-feedstock} = Em_{UP_{bio-feedstock}} + Em_{RE_{Replaced fossil share}} - TEm_{bio-feedstock} \quad 3.46$$

### 3.6. OVERVIEW OF ANALYSES THAT CAN BE CONDUCTED BY THE MODEL

The model enables the following analyses for CCS and bio-based feedstock mitigation options.

#### Carbon Capture and Storage:

Based on the procedure described in Section 3.3, the on-site CO<sub>2</sub> emissions from each unit process and in total are calculated. Therefore, the emissions associated with unit processes can be monitored by the user to decide whether to deploy CCS in all process units or in selected units. Thereafter, based on the selected units to which CCS is to be applied, the total on-site CO<sub>2</sub> emissions captured, the CO<sub>2</sub> mitigation potential, and the energy consumption related to CCS, can be quantified according to the procedure described in Section 3.4.

In addition, the model can account for the opportunity to use available excess heat at the refinery to supply the heat demand of the CC unit. It should be noted that the amount of excess heat available in a refinery could be affected by co-processing bio-feedstock. Therefore, the option to use available refinery excess heat, which is estimated in the absence of co-processing of bio-feedstock, should be considered only when CCS is the only mitigation option, and not in combination with the bio-feedstock mitigation option.

**Bio-based feedstock:**

The module is based on the procedure described in Section 3.5. The type of bio-based feedstock, the fraction of bio-based feedstock in the feed to the unit as well as the targeted product need to be defined as inputs to the model.

The general idea of the analysis is that the bio-feedstock composition is supposed to be determined by the model considering the type of bio-feedstock specified by the user. Then the general idea is that based on the type of bio-feedstock and products, the model is supposed to select the insertion point of the bio-feedstock (as discussed previously, different types of feedstock are suitable for different insertion points) and the associated reaction sets taking place within the upgrading process of the bio-feedstock to biofuels. Due to limited time, the scope of the work was restricted to one product and one suitable insertion point.

As described previously, the change in energy demand of the units in focus resulting from co-processing bio-feedstock is then calculated, followed by estimating the associated CO<sub>2</sub> mitigation potential.

**Combinations of mitigation options:**

The model provides the opportunity to combine the two mitigations options to derive the total CO<sub>2</sub> mitigation potential and changes in the energy demand.

### 3.7. INPUT DATA TO THE MODEL

Important input parameter values are defined in Table 13. In this research, a case study is conducted on Preemraff Lysekil refinery, therefore the input variables are based on the corresponding data from this refinery, which are not revealed due to confidentiality. It should be noted that all the given input data listed in Table 13 can be revised by users based on the specific data of any certain refinery and other generic data according their sources of data collection. Each module is modelled based on the method described for the corresponding module.

Table 13: Input parameter values to the model

Input parameters to the model	Unit	Value	Reference
$FC_{u,f}$ - Consumption of fuel $f$ in process units <sup>a</sup>	$10^6$ GJ/year	Confidential	Preemraff Lysekil
$\sum_u \sum_E EC_u \times Sh_E / OE_E$ - Electricity consumption of all process units <sup>b</sup>	GWh/year	522	[8]
$V_{u,bp}$ - volume flow of refinery by-product $bp$ , used as a fuel in each process unit $u$	$10^6$ Sm <sup>3</sup> /year	Confidential	Preemraff Lysekil
$V_p$ - volume of each refinery product, $p$	$10^6$ Sm <sup>3</sup> /year	Confidential	Preemraff Lysekil
$EF_f / EF_{bp} / EF_p$ - CO <sub>2</sub> emission factor	kg CO <sub>2</sub> /GJ	Grid electricity: 13.1 Liquefied Natural Gas (LNG): 57 Cracker coke: 103 Gasoline: 72.6 MK1 diesel: 72 Diesel: 75.3 Heavy fuel oil: 79 LPG: 65.1	[33] [34], [35], [36] [34], [35], [36] [37] [38] [37] [39] [37]
CR <sub>u</sub> - CO <sub>2</sub> capture rate	t/t reference emission (%)	85	[6], [40]
Specific energy requirements and CO <sub>2</sub> emissions (Em <sub>CS</sub> ) for compression, transport and storage of captured CO <sub>2</sub> -based on permanent storage beneath seabed off Norwegian coast	tCO <sub>2</sub> /tCO <sub>2</sub> captured	0.019-0.024 (avg.: 0.021)	Adapted from [41], [33]
	MWh//tCO <sub>2</sub>	0.4-0.5 (avg.: 0.45)	[41]
FP- CO <sub>2</sub> capture fuel penalty Based on:	GJ/t CO <sub>2</sub>	4.5	
- CC heat demand	GJ/t CO <sub>2</sub>	3.3-4.4 (avg.: 3.85)	[6]
- CC boiler efficiency	(%)	85	[42]

