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# **Integrating biomass gasification with electric arc furnace steel making**

**KTH Thesis Report**

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# Abstract

Greenhouse gas emissions are increasing worldwide, and new techniques are being adopted to suppress the emissions. The steel sector is responsible for 7% of the emissions. 25% of the world's steel production is made through the recycling technique Electric arc furnace (EAF). Throughout the recycling process, 500 kg CO<sub>2</sub> gets emitted per ton of liquid steel produced. An opportunity to lower these direct emissions is to couple the EAF process to biomass gasification and CO<sub>2</sub> utilisation process. The proposed solution in this thesis is to utilise the off-gases in the gasification process and create high-valuable products. The project evaluates the technical feasibility via energy efficiency and carbon utilisation. The proposed process was simulated using Aspen Plus.

A problem with the off-gases from EAF gasification is the fluctuation in composition. Three cases of off-gas composition were therefore investigated. Case 1 was the average off-gas composition, while cases 2 and 3 were extreme with high CO and CO<sub>2</sub> content, respectively. The result showed that the syngas composition strongly depends on the gasifying agent. In all cases, the energy efficiency increased, and the direct emissions decreased. Case 1 generally showed the highest efficiency and carbon utilisation, while the CO<sub>2</sub> heavily case (case 3) had the lowest.

A continuous flow of gasifying agents is required to run the gasification process. Since EAF is a batch process, air gasification runs when off-gases are unavailable. The desired outcome of air gasification is to produce syngas similar to off-gas gasification. The results showed that air infiltration in off-gases is favourable for more similar syngas.

## Keywords

EAF, EAF off-gas, gasification, CCU

# Abstract

Utsläppen av växthusgaser ökar över hela världen och nya tekniker används för att minska utsläppen. 7% av utsläppen kommer från stålsektorn. 25% av världens stålproduktion görs via återvinningstekniken ljusbågsugn. Genom återvinningsprocessen släpps det ut 500 kg CO<sub>2</sub> per ton producerat flytande stål. En möjlighet att sänka dessa direkta utsläpp är att koppla ljusbågsugnsprocessen med biomassa förgasnings och koldioxidavskiljning. Den föreslagna lösningen i denna avhandling är att utnyttja avgaserna från stålsmältningen i förgasningsprocessen och skapa värdefulla produkter. Projektet utvärderar den tekniska genomförbarheten i form av energieffektivitet och kolutnyttjande. Den föreslagna processen simulerades med Aspen Plus.

Ett problem med ljusbågsugnens avgaser är fluktuationen i sammansättningen. Tre fall av avgassammansättning undersöktes. Fall 1 var den genomsnittliga avgassammansättningen, medan fall 2 och 3 var extrema med högt CO- respektive CO<sub>2</sub>-innehåll. Resultatet visade att syntetgassammansättningen starkt beror på förgasningsmedlet. I samtliga fall ökade energieffektiviteten och de direkta utsläppen minskade, jämfört med nuvarande process. Fall 1 visade generellt högst effektivitet och kolutnyttjande, medan det CO<sub>2</sub> rika fallet (fall 3) hade lägst.

Ett kontinuerligt flöde av förgasningsmedel krävs för att driva förgasningsprocessen. Eftersom ljusbågsugn är en satsvis process, sker luftförgasning när avgaser inte är tillgängliga. Det önskade resultatet av luftförgasning är att producera syntetgas som liknar avgasförgasningens syntesgas. Resultaten visade att luftinfiltration i avgaser är gynnsamt för mer liknande syntesgas .

## Nyckelord

Ljusbågsugn, ljusbågsugn avgas, förgasningsprocess, kolavskiljning

# Acknowledgements

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# Acronyms

**EAF** Electric arc furnace

**FT** Fischer-Tropsch

**GHG** Greenhouse gas

**KPI** Key Performance indicators

**LHV** Lower Heating Value

**MeOH** Methanol

**PG** Producer Gas

**r-WGS** reversed water gas shift

**WGS** Water gas shift

# Contents

<b>1</b>	<b>Introduction</b>	<b>8</b>
1.1	Background . . . . .	8
1.2	Aim . . . . .	9
1.3	Delimitations . . . . .	9
1.4	Outline . . . . .	9
<b>2</b>	<b>Background</b>	<b>11</b>
2.1	Electric Arc Furnace (EAF) for steel making . . . . .	11
2.1.1	Composition of Off-gas . . . . .	12
2.2	Gasification of biomass . . . . .	14
2.2.1	Gasifying agent . . . . .	14
2.2.2	Catalyst . . . . .	16
2.3	Cleaning and upgrading of producer gas . . . . .	16
2.4	Proposed process description . . . . .	17
<b>3</b>	<b>Methodologies and Assumptions</b>	<b>19</b>
3.1	Modelling approach . . . . .	19
3.1.1	Energy balance . . . . .	20
3.1.2	Delimitations and assumptions . . . . .	20
3.2	Design parameters . . . . .	21
3.2.1	Assumptions . . . . .	23
3.3	Model Validation . . . . .	23
3.3.1	Gasifier . . . . .	23
3.3.2	Reverse Water-Gas Shift process (r-WGS) . . . . .	24
3.4	Key Performance Indicators . . . . .	24
<b>4</b>	<b>Results and discussion</b>	<b>26</b>

4.1	Gasifying agent conditions . . . . .	26
4.1.1	EAF off-gas as gasifying agent . . . . .	26
4.1.2	Conditions for air as gasifying agent in the absence of EAF off-gas	28
4.2	Composition of Producer gas and syngas . . . . .	29
4.2.1	Producer gas composition . . . . .	29
4.2.2	Syngas Composition . . . . .	31
4.2.3	Carbon utilisation in the process . . . . .	37
4.3	Energy balance for the process . . . . .	38
4.3.1	Off-gas gasification . . . . .	38
4.3.2	Air/steam gasification . . . . .	45
4.4	Overall evaluation of process . . . . .	49
<b>5</b>	<b>Conclusions</b>	<b>50</b>
	<b>References</b>	<b>52</b>



# Chapter 1

## Introduction

### 1.1 Background

The production of Greenhouse gas (GHG) emissions is a rapidly growing problem, and the effects of climate change have started to be seen. The major source of GHG emissions, especially CO<sub>2</sub> emissions, comes from fossil sources utilised for energy. The change from fossil to renewable energy is crucial [1]. Biomass is a renewable carbon-neutral source. The emissions produced during biomass utilisation are captured by the growth of biomass via photosynthesis [2].

Biomass gasification is a well-known technique for utilising energy from biomass. Biomass is converted to Producer Gas (PG), a mixture consisting mainly of hydrogen (H<sub>2</sub>), carbon monoxide (CO), methane (CH<sub>4</sub>), carbon dioxide (CO<sub>2</sub>) and air. The PG can be utilised and upgraded to syngas, fuels and electricity [2].

In work towards carbon neutralisation, CO<sub>2</sub> has been investigated as a gasification agent in the gasification process, as a Carbon-Capture Utilisation. The CO<sub>2</sub> gasification has shown promising results for decreasing emissions. By coupling the gasification process to another process with high CO<sub>2</sub> emissions, clean energy and decreased emissions can be a result. The emissions can hence be observed as a raw material instead of waste [3].

A sector with large emissions is the steel industry, responsible for 7% of the world's total emissions [1]. One-quarter of the world's steel is produced through EAF. EAF is the steel recycling process, however it can also treat the reduced iron-ore and convert it into steel. The process also has emissions of CO<sub>2</sub>, and CO in the off gas produced and leaving the process at high temperature. The emissions is mixed with air and combusted for electricity production

[4].

An opportunity for utilisation the energy content of EAF off-gasses in biomass gasification, in addition to converting the CO<sub>2</sub> generated from the process, is a proposed solution in this thesis for increasing system efficiency and reducing the direct emissions from the process.

## **1.2 Aim**

The project aims to determine the technical feasibility of integrating biomass gasification with EAF-process. The feasibility is determined by the energy efficiency and is measured by comparing the current electricity production from off-gas with the proposed solution. Further, the feasibility is measured in the carbon recovery, where the goal is to decrease the direct CO<sub>2</sub> emissions from EAF and instead convert the emissions to high-value products.

## **1.3 Delimitations**

The project is delimited to

- No experimental work has been performed in this thesis. However, the models developed have been validated with available experimental data in literature.
- EAF off-gas composition is assumed from litterature. There is a lot of variability in EAF off-gas composition reported in literature. Therefore, analysis has been performed for three different compositions of EAF off-gas.
- All the analysis in this study are for steady state conditions. Dynamic analysis is not part of this study.

## **1.4 Outline**

Chapter 2 provides background information on EAF process for understanding off-gas composition and energy demand. The chapter further provides information on the gasification process. Finally, upgrading solutions of PG is presented.

Chapter 3 provides the methodology, including the project's boundaries and limitations.

Chapter 4 presents the results and provides a discussion about them.

Finally, chapter 5 presents the conclusions drawn from the project and what further is recommended for investigation after this study.

# Chapter 2

## Background

This chapter describes a description of EAF and the gasification process. Understanding the EAF process gives insight into the composition of off-gas and energy balance. Important parameters in gasification provides understanding of the technique and furthermore the result after simulation in addition to ways of integrating it with EAF.

### 2.1 Electric Arc Furnace (EAF) for steel making

EAF is the most used technique for steel recycling. EAF produces crude steel from scrap iron, pig iron, and alloying materials by applying a high electric current. EAF allows for the recycling of steel scrap and the processing of directly reduced iron. The main process steps in EAF consist of melting, refining, steel and slag tapping, decarburization, ladle treatments and casting [5].

EAF is a batch process consisting of one charging door, one or three electrodes, three water-cooling parts, a roof, panels and an exhaust gas duct. The melted steel is tapped from a tilting mechanism under the furnace. The electrodes provide the electric power. Between the tips of the electrodes, the temperature is increased, due to the current, melting the iron. Steel melts at around 1200-1500°C, depending on steel composition, and the EAF process needs to exceed the melting point. The tap-to-tap time of the batch process is between 40-60 minutes [6, 7].

Indirect energy and secondary energy in EAF come from the chemical energy in the process, the exothermic reactions and liquid fuel from oxygen-burners, respectively [7]. Oxygen is added to purify the steel as well to oxidise the impurities. The oxygen accelerates the melting

and increases the mixing effect. The oxygen is added directly or with oxyfuel burners [5, 8]. Oxyfuel burners combust natural gas with pure oxygen [5]. The oxygen requirement per ton of steel is  $32\text{m}^3 \text{O}_2/\text{ton steel}$  [9]. The energy sources in EAF is presented in figure 2.1.1.

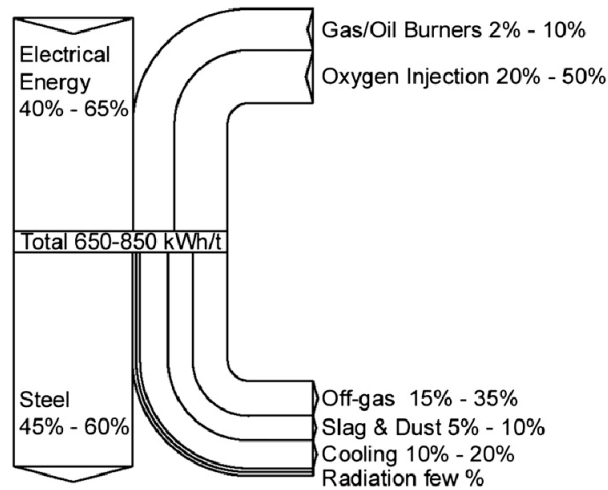


Figure 2.1.1: Energy sources in EAF, [9]

Carbon injection in the melt and slag facilitates the chemical reactions in EAF. The injection of carbon and oxygen creates a foam, increasing the energy efficiency. The carbon comes mainly from fossil sources.

EAF produces, apart from melted steel, the by-products slag, dust and off-gas. Slag from EAF is characterized as highly calcareous, siliceous and ferrous. The slag composition varies depending on steel input in EAF but usually consists in different ratios of iron-, silicon-aluminium- and calcium oxides [10, 11].

Three different types of dust are generated from the different steel-making processes: stainless steel dust, carbon steel dust and ferrochrome dust. The dust contains different metals; iron, zinc, calcium, magnesium, and lead [12]. Most metals occur as oxides since the dust is formed under oxide conditions [13]. The main compound present in the dust is iron and zinc [12, 13]. The dust content in the off-gas varies between 15-30 to 50-60 g/m<sup>3</sup> off-gas.

### 2.1.1 Composition of Off-gas

The EAF off-gas contains chemical energy, mainly unburned CO and H<sub>2</sub>, in addition to the thermal energy content. The energy output in the off-gas is around 15-35% of the total energy leaving the system [9]. The energy lost with the off-gas can be post-combusted for energy recovery. The off-gas is blended with air before the combustion [14].

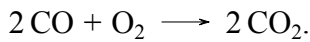
The composition of off-gas is dynamic. The main species are CO<sub>2</sub>, CO, H<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub> [6]. The

composition of off-gas varies due to different combustion processes in the furnace and various flow rates of oxygen and carbon injection. The average primary off-gas composition (for the dry gases) is 10–15% CO<sub>2</sub>, 5–15% O<sub>2</sub>, 5–25% CO, 5–10% H<sub>2</sub>, and 50–70% N<sub>2</sub>. The primary gas is measured before the air is added to the stream for combustion[15]. Steam is formed from the water cooling parts inside EAF and will be in the off-gas [4, 9].

Within the process, the off-gas temperature fluctuates and is between 1100-2100°C. [6, 16].

The CO and CO<sub>2</sub> in the off-gas are formed from the decarburization process. When the O<sub>2</sub> is injected, it acts as an oxidant and reacts with C in the steel. The oxidation reactions are divided into two types, direct and indirect oxidation. In direct oxidation, all O<sub>2</sub> is consumed, and CO is formed.

Air is infiltrated through slag doors, gaps, or electrode openings during the melting process to ensure an oxygen-enriched environment. The formed CO is post-combusted and forms CO<sub>2</sub> accordingly



As mentioned, the off-gas composition varies between processes and depends on the input. The measuring point of off-gas varies as well. Three different off-gas compositions, measured directly after the EAF elbow duct, are presented in table 2.1.1.

Table 2.1.1: Composition of off-gas

Component	Case 1 (vol%) [15]	Case 2 (vol%) [4]	Case 3 (vol%) [17]
CO <sub>2</sub>	15	20	98.4
CO	15	40	0.8
O <sub>2</sub>	15	15	0
H <sub>2</sub>	5	0	0
N <sub>2</sub>	50	40	0.8

As presented in the table, the composition significantly differs between cases. The first case is the average composition, and cases 2 and 3 are extreme cases with high CO and CO<sub>2</sub> content, respectively.

## 2.2 Gasification of biomass

Gasification is the thermochemical process where biomass is converted, without combustion, to syngas ( $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{CH}_4$ ) and char at high temperatures. The gasification process exist in several techniques, and depending on biomass and technique, is beneficial under different conditions. The conversion of biomass occurs in four steps, heating/drying, pyrolysis, gas-solids reactions, and gas-phase reactions. The pyrolysis step is where biomass is converted into tars, char and gases. Due to the large fractions of volatiles in biomass, pyrolysis is an important step. The main gas and solid reactions taking place inside the gasifier are presented in table 2.2.1 [18, 19].

Table 2.2.1: Main reactions inside gasifier [18].

Name of reaction	Chemical reaction	$\Delta H(\text{kJ/mol})$
Partial oxidation	$\text{C} + \text{O}_2 \longrightarrow \text{CO}_2$	-394
	$\text{CO} + 0.5 \text{O}_2 \longrightarrow \text{CO}_2$	-284
	$\text{CH}_4 + 2 \text{O}_2 \longrightarrow \text{CO}_2 + 2 \text{H}_2\text{O}$	-803
	$\text{O}_2 + 2 \text{H}_2 \longrightarrow 2 \text{H}_2\text{O}$	-242
Boudouard	$\text{C} + \text{CO}_2 \longrightarrow 2 \text{CO}$	+172
Water-gas (primary)	$\text{C} + \text{H}_2\text{O} \longrightarrow 2 \text{CO} + \text{H}_2$	+131
Water-gas (secondary)	$\text{C} + 2 \text{H}_2\text{O} \longrightarrow \text{CO}_2 + 2 \text{H}_2$	+88
WGS	$\text{CO} + \text{H}_2\text{O} \longrightarrow \text{CO}_2 + \text{H}_2$	-42.3
Methanation	$\text{C} + 2 \text{H}_2 \longrightarrow \text{CH}_4$	-74.8
Methane reforming	$\text{CH}_4 + \text{H}_2\text{O} \longrightarrow \text{CO} + 3 \text{H}_2$	+206
$\text{H}_2\text{S}$ formation	$\text{H}_2 + \text{S} \longrightarrow \text{H}_2\text{S}$	-20.2

The gasification depends on several parameters; temperature, gasifying agent, biomass and catalyst. Investigated and discussed in this report is gasifying agent and catalyst.

### 2.2.1 Gasifying agent

The selection of gasifying agents impacts the production of syngas. The gasifying agents used are  $\text{CO}_2$ , steam, oxygen, air or mixtures.

### **Using CO<sub>2</sub> as gasifying agent**

Using CO<sub>2</sub> as gasifying agent is novel and comes as a solution to decrease the GHG emissions. By using CO<sub>2</sub>, high-valuable products can be produced while direct emissions can be reduced. The CO<sub>2</sub> in gasifying agent promotes the Boudouard reaction, producing a CO-rich gas. The endothermic reaction makes the temperature inside the gasifier of importance. Below 650°C, CO<sub>2</sub> acts as an inert gas [18, 20].