Global volume-weighted average upstream (well-to-refinery) carbon intensity	gCO <sub>2eq</sub> /MJ	10.3	[43]
SpecEm <sub>Make-up f</sub> - Specific resource extraction emissions for LNG -based on Higher Heating Value (HHV)	gCO <sub>2eq</sub> /MJ HHV	18.3	[44]
Crude oil input to the refinery	10 <sup>6</sup> GJ/year	416.2	Adapted from [8]
Heat sources to supply CC unit: - Steam rates - Operation hours	t/h h/year	Confidential 8500	A study on Preemraff Lysekil
Relative hydrogen consumption	L/kg Rapeseed oil	294	[45]
Y <sub>LP</sub> - Estimated liquid product yield related to hydrotreating of rapeseed oil	wt%	94	[29], [32], [46], [31]
Y <sub>water</sub> - Estimated water yield related to hydrotreating of rapeseed oil	wt%	5	[45], [46], [32]
Estimated compositions of liquid and gas products	wt%	Appendix A	Adapted from [47], [48]
Specific emissions from extraction phase to production of refined rapeseed oil	kgCO <sub>2eq</sub> /t refined rapeseed oil	262	[49]
m <sub>tot</sub> - Mass flow of the liquid input to the hydrotreating unit process	10 <sup>6</sup> t/year	Confidential	Preemraff Lysekil
Composition of rapeseed oil in terms of fatty acids	wt%	Table 6	[29], [30]

<sup>a</sup> Fuel *f* is inclusive of fossil fuels and the byproducts of the refinery that can be used as fuels for different unit processes (e.g. fuel gas)

<sup>b</sup> Power source can be electricity purchased from grid or electricity generated on-site by combined heat and power (CHP) or steam turbines.

## 4. RESULTS AND DISCUSSION

The model was constructed based on the methodology described in the previous sections. Thereafter the model was applied to quantify CO<sub>2</sub> emissions and analyze the effect of mitigation options including CCS, bio-feedstock co-processing, and combinations thereof in terms of changes in the refinery energy demand and CO<sub>2</sub> mitigation potential. The effect of recovering excess heat to satisfy the heat demand of the CC unit was also investigated. The results are presented in this chapter.

### 4.1. CO<sub>2</sub> EMISSIONS OF THE HYDROGEN PRODUCTION UNIT (HPU)

Based on the specified rate of input feed and corresponding fuel consumptions, on-site CO<sub>2</sub> emissions in flue gases were quantified using the CO<sub>2</sub> quantifying module. In order to validate the model, the estimated amount of CO<sub>2</sub> emissions was compared with the corresponding site data for the Preemraff refinery [15] in Table 14. It can be concluded that the amount of estimated emissions is satisfactorily in agreement with the real data.

Table 14: Comparison between CO<sub>2</sub> emissions from HPU estimated by the model and the real site data

On-site CO <sub>2</sub> emissions from HPU	Estimated by the model	Site data
10 <sup>6</sup> t/year	0.624	0.6

### 4.2. CO<sub>2</sub> MITIGATION POTENTIAL AND ENERGY CONSUMPTION OF CC TECHNOLOGY FOR THE HPU

The CO<sub>2</sub> mitigation potential and required energy for CC technology were calculated using the CCS module. Input data was taken from a previous confidential study on the Preemraff Lysekil refinery regarding availability of excess heat which could be recovered to supply heat to the CC unit. The results regarding the CO<sub>2</sub> mitigation potential and energy requirement of CC technology for the two cases of supplying CC technology with/without available excess heat are shown in Table 15. The share of the CO<sub>2</sub> mitigation potential regarding the total on-site CO<sub>2</sub> emissions from the Preemraff Lysekil refinery [7] are also shown.

Table 15: CO<sub>2</sub> mitigation potential and energy requirement of CC technology, applied to the HPU, with and without the effect of using excess heat

CCS mitigation option	Total on-site emissions (10 <sup>6</sup> tCO <sub>2</sub> /year)	HPU on-site emissions (10 <sup>6</sup> tCO <sub>2</sub> /year)	CO <sub>2</sub> mitigation potential (10 <sup>6</sup> tCO <sub>2</sub> /year)	Percentage of HPU on-site emissions mitigated (%)	Percentage of total on-site emissions mitigated (%)	CC primary energy consumption (10 <sup>6</sup> GJ/year)
Without excess heat	1.625	0.624	0.334	53.5	20.6	2.404
With excess heat	1.625	0.624	0.52	83.3	32	0

The CC unit's energy demand adds around 62% to the total energy consumption of the HPU in the Preemraff Lysekil refinery, which is supplied by 2 MW of electricity [50], 29.4 MW of fuel gas [50], and offgas from PSA that is calculated based on the available site data. The use of excess heat reduces or eliminates the required primary energy supply for CC. As can be seen, in this case it was sufficient to fully cover the energy demand of CC. Therefore, the emissions related to the CC fuel penalty (defined in Equation 3.9) are eliminated, leading to a considerable increase in the CO<sub>2</sub> mitigation potential. As can be seen in this case, the percentage of the HPU on-site emissions mitigated is slightly below 85%, which is the carbon capture rate applied. This is because there are some emissions associated with the compression, transport and storage, which are subtracted from the total carbon captured. By applying CC technology to the HPU, a significant share of the total on-site emissions of the refinery can be mitigated, and the mitigation potential can also be increased by using the available excess heat for supplying energy to the CC technology.

### 4.3. CO<sub>2</sub> MITIGATION POTENTIAL AND ENERGY CONSUMPTION OF CC TECHNOLOGY FOR THE REFINERY

The case study on the effect of excess heat on CO<sub>2</sub> mitigation potential and the primary energy requirement of the CC unit was extended to investigate the effect of applying CC technology to the total on-site CO<sub>2</sub> emissions from the Preemraff Lysekil refinery. Note that the input data to the model does not include data for all refinery process units, therefore, the value of the total on-site emissions was retrieved from Preem's sustainability report [7]. The CO<sub>2</sub> mitigation potential and the CC energy demand were estimated by the CCS module for the two cases of supplying CC technology with/without excess heat. The maximum available excess heat in the refinery that can be used to supply the CC unit was considered, which is around  $2.3 \times 10^6$  GJ/year that approximately corresponds to 73 MW (a conservative value considering the CC operating conditions estimated based on [51]). The results are shown in Table 16. It can be seen that utilizing excess heat for this purpose can cover around 43.5% of the CC primary energy demand. This leads to a 13% increase in the CO<sub>2</sub> mitigation potential of the CC technology.

Table 16: CO<sub>2</sub> mitigation potential and energy requirement of CC technology, applied to the refinery, estimated by the model and the effect of using excess heat on them

CCS mitigation option	Total on-site emissions (10 <sup>6</sup> tCO <sub>2</sub> /year)	CO <sub>2</sub> mitigation potential (10 <sup>6</sup> tCO <sub>2</sub> /year)	CO <sub>2</sub> mitigation potential (% of total on-site emissions)	CC primary energy consumption (10 <sup>6</sup> GJ/year)	Percentage of CC primary energy consumption covered by excess heat (%)
Without excess heat	1.625	0.868	53.4	6.256	0
With excess heat	1.625	1.079	66.4	3.533	43.5

#### 4.4. CO<sub>2</sub> MITIGATION POTENTIAL OF CO-PROCESSING RAPESEED OIL IN THE HYDROTREATING UNIT

Co-processing was evaluated for a feedstock mix consisting of rapeseed oil and light gas oil (LGO) with a ratio of 17:83 wt%. The hydrotreating was assumed to be conducted at 340 °C and 4 MPa over NiMo/Al<sub>2</sub>O<sub>3</sub>, which is a common commercial catalyst for hydrotreating. The results for CO<sub>2</sub> mitigation potential, change in energy demand for the refining process as well as the amount of biogenic CO<sub>2</sub> emissions generated within the process units involved in upgrading the bio-based feedstock are summarized in Table 17.