In rich CO<sub>2</sub> gas, the CO<sub>2</sub> is not completely converted and is left in produced gas. Using CO<sub>2</sub> increases the carbon conversion [18, 20]. Increased CO<sub>2</sub> in gasifying agent decreases the H<sub>2</sub>/CO ratio, decreasing the Lower Heating Value (LHV). The effect can be hindered by mixing CO<sub>2</sub> with oxygen and instead promote H<sub>2</sub> and CO formation [18]. A higher temperature does also increase the H<sub>2</sub>/CO ratio. By injecting steam in CO<sub>2</sub> gasification, the H<sub>2</sub> production can be increased. The steam is not fully converted and remains in producer gas [20].

### **Steam as gasifying agent**

The injection of steam emphasizes the Water gas shift (WGS) reaction, improving H<sub>2</sub> yield [21–24].

The steam-to-biomass ratio is important when injected into the gasifier. However, the result in the literature is inconsistent and depends on the composition of the feedstock. A steam-to-biomass ratio between 0.1-3 has been reported as favourable. A lower ratio favors the Boudouard reaction, while a higher one promotes H<sub>2</sub> formation. For H<sub>2</sub> production, higher temperature is favorable (850-1350°C), due to the endothermic steam gasification reaction [21–24].

### **Oxygen as gasifying agent**

Oxygen as gasifying agent favors the complete conversion and partial combustion reaction [25]. With a high oxygen concentration, the furnace temperature is higher. The oxygen facilitates then the CO<sub>2</sub> reduction reaction, hence favors the CO formation [26]. H<sub>2</sub> production is higher in oxygen enriched environment [18].

### **Air as gasifying agent**

The use of air as gasifying agent is a cheaper option than pure oxygen. Nitrogen acts as inert gas and dilutes the oxygen concentration. Research has shown that an increased flow rate of



gasifying agent increases the syngas yield due to the increased oxygen concentration. Increased temperature is beneficial for H<sub>2</sub> generation [19, 27–30]

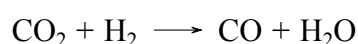
### 2.2.2 Catalyst

The gasification reactions can be emphasised by adding a catalyst inside the gasifier. Relevant in this work is the utilisation of dust and slag from EAF process. Adding the EAF slag can increase the carbon conversion efficiency and benefit the coal gasification reaction [31]. Zinc oxides, found in EAF off-gas, can increase the H<sub>2</sub> production [32].

## 2.3 Cleaning and upgrading of producer gas

The PG from gasification needs to be cleaned from contaminants. Biomass contains sulphur that will form H<sub>2</sub>S and COS. The concentration of H<sub>2</sub>S is generally around 100ppm in PG. Despite the low content, the gas need to be cleaned due to the possibility of deactivating the catalyst used for the water-gas shift reaction. The limit for H<sub>2</sub>S in gas turbines is 8ppm. Sulphur can be removed in situ, i.e. inside the gasifier or downstream. In situ, calcium sorbents are the most used. Downstream cleaning is mainly done by different metals, where the most dominant is ZnO [33]. The sulphur cleaning can hence be done from steel dust from EAF-process, having a high ZnO content.

For upgrading the PG to syngas, which can be further upgraded to fuels, reversed water gas shift (r-WGS) reaction is of importance.



The r-WGS reaction favours higher temperatures at atmospheric pressure. The temperature needs to exceed 800°C [34, 35]. The r-WGS reactor uses catalysts that emphasise the conversion of CO<sub>2</sub>.

The syngas can be further utilised for Fischer-Tropsch (FT) process and Methanol (MeOH) production. FT process is the well-developed process of producing liquid fuels from higher hydrocarbons. The hydrocarbons are produced from CO and H<sub>2</sub> [36].

MeOH synthesis is generated by CO. The reaction follows



## 2.4 Proposed process description

Based on the literature review, a proposed process is derived. The EAF off-gases can be utilised in the gasification process. The oxygen demand for EAF can be produced from electrolysis and while producing  $H_2$  used in r-WGS reactor.

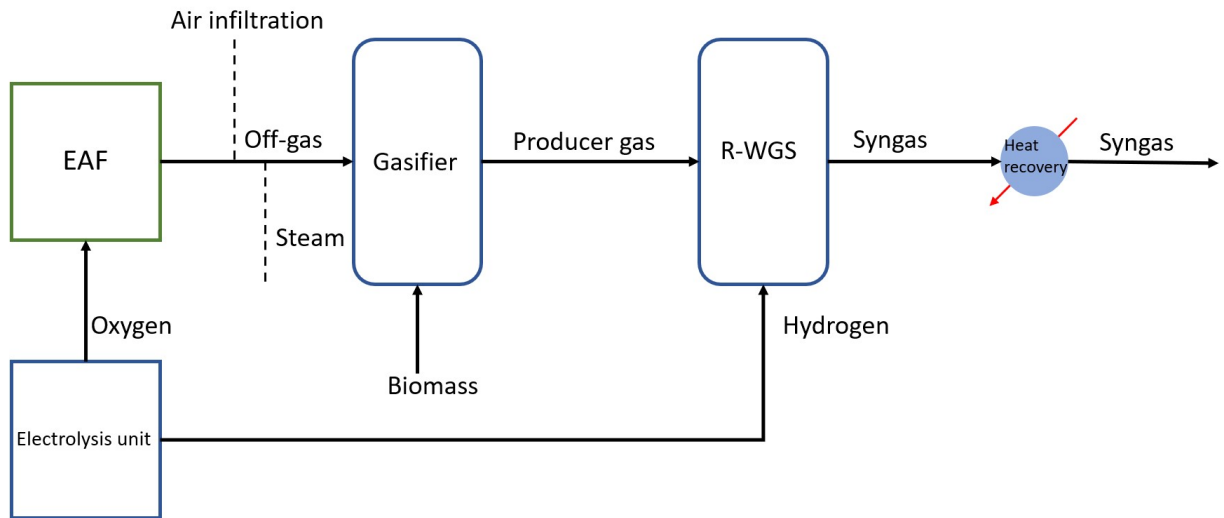


Figure 2.4.1: Proposed process description, material streams

The high temperature in off-gas will provide thermal energy to the gasifier. The gasifier will be run autothermal. Excess thermal energy will be useful for the endothermic reactions and promote CO formation. The producer gas will be treated in an r-WGS reactor to convert  $CO_2$  further and produce syngas. The syngas will either be used as it is or used in the FT or MeOH process.

The added electrolysis unit provides EAF with oxygen and the r-WGS reactor with  $H_2$ .

EAF is a batch process, and gasification is a continuous process. When off-gases are not available, different compositions of air will be used. The gasification process runs in two modes, with off-gas as the gasifying agent and air as the gasifying agent. The produced syngas leave process at high temperature. The thermal energy in syngas will be utilised in electricity production.

The proposed process is compared the reference process as shown in 2.4.2. The reference process consists of EAF which takes oxygen from the electrolyser unit. The  $H_2$  generated from the electrolyser is stored and can be sold. Heat from the EAF off-gas is recovered by generating steam. Steam is expanded on the steam turbines to generate electricity.

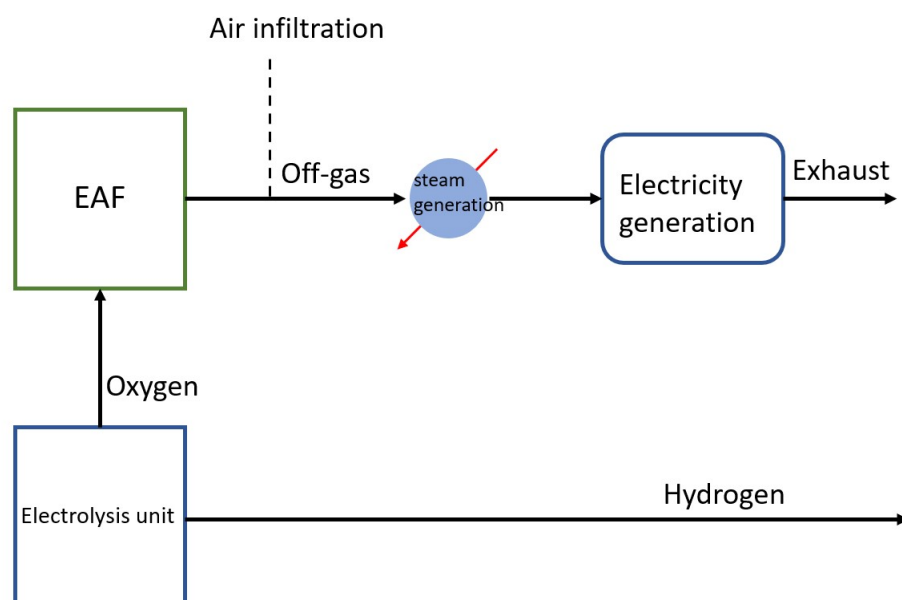


Figure 2.4.2: Reference process, material streams

# Chapter 3

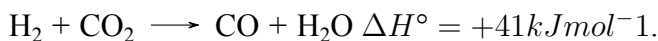
## Methodologies and Assumptions

In this section, the methodology and assumptions of the project are presented.

### 3.1 Modelling approach

The gasification process is simulated using Aspen Plus. The restricted equilibrium method is used in Aspen Plus. The Aspen Plus model was built on the study from Doherty, Reynolds and Kennedy [38]. Alterations are done where all reactions in 2.2.1 are specified in restricted equilibrium. The model approach is first to decompose biomass and then gasify biomass. The gasifier reactor temperature is set to 850°C and pressure 1 bar.

In addition to the gasifier reactor, an r-WGS reactor is added. The reactor is based on the restricted equilibrium method. The reaction considered is the r-WGS reaction



Temperature of the r-WGS reactor is set to 850°C and pressure 1 bar [39].

Additional  $\text{H}_2$  is added to the r-WGS reactor for  $\text{CO}_2$  conversion, according to the r-WGS reaction. Hydrogen is added in three different ratios per case of the gasifying agent. First, the  $\text{H}_2$  available from the electrolyser based on the  $\text{O}_2$  required for EAF is added. The  $\text{H}_2$  is assumed to be produced in 2:1  $\text{O}_2$  produced.

Secondly,  $\text{H}_2$  is added to the r-WGS reactor to allow the composition of syngas to be used in the FT process. The molar ratio of  $\text{H}_2/\text{CO}$  in syngas needs to be 1.6-2 [40, 41]. The ratio is decided to be 2.

$$\frac{H_2}{CO} = 2 \quad (3.1)$$

Finally, the added H<sub>2</sub> allows the syngas to be used in methanol production. The optimal molar ratio of H<sub>2</sub>/CO/CO<sub>2</sub> for methanol production is presented in equation 3.2 [42]

$$\frac{H_2 - CO_2}{CO + CO_2} = 2.1 \quad (3.2)$$

### 3.1.1 Energy balance

Energy balance over the whole system, including the electrolyser, is conducted. Electrolyser is added for O<sub>2</sub> production to EAF, as well H<sub>2</sub> production for the r-WGS reactor.

The result is compared to the energy output from the EAF process without the gasifying process added. The first step in the energy balance is to analyse the energy content in off-gases from EAF. The chemical composition, temperature and the required amount per 100 kg of biomass are used. From the energy content in off-gas, the amount of steel processed in EAF is known. This is done by comparing the average energy content leaving the EAF process in off-gases to the energy in specific cases. Once the amount of ton steel is decided, the required amount of oxygen from electrolysis can be decided, hence the available amount of hydrogen. The electricity demand for the electrolyser is then calculated.

The heat in the syngas is utilised for electricity generation. The generation is simulated using Aspen HYSIS. The heat in the syngas is used for steam generation when steam is used in the gasifying agent. The LHV of syngas is calculated.

The off-gas from EAF, without gasifier, is combusted, and electricity production is generated in Aspen HYSIS for reference case.

### 3.1.2 Delimitations and assumptions

- The gasifier is modeled for 850°C and 1 bar.
- Biomass gasification is simulated using Aspen Plus
- Electricity production from heat recovery is simulated using Aspen HYSIS.

- The system boundaries are the gasifying system, including the r-WGS upgrading. For EAF process, only the energy content in off-gases is considered. The energy input to the EAF and the energy flow via molten products from EAF is not considered in this analysis.
- Reference case off-gas energy is the average as provided in [9].
- Electrolyzer is an Alkaline water electrolyser with specific energy consumption of  $4.5 \text{ kWhNm}^{-3} \text{ H}_2$  [43]. The temperature of produced  $\text{O}_2$  and  $\text{H}_2$  is  $65^\circ\text{C}$ .
- Ratio of produced  $\text{H}_2$  and  $\text{O}_2$  in electrolyser is 2:1.
- Reactions reach equilibrium.
- Ratio of  $\text{H}_2:\text{CO}$  in syngas for FT process is 2.
- Ratio of  $(\text{H}_2-\text{CO}_2)/(\text{CO}+\text{CO}_2)$  in syngas for MeOH process is 2.1.

## 3.2 Design parameters

The available literature is used to select three cases of off-gas composition which is investigated in this work. The off-gas composition is presented in 3.2.1.

Table 3.2.1: Composition of EAF off-gas

Component	Case 1 (vol%) [15]	Case 2 (vol%) [4]	Case 3 (vol%) [17]
$\text{CO}_2$	15	20	98.4
$\text{CO}$	15	40	0.8
$\text{O}_2$	15	15	0
$\text{H}_2$	5	0	0
$\text{N}_2$	50	40	0.8

The composition of the base cases is the primary off-gas composition, hence before air infiltration. The composition is dry. However, there might be smaller composition of water vapor present in primary off-gas from EAF. This case will be similar to the case where we analyse steam and off-gas gasification, assuming that a fraction of steam is coming from EAF off-gas. Case 1 is selected as it is the average composition. Cases 2 and 3 are selected due to extreme cases, with high  $\text{CO}$  and  $\text{CO}_2$  content, respectively. The different off-gas compositions are hereafter called cases 1, 2 and 3, according to table 3.2.1.

The three base cases are further investigated with air infiltration, with steam and finally with air infiltration combined with added steam. Hence, four modes are investigated and modelled for each case, giving a total of 12 cases investigated. The 12 cases investigated are presented

in table 3.2.2.

Table 3.2.2: Modes investigated in off-gas gasification simulation

Case	Off-gas	Off-gas + air	Off-gas + steam	Off-gas + air + steam
Case 1	X	X	X	X
Case 2	X	X	X	X
Case 3	X	X	X	X

The air infiltration is investigated since this occurs in EAF, for off-gas post-combustion. The steam is investigated to account for the steam formed in EAF from the water cooling parts. Since there is no available literature on the amount of steam in off-gas, the amount is assumed. Steam is also added to increase the H<sub>2</sub> generation in producer gas and hence decrease the demand for extra H<sub>2</sub> in the r-WGS reactor.

The flow rate of the gasifying agent is set to allow the gasification process to run autothermal when the biomass feeding rate is fixed to 100 kg/h. The temperature of the off-gas is the average 1600°C. For off-gas with air infiltration, the temperature decreases due to the lower temperature of the air. The air temperature is set to 65°C. The temperature of the gasifying agent is investigated by simulating a mixer in Aspen Plus. The mass of air infiltrated is assumed to be equal to 0.9 of off-gas mass in all cases with air infiltration, according to Kirschen et. al (2005) [4]. The steam flow in cases with steam and off-gas is assumed to be equal to 10wt% of gasifying agent and has a temperature of 150°C.

The EAF process is a batch process. For running gasification, a continuous flow of gasifying agents is required. When off-gas is not available, air is used as gasifying agent. For each mode of off-gas investigated, air gasification is investigated. The composition of the gasifying agent is adjusted to produce a similar composition of produced gas as when off-gas is used, where CO<sub>2</sub>, CO and H<sub>2</sub> are the species focused on. The gasifying agent is, in these cases, either air, enriched air, oxygen and/or steam in different ratios. The temperature of air/oxygen is 65°C. When combined with steam, the temperature is 150°C. The flow rate is decided to allow the gasification process to run auto-thermal for a biomass feeding rate of 100 kg/h.

### 3.2.1 Assumptions

- No fluctuation in off gas composition.
- No temperature fluctuation in the off-gas. The temperature is 1600°C
- The mass of air infiltration is equal to 0.9 of off-gas mass, in all cases [4]
- Steam makes 10% of mass as gasifying agent going in.
- Three cases of primary off-gas composition are investigated
- Biomass feeding rate is fixed to 100 kg/h. The biomass is pine.
- Steam temperature is 150°C at 1 bar.
- Air temperature is 65°C.
- Pressure drop in the process steps are neglected in this study.

## 3.3 Model Validation

For validation of the gasification process model in Aspen plus, experimental results found in the literature are used. The same design conditions as in experiments were inserted into the Aspen model, and results could be compared. Due to the Aspen model reaching equilibrium, and in reality, there are fluctuations in produced gas, the accepted error between the Aspen and experiment is set to 15%.

### 3.3.1 Gasifier

The gasifier in Aspen Plus is validated against literature from four experiments using different gasifying agents: air, enriched air + steam, steam, and CO<sub>2</sub>. The experimental parameters from experiments can be seen in table 3.3.1.

Table 3.3.1: Parameters used for validation of aspen model

Parameters	Air [44]	Air+Steam [45]	Steam [45]	CO <sub>2</sub> [46]
Flow rate of gasifying agent [kg/h]	0.7	17.4	2.16	8
Biomass feeding rate [kg/h]	0.6	21.6	21.6	8
Temperature [°C]	1000	840	840	840

The results from validation are observed in 3.3.2.