Table 17: Model outcomes for co-processing of rapeseed oil and LGO in the hydrotreating unit

Co-processing rapeseed oil and LGO	CO <sub>2</sub> mitigation potential (10 <sup>6</sup> tCO <sub>2</sub> /year)	Increased energy demand for HPU (10 <sup>6</sup> GJ/year)	Biogenic CO <sub>2</sub> emissions (10 <sup>6</sup> tCO <sub>2</sub> /year)
17:83 wt%	0.82	0.23	0.043

Compared to the results for CCS applied to the HPU described under Section 4.2, the co-processing mitigation option has a CO<sub>2</sub> mitigation potential that is around 2.5 times higher whereas the increase of refining energy demand is around 9.6% of the corresponding value for the CCS option applied only to the HPU. This is to a large extent due to the fact that co-processing has reduction effect on the emissions in the user phase (Scope 3), which accounts for the major contribution to the decrease of value chain emissions.

#### 4.5. INTERPLAY BETWEEN CCS AND CO-PROCESSING OF RAPESEED OIL

In order to evaluate the combined effect of the CCS and co-processing mitigation options, a number of test points were considered, as defined in Table 18. The High value for CCS assumes that the technology is applied to the total on-site emissions from the HPU. The Low value assumes that the technology is applied to a fraction of the HPU flue gases for which the CC energy demand can be covered by excess heat from the refinery's heat collection network (HCN).-. This was considered as a basis to define

a low value for CCS. However, in the analysis only the aforementioned fraction (62.2%) is applied as the Low value, and the energy for the CC technology was not satisfied by the HCN to be able to monitor the pure effect of the CC. The High value for the rapeseed oil co-processing corresponds to the indicative value of the maximum amount that can be co-processed according to results reported in the literature. The Low value of 0 wt.% for co-processing determines a Benchmark case corresponding to application of carbon capture as sole mitigation technology.

Table 18: Test points for analyzing the interplay between the mitigation options

Mitigation option	Low (-)	High (+)
CC for HPU (%)	62.2	100
Rapeseed oil : crude oil ratio in feed (wt-%)	0	17

The analysis was conducted based on a 2<sup>2</sup> factorial design, as shown in Table 19.

Table 19: Factorial design of the test points for analyzing the interplay between the mitigation options

Rapeseed oil wt % for co-processing	CC applied (partial capture %)
-	-
-	+
+	-
+	+

Table 20 presents the results for CO<sub>2</sub> mitigation potential and total energy added to the refining process for each set of combination of mitigation options. Figure 4-1 illustrates the difference with respect to the reference case (without mitigation options).

Table 20: The results considering interplay between CCS and rapeseed oil co-processing

Set No.	CCS	Bio-feedstock	Total CO <sub>2</sub> mitigation potential (10 <sup>6</sup> tCO <sub>2</sub> /year)	Total addition to the refinery energy demand (10 <sup>6</sup> GJ/year)
1	-	-	0.208	1.495
2	-	+	1.031	1.757
3	+	-	0.334	2.404
4	+	+	1.16	2.685

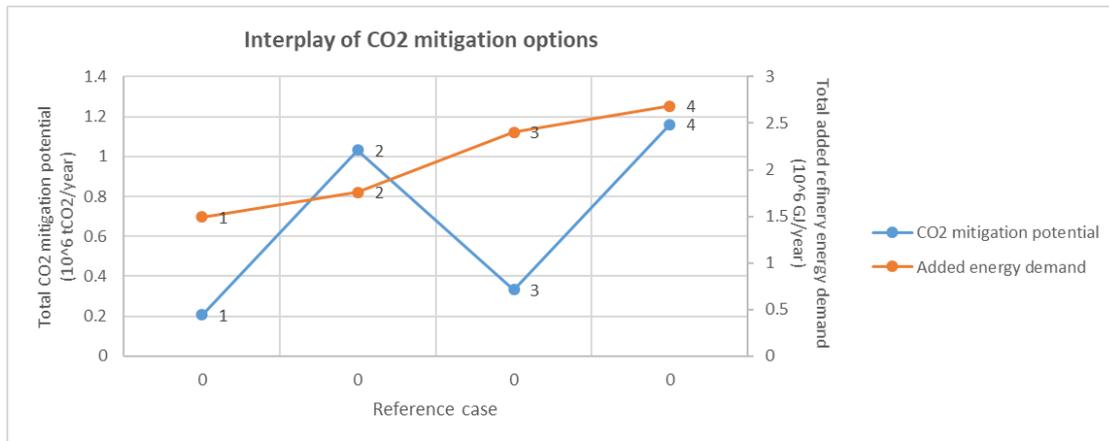


Figure 4-1: The interplay between the mitigation options compared with the reference case

As can be seen in Table 20, the CO<sub>2</sub> mitigation potential for Set 2 is 4.97 times greater than that for Set 1, while the increase in the refining energy demand is almost 17.5%. For Set 3, both the mitigation and the energy demand increase by around 61% compared to Set 1. For Set 4, the CO<sub>2</sub> mitigation potential is 5.6 times more than that of Set 1, and the increase in the energy demand is approximately 80%.