Table 3.3.2: Validation results for different gasifying agent with errors



Comp.	Air			Air+ Steam			Steam			CO2		
	Exp. [%]	Asp. [%]	Error [%]	Exp. [%]	Asp. [%]	Error [%]	Exp. [%]	Asp. [%]	Error [%]	Exp. [%]	Asp. [%]	Error [%]
CO2	12	10	<b>13.3</b>	23	25	<b>6</b>	23	25	<b>6</b>	21	18	<b>14</b>
CO	23	22	<b>4.3</b>	39	36	<b>8</b>	39	36	<b>8</b>	58	57	<b>2</b>
H2	13.5	15	<b>10</b>	27	28	<b>5</b>	27	28	<b>5</b>	21	22	<b>5</b>
CH4	1.15	0	<b>100</b>	11	11	<b>0</b>	11	11	<b>0</b>	1	12	<b>92</b>

The model shows good prediction. However, as observed in the table, the error for CH<sub>4</sub> is large. Previous research has found the same problem when validating biomass gasification in an equilibrium model. The underestimation of CH<sub>4</sub> is due to the differences between existing biomass gasification and an ideal reactor at chemical equilibrium [47–49].

### 3.3.2 Reverse Water-Gas Shift process (r-WGS)

The r-WGS reactor is validated by comparing the modelled CO<sub>2</sub> conversion to experimental results available in literature. The parameters from the experimental can be seen in table 3.3.3

Table 3.3.3: Parameters from experiment used for r-WGS validation [50]

H <sub>2</sub> :CO <sub>2</sub> ratio	8:1
Temperature [°C]	750

The result from validation is presented in table 3.3.4.

Table 3.3.4: Result for r-WGS validation

	Literature [50]	Model in this work	Error [%]
CO <sub>2</sub> Conversion	87	92	<b>5.4</b>

The table shows that the error in the r-WGS reactor is close to 5%, and the model shows good prediction.

## 3.4 Key Performance Indicators

The Key Performance indicators (KPI) in this project evaluate the process performance in terms of emissions and energy efficiency.

C utilisation is measured to compare the C in CO<sub>2</sub> out from process to all carbon put in process,

from biomass and gasifying agent. The higher the C utilisation, the more profitable since carbon input is converted to CO and not CO<sub>2</sub>.

$$C_{recovery} = \frac{C_{in} - C_{in}C_{outinCO2}}{C_{in}} \times 100\% \quad (3.3)$$

CO<sub>2</sub> out is measured in syngas, and C is the total carbon in the gasifying agent and biomass.

The energy efficiency is measured as the energy input divided by the energy output. This project aims to increase efficiency by integrating the gasifier with the EAF.

$$System\ efficiency = \frac{Energy_{out}}{Energy_{in}} \times 100\% \quad (3.4)$$

Where energy out is the energy of syngas and the electricity production from the heat recovery stream. Energy is the energy in gasifying agent, electricity demand for electrolysis, the LHV of biomass and energy demand for the r-WGS reactor.

# Chapter 4

## Results and discussion

In this chapter, the results for different design conditions and cases are presented and discussed briefly. Firstly, the flowrates for different gasifying agents is presented for different cases outlined in Table 4.1.4- 4.1.6. The result is evaluated.. Then the composition of producer gas from biomass gasification and syngas after r-WGS is presented. The C utilization is evaluated for different cases and presented thereafter. The energy balance results are then presented along with system efficiencies in different cases.

### 4.1 Gasifying agent conditions

The gasification process, without an r-WGS reactor, was modelled autothermal.

#### 4.1.1 EAF off-gas as gasifying agent

The flow rate was decided for the three cases of primary off-gas composition. The flow rate for air infiltration, steam and finally off-gas with steam and air infiltration was decided. The composition of the gasifying agent, temperature and flow rates of gasifying agent for the different cases are presented in table 4.1.4.

Table 4.1.1: Composition, temperature and flow rate of gasifying agent for case 1

Comp.	Case 1	Case 1 + air	Case 1 + steam	Case 1 + air + steam
CO <sub>2</sub>	15%	7.5%	10%	7.4%
CO	15%	6.4%	10%	7.4%
H <sub>2</sub>	5%	0.5%	0.6%	-
H <sub>2</sub> O	-	-	15%	5%
O <sub>2</sub>	15%	18.7%	10%	17%
N <sub>2</sub>	50%	67.4%	55 %	63%
Temp. [°C ]	1600	937	1202	891
Mass flow kg/h	120	138	204	150

Table 4.1.2: Composition, temperature and flow rate of gasifying agent for case 2

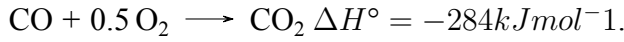
Comp.	Case 2	Case 2 + air	Case 2 + steam	Case 2 + air + steam
CO <sub>2</sub>	20%	10%	17.3%	9.3%
CO	40%	20%	34.6%	18.8%
H <sub>2</sub>	-	-	-	-
H <sub>2</sub> O	-	-	14.7%	8%
O <sub>2</sub>	-	10%	-	9.1%
N <sub>2</sub>	40%	60%	33.6%	54.3%
Temp. [°C ]	1600	929	1380	863
Mass flow kg/h	508	262	567	300

Table 4.1.3: Composition, temperature and flow rate of gasifying agent for case 3

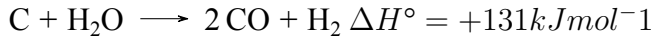
Comp.	Case 3	Case 3 + air	Case 3 + steam	Case 3 + air + steam
CO <sub>2</sub>	98.4%	41.6%	77%	37.8%
CO	0.8%	0.7%	0.7%	0.3%
H <sub>2</sub>	-	-	-	-
H <sub>2</sub> O	-	-	21.6%	13.4%
O <sub>2</sub>	-	12%	-	11%
N <sub>2</sub>	0.8%	45.7%	0.7%	37.5%
Temp. [°C ]	1600	946	1389	879
Mass flow kg/h	723	327	900	370

As the table shows, the higher the oxygen content, the less gasifying agent is required. The reason for this is that oxygen favors the exothermic reactions, allowing endothermic reactions to occur





Oxygen in gasifying agent increases the biomass gasified per kg of the gasifying agent. Conversely, more gasifying agent is required when the steam is present. The endothermic steam reactions can explain this



Air infiltration is advantageous for off-gas with high  $\text{CO}_2$  since more biomass can be gasified per kg of off-gas. However, a higher  $\text{N}_2$  content in gasifying agent dilutes the agent and can increase the required flow of gasifying agent. When steam is present in off-gas, an increased flow is required for biomass gasification. Hence, less biomass can be gasified per kg of off-gas.

#### 4.1.2 Conditions for air as gasifying agent in the absence of EAF off-gas

For air gasification, the flow rates were decided to run autothermal for 100 kg biomass/h. The composition of the gasifying agent in air and steam gasification was based on the composition of produced gas from the off-gas process, i.e. composition before the r-WGS reactor. To enable continuity in the gasification process, the composition of produced gas should be similar to that of producer gas when off-gas is used as gasifying agent. The composition of the gasifying agent, temperature and flow rates can be seen in 4.1.4-4.1.6.

Table 4.1.4: Composition, temperature and flow rate of gasifying agent for air gasification, case 1

Comp.	Case 1	Case 1 + air	Case 1 + steam	Case 1 + air + steam
O <sub>2</sub>	60%	45%	30%	30%
N <sub>2</sub>	40%	55%	40%	40%
H <sub>2</sub> O	-	-	30%	30%
Temp. [°C]	65	65	150	150
Mass flow kg/h	44	61	92	92

Table 4.1.5: Composition, temperature and flow rate of gasifying agent for air gasification, case 2

Comp.	Case 2	Case 2 + air	Case 2 + steam	Case 2 + air + steam
O <sub>2</sub>	100%	100%	100%	40%
N <sub>2</sub>	-	-	-	30%
H <sub>2</sub> O	-	-	-	30%
Temp. [°C]	65	65	150	150
Mass flow kg/h	26	61	61	62

Table 4.1.6: Composition, temperature and flow rate of gasifying agent for air gasification, case 3

Comp.	Case 3	Case 3 + air	Case 3 + steam	Case 3 + air + steam
O <sub>2</sub>	21%	45%	21%	21%
N <sub>2</sub>	79%	55%	79%	79%
H <sub>2</sub> O	-	-	-	-
Temp. [°C]	65	65	65	150
Mass flow kg/h	180	61	180	92

As observed in the tables, the flow rates decrease when the oxygen content in gasifying agent increases. The results follow when different mixtures of the gasifying agent from off-gas are present. When steam is used in gasifying agent, the flow rates increase.

## 4.2 Composition of Producer gas and syngas

### 4.2.1 Producer gas composition

Producer gas is the gas at the outlet of the biomass gasification step. The influence on producer gas composition of varying gasifying agent composition was investigated. The inert free producer gas composition, i.e. before the r-WGS reactor, for the different cases can be seen in the table 4.2.1- 4.2.3.

As observed from case 1, air gasification is fairly similar to off-gas gasification. The more extreme cases, case 2 and 3, is not as straightforward to fit, seen in table 4.2.2- 4.2.3.

Table 4.2.1: Composition of producer gas for off-gas and air gasification, case 1

Components of PG	Case 1		Case 1+air		Case 1+ steam		Case 1+air+steam	
	Off-gas	Air	Off-gas	Air	Off-gas	Air	Off-gas	Air
<b>CO<sub>2</sub></b>	0.12	0.15	0.11	0.15	0.17	0.17	0.15	0.17
<b>CO</b>	0.53	0.45	0.37	0.45	0.42	0.33	0.46	0.33
<b>H<sub>2</sub>O</b>	0.04	0.05	0.05	0.05	0.10	0.15	0.08	0.15
<b>H<sub>2</sub></b>	0.18	0.19	0.15	0.20	0.23	0.26	0.22	0.26
<b>CH<sub>4</sub></b>	0.13	0.16	0.07	0.15	0.08	0.09	0.10	0.09
<b>LHV [kWh]</b>	564	471	507	458	569	478	525	478

Table 4.2.2: Composition of producer gas for off-gas and air gasification, case 2

Components of PG	Case 2		Case 1+air		Case 2+ steam		Case 2+air+steam	
	Off-gas	Air	Off-gas	Air	Off-gas	Air	Off-gas	Air
<b>CO<sub>2</sub></b>	0.15	0.15	0.15	0.15	0.22	0.15	0.19	0.18
<b>CO</b>	0.70	0.46	0.56	0.46	0.50	0.46	0.47	0.35
<b>H<sub>2</sub>O</b>	0.01	0.04	0.05	0.04	0.07	0.04	0.09	0.10
<b>H<sub>2</sub></b>	0.09	0.17	0.17	0.17	0.16	0.17	0.20	0.24
<b>CH<sub>4</sub></b>	0.05	0.18	0.07	0.18	0.05	0.18	0.06	0.13
<b>LHV [kWh]</b>	1017	474	603	456	1106	456	645	469

Table 4.2.3: Composition of producer gas for off-gas and air gasification, case 3

Components of PG	Case 3		Case 3+air		Case 3+ steam		Case 3+air+steam	
	Off-gas	Air	Off-gas	Air	Off-gas	Air	Off-gas	Air
<b>CO<sub>2</sub></b>	0.56	0.35	0.32	0.35	0.53	0.17	0.34	0.17
<b>CO</b>	0.32	0.34	0.41	0.34	0.22	0.33	0.34	0.33
<b>H<sub>2</sub>O</b>	0.07	0.14	0.12	0.14	0.18	0.15	0.16	0.15
<b>H<sub>2</sub></b>	0.05	0.16	0.14	0.16	0.07	0.26	0.15	0.26
<b>CH<sub>4</sub></b>	0.002	0.01	0.01	0.01	0.001	0.09	0.012	0.09
<b>LHV[kWh]</b>	714	276	496	276	733	276	486	480

The tables show that the gasifying agent strongly affects the producer-gas composition. Off-gas with high CO or CO<sub>2</sub> content (case 2 and 3 respectively) gives high content in producer gas. The high content of CO and CO<sub>2</sub> in the case with EAF off-gas gasification cannot be matched with air gasification. When air is infiltrated in off-gases, producer gas composition is more similar to air gasification. For continuity in the process, in terms of producer gas composition, air infiltration in off-gases is hence favorable.

Adding steam increases the  $H_2$  production compared to when dry off-gases are used. Interestingly noteworthy, for case 3,  $H_2$  production increases slightly more when air is infiltrated compared to steam. The increased  $H_2$  and CO production when oxygen is supplied to  $CO_2$  gasification has previously been shown in the literature.

In all cases observed, a r-WGS reactor is required to decrease the  $CO_2$  in gas and increase  $H_2$  ratio for further use in the FT and MeOH process.

### **4.2.2 Syngas Composition**

The producer gas was treated in the r-WGS reactor. In addition to the r-WGS reactor,  $H_2$  is supplied. . The resulting product from the r-WGS reactor is syngas. The addition of  $H_2$  is done in three different ratios, available  $H_2$  from energy balance, to allow syngas to be used in FT and finally, to allow syngas to be used in MeOH production. For FT and MeOH production,  $H_2$  is added subsequently until the composition of syngas fulfils equation 3.1 and 3.2.

#### **Syngas conditions during off-gas gasification**

The different syngas compositions after available  $H_2$  addition for each off-gas case and the addition of  $H_2$  can be seen in table 4.2.2-4.2.6.



Table 4.2.4: Syngas compositions after r-WGS reactor from available H<sub>2</sub>, to FT and MeOH for case 1.

Components in syngas	Case 1			Case 1+air			Case 1+ steam			Case 1+air+steam		
	Syngas	FT	MeOH	Syngas	FT	MeOH	Syngas	FT	MeOH	Syngas	FT	MeOH
CO <sub>2</sub>	0.02	0.01	0.01	0.04	0.01	0.01	0.08	0.11	0.03	0.05	0.02	0.02
CO	0.57	0.33	0.31	0.54	0.34	0.31	0.45	0.57	0.30	0.50	0.32	0.30
H <sub>2</sub> O	0.01	0.02	0.02	0.03	0.03	0.03	0.08	0.10	0.07	0.05	0.04	0.04
H <sub>2</sub>	0.39	0.63	0.66	0.40	0.61	0.65	0.39	0.49	0.59	0.39	0.61	0.64
CH <sub>4</sub>	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Added H <sub>2</sub>	2.04	7.00	8.90	2.34	5.60	7.20	3.50	5.30	7.00	2.53	6.00	7.40
LHV[kWh]	646	1071	1164	571	921	1028	657	999	1092	589	949	1036

Table 4.2.5: Syngas compositions after r-WGS reactor from available H<sub>2</sub>, to FT and MeOH for case 2.

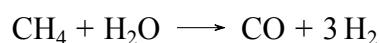
Components in syngas	Case 2			Case 2+air			Case 2+ steam			Case 2+air+steam		
	Syngas	FT	MeOH	Syngas	FT	MeOH	Syngas	FT	MeOH	Syngas	FT	MeOH
CO <sub>2</sub>	0.07	0.01	0.01	0.08	0.02	0.02	0.13	0.03	0.03	0.10	0.03	0.03
CO	0.67	0.32	0.31	0.56	0.31	0.31	0.51	0.29	0.27	0.48	0.30	0.28
H <sub>2</sub> O	0.03	0.03	0.03	0.04	0.04	0.04	0.08	0.07	0.07	0.08	0.07	0.07
H <sub>2</sub>	0.24	0.64	0.64	0.33	0.64	0.64	0.28	0.60	0.63	0.34	0.60	0.63
CH <sub>4</sub>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Added H <sub>2</sub> [kmol]	5	25	25.4	1.6	11.00	11.50	8	23.00	28.00	2	10.50	12.20
LHV[kWh]	1290	2837	2927	721	1378	1384	1332	3040	3239	742	1390	1510

Table 4.2.6: Syngas compositions after r-WGS reactor from available H<sub>2</sub>, to FT and MeOH for case 3.

Components in syngas	Case 3			Case 3+air			Case 3+ steam			Case 3+air+steam		
	Syngas	FT	MeOH	Syngas	FT	MeOH	Syngas	FT	MeOH	Syngas	FT	MeOH
CO <sub>2</sub>	0.43	0.07	0.05	0.24	0.06	0.04	0.42	0.10	0.06	0.26	0.08	0.05
CO	0.35	0.25	0.22	0.42	0.27	0.24	0.24	0.23	0.19	0.35	0.25	0.22
H <sub>2</sub> O	0.13	0.16	0.14	0.13	0.13	0.12	0.22	0.22	0.18	0.17	0.17	0.15
H <sub>2</sub>	0.09	0.51	0.59	0.21	0.54	0.61	0.12	0.46	0.57	0.22	0.50	0.59
CH <sub>4</sub>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Added H <sub>2</sub> [kmol]	4.9	39.00	54.00	1.8	13.30	18.00	6.2	39.00	60.00	2.0	13.00	19.40
<b>LHV</b> [kWh]	950	4008	5267	605	1549	1829	1033	4486	6219	623	1557	2121

The addition of H<sub>2</sub> increases the CO<sub>2</sub> conversion. The result is expected according to the r-WGS reaction. The results show that higher CO<sub>2</sub> content in gasifying agent increases the need for H<sub>2</sub> in r-WGS reactor to be used in FT or MeOH production. Once all CO<sub>2</sub> reacted, H<sub>2</sub> did not further react, and the ratio of H<sub>2</sub> increased in syngas. For increasing the carbon utilisation, the addition of H<sub>2</sub> is preferable. Observed from case 3, the CO<sub>2</sub> content in syngas decreases from 43mol-% to 7 mol-% and 5mol-% for FT and MeOH, respectively.

Observed in all cases, CH<sub>4</sub> and steam decrease in the r-WGS reactor. This implies that a steam reforming reaction occurs.