It can be concluded that the combination of the low share of CCS with the co-processing is the best trade-off between the mitigation options with a considerable increase in CO<sub>2</sub> mitigation potential and the lowest increase in the energy demand. This is because the emissions associated with CCS related to the energy demand of the CC technology as well as the compression, transport, and storage of the captured carbon are significant and grow as the extent of CC is increased. Thus, although a higher degree of CC leads to decreased CO<sub>2</sub> emissions, it is accompanied by an increase in the emissions related to satisfying the energy demand for the complete CCS, i.e. including emissions related to compression, transport and storage. However, if excess heat is available and recovered, the energy demand of the CC technology can be fully or partly satisfied without combustion of additional fuel, which moderates the effect of the CC energy demand. Based on the results, it is also clear that introducing bio-feedstock co-processing leads to significantly larger mitigation potential and a lower rate of increase in energy demand, as discussed in Section 4.4. The aforementioned trade-off corresponds to the share of CCS that leads to a reasonable balance between the total CO<sub>2</sub> mitigation potential and the added energy demand.

#### 4.6. ANALYSIS OF THE INTERPLAY BETWEEN CCS AND CO-PROCESSING RAPESEED OIL INCLUDING BIOGENIC CO<sub>2</sub> EMISSIONS

As discussed in Section 3.5.2, there are some biogenic CO<sub>2</sub> emissions generated within the upgrading of rapeseed oil. In order to assess the effect of capturing these emissions, the same analysis as that described in Section 4.5 was conducted while biogenic emissions are also included in the on-site emissions of the HPU. The results on CO<sub>2</sub> mitigation potential and total energy added to the refining process for each combination of mitigation options are summarized in Table 21 and illustrated versus the reference case (with no mitigation option applied) in Figure 4-2.

Table 21: The results of the interplay between CCS and the rapeseed oil co-processing including the biogenic CO<sub>2</sub> emissions

Set No.	CCS	Bio-feedstock	Total CO <sub>2</sub> mitigation potential (10 <sup>6</sup> tCO <sub>2</sub> /year)	Total addition to the refinery energy demand (10 <sup>6</sup> GJ/year)
1	-	-	0.208	1.495
2	-	+	1.046	1.859
3	+	-	0.334	2.404
4	+	+	1.183	2.849

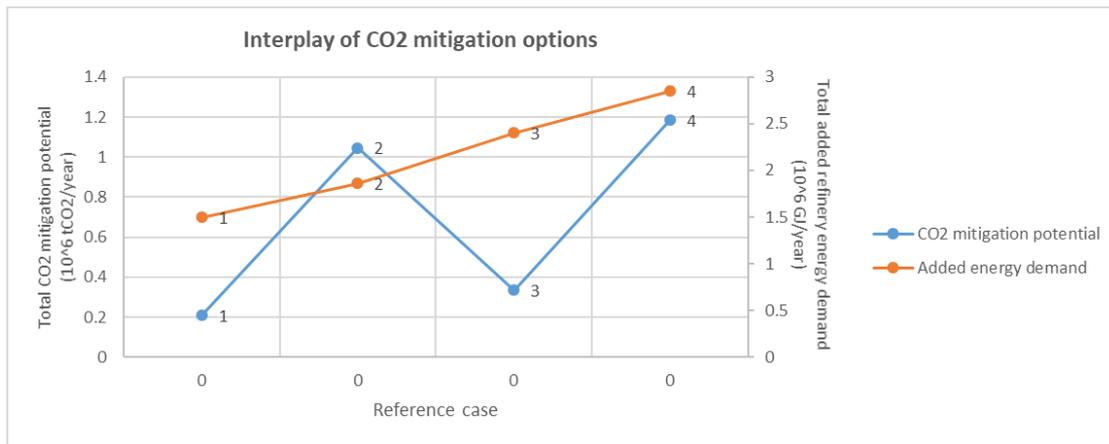


Figure 4-2: The interplay between the mitigation options compared with the reference case including the biogenic CO<sub>2</sub> emissions