The result shows that off-gases can be used in biomass gasification to form high-valuable gases that can further be used in FT or MeOH production. The addition of H<sub>2</sub> significantly increases the LHV of syngas.

### **Syngas conditions for air gasification cases**

The producer gas was for air gasification treated in r-WGS reactor for syngas production (only available H<sub>2</sub> used), FT and MeOH production. The result for each case can be seen in table 4.2.7-4.2.9.

Table 4.2.7: Compositions for air gasification, case 1, for syngas FT and MeOH

Components in syngas	Case 1			Case 1+air			Case 1+ steam			Case 1+air+steam		
	Av. H <sub>2</sub>	FT	MeOH	Av. H <sub>2</sub>	FT	MeOH	Available H <sub>2</sub>	FT	MeOH	Av. H <sub>2</sub>	FT	MeOH
CO <sub>2</sub>	0.01	0.01	0.01	0.02	0.01	0.01	0.06	0.04	0.03	0.06	0.04	0.03
CO	0.45	0.32	0.31	0.44	0.32	0.32	0.34	0.29	0.26	0.34	0.29	0.26
H <sub>2</sub> O	0.02	0.01	0.01	0.02	0.02	0.02	0.10	0.09	0.09	0.10	0.09	0.09
H <sub>2</sub>	0.51	0.64	0.66	0.51	0.65	0.65	0.51	0.58	0.62	0.51	0.58	0.62
CH <sub>4</sub>	0.01	0.01	0.01	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00
Added H <sub>2</sub>	2.90	5.20	5.80	2.50	5.40	5.40	2.90	3.90	5.40	2.90	3.90	5.40
LHV[kWh]	508.00	816.80	840.40	495.00	830.49	830.49	518.00	793.60	889.60	518.00	793.60	889.60

Table 4.2.8: Compositions for air gasification, case 2, for syngas FT and MeOH

Components in syngas	Case 2			Case 2+air			Case 2+ steam			Case 2+air+steam		
	Av. H <sub>2</sub>	FT	MeOH	Av. H <sub>2</sub>	FT	MeOH	Available H <sub>2</sub>	FT	MeOH	Av. H <sub>2</sub>	FT	MeOH
CO <sub>2</sub>	0.02	0.01	0.01	0.02	0.01	0.01	0.02	0.01	0.01	0.16	0.03	0.02
CO	0.49	0.32	0.32	0.49	0.32	0.32	0.49	0.32	0.32	0.37	0.30	0.29
H <sub>2</sub> O	0.02	0.01	0.01	0.02	0.01	0.01	0.02	0.01	0.01	0.11	0.06	0.06
H <sub>2</sub>	0.45	0.64	0.65	0.45	0.64	0.65	0.45	0.64	0.65	0.24	0.61	0.63
CH <sub>4</sub>	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.12	0.00	0.00
Added H <sub>2</sub>	1.60	5.20	5.40	1.60	5.20	5.40	1.60	5.20	5.40	1.50	4.50	5.20
LHV	564.14	791.00	932.40	564.14	791.00	932.40	564.14	791.00	932.40		797.63	860.44

Table 4.2.9: Compositions for air gasification, case 3, for syngas FT and MeOH

Components in syngas	Case 3			Case 3+air			Case 3+ steam			Case 3+air+steam		
	Available H <sub>2</sub>	FT	MeOH	Av. H <sub>2</sub>	FT	MeOH	Av. H <sub>2</sub>	FT	MeOH	Av. H <sub>2</sub>	FT	MeOH
CO <sub>2</sub>	0.08	0.03	0.02	0.02	0.01	0.01	0.08	0.03	0.02	0.08	0.03	0.02
CO	0.49	0.30	0.28	0.44	0.32	0.32	0.49	0.30	0.28	0.49	0.30	0.28
H <sub>2</sub> O	0.07	0.06	0.06	0.02	0.02	0.02	0.07	0.06	0.06	0.07	0.06	0.06
H <sub>2</sub>	0.36	0.61	0.63	0.51	0.65	0.65	0.36	0.61	0.63	0.36	0.61	0.63
CH <sub>4</sub>	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00
Added H <sub>2</sub>	0.00	5.30	6.30	2.50	5.40	5.40	0.00	5.30	6.30	0.00	5.30	6.30
LHV	433.00	798.51	846.12	495.00	830.49	830.49	433.00	798.51	846.12	433.00	798.51	846.12

The syngas composition from air gasification treated for use in FT and MeOH is very similar to syngas from off-gases, valid for all cases. Syngas produced with available  $H_2$ , vary. For continuously syngas production between air and off-gas gasification, FT and MeOH is preferred.

Further comparing air gasification with off-gas gasification, the LHV of off-gas gasification is significantly higher. The explanation is the higher required flow of off-gases for biomass gasification. For air gasification, the lower flow rate of the gasifying agent is required per LHV of biomass.

### 4.2.3 Carbon utilisation in the process

Carbon utilisation was evaluated for all cases of syngas production from off-gas gasification.

Table 4.2.10: Carbon utilisation for case 1

<b>C source [kg]</b>	<b>EAF</b>	<b>Off-gas</b>	<b>Off-gas + Air</b>	<b>Off-gas + steam</b>	<b>Off-gas+ air+steam</b>
C in off-gas	43.6	43.6	23.5	33.1	27.7
C from biomass	0.0	51.2	51.2	51.2	51.2
C in CO <sub>2</sub> syngas	43.6	7.9	13.4	38.4	21.3
<b>C utilisation [%]</b>	0.0	91.7	82.1	54.4	73.0

Table 4.2.11: Carbon utilisation for case 2

Table 4.2.12: C utilisation of Case 2

<b>C source [kg]</b>	<b>EAF</b>	<b>Off-gas</b>	<b>Off-gas + Air</b>	<b>Off-gas + steam</b>	<b>Off-gas+ air+steam</b>
C in offgas	326.0	326.0	87.8	334.5	96.0
C from biomass	0.0	51.2	51.2	51.2	51.2
C in CO <sub>2</sub> syngas	326.0	55.2	31.5	128.3	53.3
<b>C utilisation [%]</b>	0	85.4	77.4	66.7	63.8

Table 4.2.13: Carbon utilisation for case 3

<b>C source [kg]</b>	<b>EAF</b>	<b>Off-gas</b>	<b>Off-gas + Air</b>	<b>Off-gas + steam</b>	<b>Off-gas+ air+steam</b>
C in offgas	719.4	719.4	170.8	805.5	184.1
C from biomass	0	51.2	51.2	51.2	51.2
C in CO <sub>2</sub> syngas	719.4	502.4	129.2	627.7	156.3
<b>C utilisation [%]</b>	0	34.8	41.8	26.7	33.6

The analysis shows the desirable result of decreasing CO<sub>2</sub> emissions and converts into CO. It is observed, that in the presence of steam, the C utilisation is less. This is because it favors

the water gas shift reaction producing more  $\text{CO}_2$ . The C utilisation is lowest for case 3 but increases with air infiltration. However, for cases 1 and 2, air infiltration decreases carbon utilisation.

### 4.3 Energy balance for the process

Energy balance for off-gas and air gasification was performed.

#### 4.3.1 Off-gas gasification

The energy balance for the different cases was performed and compared to the reference case, i.e. case without the gasifier. Chemical, thermal and electrical energy was considered. The energy for EAF operation was not considered, but only the energy in off-gas is considered.

The energy content in EAF off-gas was set to the average (187.5 kWh), according [9], and is hence per ton of steel. The off-gas combustion and heat recovery and electricity generation process was modelled in Aspen HYSIS. Since  $\text{H}_2$  is not utilised in any reactor in the reference case,  $\text{H}_2$  is an output. The flows in the reference case is represented in 4.3.1.

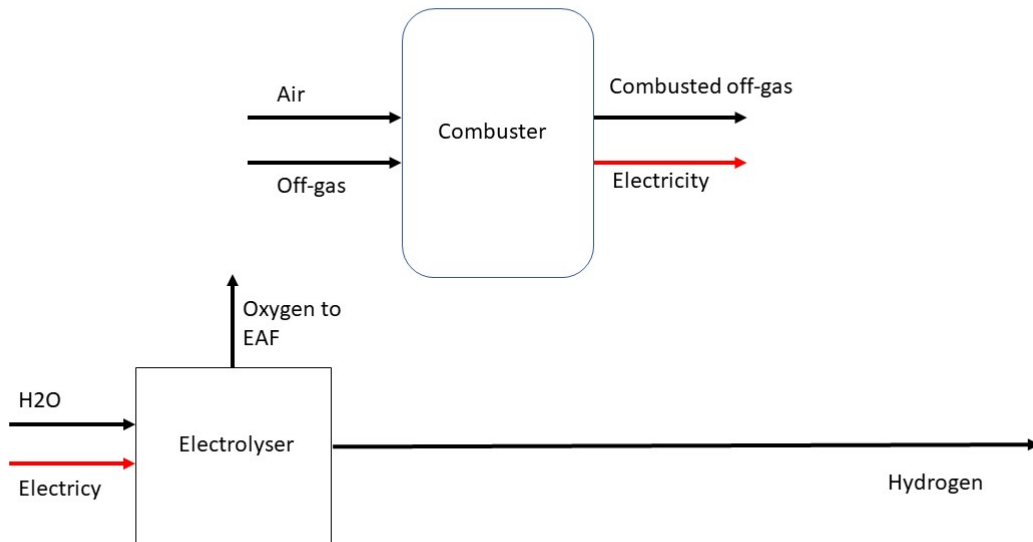


Figure 4.3.1: Energy flows of reference case

The energy in off-gases used in gasification was compared to the energy flow in off-gas in the reference case. By comparing, the known amount of steel required to produce the amount of

off-gas required and hence electricity demand for electrolyser and available  $H_2$ .