The CO<sub>2</sub> mitigation potential for Set 2 is 5.04 times higher than for Set 1, whereas the refining energy demand increases by almost 24.3%. Since biogenic CO<sub>2</sub> emissions do not occur for Set 3 conditions, the results are same as the analysis in which the biogenic emissions are not considered. For the last set of data corresponding to the combination of maximum application of CCS to the HPU combined with the co-processing of rapeseed oil, the CO<sub>2</sub> mitigation potential is 5.7 times the value for Set 1 and the increase in the energy demand is 90.5%. As in Section 4.5, the best trade-off between the mitigation options is the combination of the low share of applied CCS and co-processing, which leads to considerable increase in CO<sub>2</sub> mitigation potential and the lowest increase in the energy demand.

A comparison between the corresponding values of CO<sub>2</sub> mitigation potential and energy demands for the two analyses with and without biogenic emissions are shown in Table 22. Compared with the results presented in Section 4.5 with no biogenic CO<sub>2</sub> emissions included, there is only a slight increase in terms of the mitigation potential for both combinations of low and high share of CCS with the co-processing. However, the increase in the corresponding energy demands are more noticeable compared with corresponding increased energy demands in the previous analysis due to higher energy requirement of the CC technology.

Table 22: Comparison between the interplay results for the two analyses of with and without biogenic emissions

% Change in total CO <sub>2</sub> mitigation potential	% Change in total addition to the refinery energy demand
0.00	0.00
1.38	5.81
0.00	0.00
1.97	6.11

The slight increase in the CO<sub>2</sub> mitigation potential due to low amount of biogenic CO<sub>2</sub> emissions, is obtained at the cost of higher energy demand compared to the analysis with no biogenic CO<sub>2</sub> included. Thus, the sole application of CCS to the biogenic emissions released through the bio-feedstock co-processing may not be a proper decision especially when the cost of supplying the corresponding energy demand is taken into account. However, as mentioned in Section 4.5, the excess heat in the refinery could be utilized to completely or partly satisfy the energy demand of the CC unit. Thus, the application of CCS to the biogenic emissions released by upgrading of lipids can potentially achieve negative CO<sub>2</sub> emissions, but should be combined with usage of excess heat to moderate the associated higher increase rate of the energy demand.



## 5. SUMMARY AND CONCLUSIONS

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In this research, possible measures for mitigation of CO<sub>2</sub> emissions along the refinery value chain (Scope 1, Scope 2, and part of Scope 3) were identified, and carbon capture and storage as well as co-processing of bio-feedstock were selected for further analysis. A methodology was developed to enable quantifying the CO<sub>2</sub> mitigation potential and changes in the energy demand of the refinery related to deployment of each mitigation option. A model was built based on the proposed methodologies that enables the user to investigate the impact of implementing the mitigation measures or a combination thereof on a refinery. The model was constructed to be capable of analyzing the interplay between mitigation options. This capability was applied to quantify the total effect of the combination of the mitigation options. The model adopts a generic approach so that it can be applied to any complex refinery and factors such as rate of carbon capture, process units, energy consumptions, etc. can be tuned to the targeted case. The flexible structure of the model facilitates the addition of any other mitigation option by combining it with the model as a new module.

In this work, the Preemraff Lysekil refinery was used as a case study. The constructed model includes all the process units in the refinery, and data collection was performed on the refinery level. However, the input data required for the model was not available for some process units. Thus, considering the importance of the HPU and availability of data for it, analysis on the effect of CCS was conducted on this process unit. Post combustion using MEA absorption was considered for carbon capture and applied to total on-site emissions of the HPU. The results indicate that implementation of carbon capture can significantly decrease on-site emissions from the Hydrogen Production Unit, which accounts for a substantial share (20.6%) of the total on-site emissions of the Preemraff Lysekil refinery. The case study also considered recovery and use of excess heat available in this refinery to satisfy the energy demand of the carbon capture unit. The results indicate that available excess heat is sufficient to fully cover the heat demand of a carbon capture unit installed at the Hydrogen Production Unit, thereby increasing the CO<sub>2</sub> mitigation potential by 55.7% compared to the case in which primary energy must be used to cover the heat demand. Furthermore, use of excess heat leads to a substantial decrease in the primary carbon capture energy demand when applied to the whole refinery, resulting in a rise in CO<sub>2</sub> mitigation potential of approximately 24.3%.

The impact of co-processing bio-feedstock was investigated for hydrotreating of lipid-based feedstocks. The case study was conducted assuming hydrotreating of 17 wt% of rapeseed oil at 340 °C and 4 MPa over NiMo/Al<sub>2</sub>O<sub>3</sub>. The results showed a mitigation potential that is around 2.5 times higher compared to the Carbon Capture and Storage applied to the Hydrogen Production Unit while the increase in the energy demand is almost 9.6% of that of Carbon Capture and Storage. The interplay between the mitigation options was analysed using several test points. The best trade-off was determined to be a lower share of Carbon Capture and Storage combined with the co-processing option. The same analysis was conducted when the biogenic emissions from upgrading the bio-feedstock are captured as well. The general trend of the results was

the same as the previous analysis. It was concluded that regarding the higher growth rate in the energy demand as compared to the rate of increase in the CO<sub>2</sub> mitigation potential, capturing biogenic CO<sub>2</sub> emissions could be useful when excess heat is used to supply the energy demand to moderate the higher growth rate of it.



## 6. FUTURE WORK

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In order to continue this research, further work is recommended in the following areas:

- Model input data collection related to rapeseed oil hydrotreating for different operating conditions:

The reactions in the hydrotreating unit are sensitive to the operating conditions. Thus, more data for different operating conditions must be collected to make the model flexible in this respect.

- Model input data collection related to hydrotreating of other lipids:

The developed method for hydrotreating of bio-based feedstock is applicable to all lipids. However, input data to the model for other lipids is required to be able to apply the model for all lipid-based feedstock, which need to be collected in future studies.

- Development of the model to be more flexible at the operation unit level:

The adaptability of the developed model is at the process unit level and not at the operation unit level. Future work is needed to determine if the model can be made more flexible to changes at the operation unit level.

- Use of industrial-scale input data for hydrotreating:

The input data for yields and compositions regarding hydrotreating of rapeseed oil are estimated based on experimental laboratory-scale data from the literature. These can be revised in future studies if industrial-scale data becomes accessible. This could also be taken into account for data collection for other lipids.

- Development of the method and model for other process units as the bio-feedstock insertion point:

In this research, the method developed for the co-processing of bio-based feedstock is related to the catalytic hydrotreating unit as the insertion point. However, other potential process units for co-processing of the bio-feedstock include the catalytic hydrocracking and fluid catalytic cracking units. The methods applicable to each of them could be investigated in future studies.

- Development of the method and model for other types of bio-feedstock:

The method developed for co-processing of bio-based feedstock is related to lipid-based feedstocks. In future studies the method for upgrading other types of bio-feedstock under carbohydrates category can be investigated.

- Development of the method and model for other mitigation options such as green hydrogen produced by water electrolysis using renewable electricity as energy source:

In this project, CCS and bio-based co-processing were the mitigation options investigated. However, in order to achieve zero emissions from refineries other mitigation options such as green hydrogen from electrolyzers can also be applied. Thus, development of methodology and model for other mitigation options can be investigated in future studies as well.



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## APPENDIX A: THE RAPESEED OIL HYDROTREATING PRODUCT COMPOSITION

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The composition of the gas phase is normalized based on the compounds resulting from the hydrotreating of rapeseed oil. Since the share of fossil-based methane and propane are usually lower than that of the bio-based ones (adapted from [31]), the fossil shares of these were neglected. The composition of the liquid phase is normalized by deducting the share of fossil-based compounds and distributing the group composition of iso and cycloalkanes into n-alkanes. The latter is due to the point that some of the n-alkanes are subsequently isomerized or cyclized [47]. To account for their hydrogen consumption once they were generated as n-alkanes within the hydrotreating, their share has been allocated to n-alkanes. The low share of aromatics generated from the hydrotreating of rapeseed oil has been neglected.

Table 23: The product composition of the hydrotreating of rapeseed oil (adapted from [47], [48])

Product of hydrotreating rapeseed oil	Compound	wt%
Gas phase	CO	19.1
	CO <sub>2</sub>	30
	CH <sub>4</sub>	17.1
	C <sub>3</sub> H <sub>8</sub>	33.8
Liquid phase	n-C <sub>16</sub>	9.6
	n-C <sub>17</sub>	74.1
	n-C <sub>18</sub>	13.1
	n-C <sub>19+</sub>	3.1



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