When the gasifier is added to the process, incoming energy is from off-gas, biomass, the electricity of electrolysis units and electricity to the r-WGS reactor. The r-WGS reaction is endothermic, and the reactor needs to be supplied with heat. The additional energy required for the r-WGS reactor was decided to be electrical. However, it is possible to supply heat for the r-WGS reactor by combusting a fraction of the produced syngas. Energy flows leaving the system are the chemical energy in syngas and the electrical energy from the heat recovery system. The energy flows in gasifier cases are presented in 4.3.2.

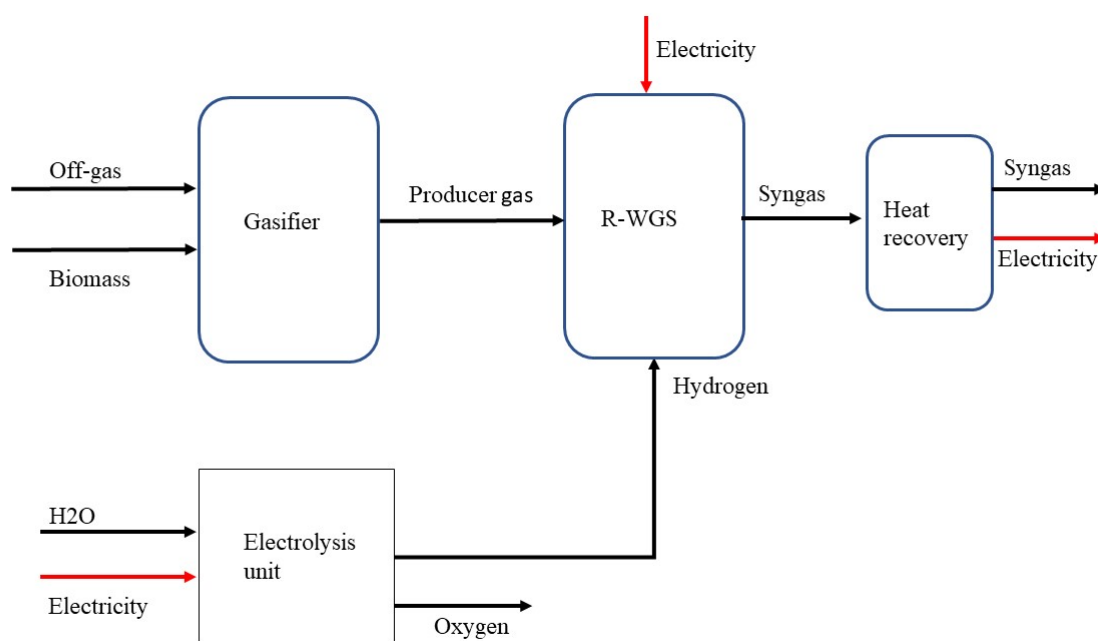


Figure 4.3.2: Caption

The energy for each component in the system, for the different cases, is presented in tables 4.3.1 -4.3.3, including the system's efficiency. The balance is for syngas production when only available hydrogen is used.



Table 4.3.1: Energy balance over system, case 1

Energy [kWh]	Ref.	Case 1	Case 1+air	Case 1+steam	Case 1 +air + steam
<b>IN</b>					
Biomass	0	530	530	530	530
Off-gas	187.5	133	58.6	114.9	102.5
Electricity for electrolyser	280	199.5	228.9	342.3	247.4
Electricity use for r-WGS	0	80.1	65.18	88.15	64.37
<b>OUT</b>					
Electricity out	42	65	69	87.9	70.7
Syngas Energy	0	643.7	571.8	657.4	589.1
Hydrogen Energy	180	0	0	0	0
<b>Efficiency</b>	47%	75%	73%	69%	70%

Table 4.3.2: Energy balance over system, case 2

Energy [kWh]	Ref.	Case 2	Case 2+air	Case 2+steam	Case 2 +air + steam
<b>IN</b>					
Biomass	0	530	530	530	530
Off-gas	187.5	307.1	105	519.76	266
Electricity for electrolyser	280	461	161	799	409
Electricity use for r-WGS	0	513.3	273.7	466.0	230.4
<b>OUT</b>					
Electricity out	55	73	183.4	280.3	197.8
Syngas energy	0	1290.0	721.2	1331.6	742.3
Hydrogen energy	180	0	0	0	0
<b>Efficiency</b>	56%	77%	85%	70%	66%

As observed from the calculated efficiencies for cases 1 and 2, adding the gasifier to the EAF process is beneficial for increasing system efficiencies. Biomass gasification increases the energy content of the syngas leaving the system. This way we are also able to utilise the energy content in EAF off-gas for the biomass gasification process. For case 3, the benefit is not as obvious (table 4.3.3).

Table 4.3.3: Energy balance over system, case 3

Energy [kWh]	Ref.	Case 3	Case 3+air	Case 3+steam	Case 3 +air + steam
<b>IN</b>					
Biomass	0	530	530	530	530
Off-gas	187.5	321	114	403	129.2
Electricity for electrolyser	280	479	170.2	602	193
Electricity use for r-WGS	0	415.6	384.8	496.2	401.2
<b>OUT</b>					
Electricity out	37.7	87.1	66.6	149.3	76.7
Syngas energy	0	950.1	604.7	1032.9	623.3
Hydrogen energy	180	0	0	0	0
<b>Efficiency</b>	46%	59%	56%	58%	56%

For case 3, the energy in the syngas is lower than in cases 1 and 2 due to the higher CO<sub>2</sub> content. Adding more H<sub>2</sub>, conversion of CO<sub>2</sub> can further occur and increase the LHV. However, the electrolyser is energy intensive, and the energy in syngas needs to exceed the demand to increase efficiency.

The efficiencies of the reference case differ due to the output electricity. Case 2 has a high CO content that can be post-combusted for electricity production. Case 3 only utilises thermal energy.

### Adjusting syngas conditions for Fischer Tropsch (FT) process

The system efficiencies were further investigated when syngas was treated to be used in FT or MeOH production. The additional need of hydrogen increases the electrical use in electrolysis.

The efficiency of different systems to produce syngas suitable for FT process is presented in table 4.3.13- 4.3.15.

Table 4.3.4: Energy balance over system adjusting syngas suitable for FT, case 1

Energy [kWh]	Case 1	Case 1+air	Case 1+steam	Case 1 +air + steam
<b>IN</b>				
Biomass in	530	530	530	530
Off-gas energy	133	58.6	114.9	102.5
Electricity for electrolyser	684.6	547.68	518.34	586.8
Electricity use for r-WGS	507.5	414.5	429.8	424.2
<b>OUT</b>				
Electricity	32	30	31	33
Syngas energy	1071.1	921.0	999.05	949.0
<b>Efficiency for FT</b>	59%	61%	65%	60%

Table 4.3.5: Energy balance over system adjusting syngas suitable for FT, case 2

Energy [kWh]	Case 2	Case 2+air	Case 2+steam	Case 2 +air + steam
<b>IN [kWh]</b>				
Biomass	530	530	530	530
Off-gas energy	307.1	105	519.76	266
Electricity for electrolyser	2445	1076	2249	1027
Electricity use for r-WGS	1821	775	1935	744.6
<b>OUT [kWh]</b>				
Electricity	40	42	39	42
Syngas energy	2837.9	1377.9	3040.2	1389.5
<b>Efficiency</b>	56%	57%	59%	56%

it is observed that hydrogen generation is the main contributor to the decrease in efficiency. This is especially true for case 2, where the CO content is high in syngas production before additional hydrogen for FT suited syngas generation. The molar ratio of H<sub>2</sub>/CO for FT process needs to be 2, and for achieving this in CO-rich gas, a prominent addition of hydrogen is required. In these cases, one could argue that the best option for syngas is to be directly combusted and not further treated for FT since the energy content is already high.

However, the system efficiencies in the case of producing syngas for FT is still higher than the reference case.

Table 4.3.6: Energy balance over system adjusting syngas suitable for FT, case 3

Energy [kWh]	Case 3	Case 3+air	Case 3+steam	Case 3 +air + steam
<b>IN</b>				
Biomass in	530	530	530	530
off-gas energy	321	114	403	129.2
Electricity for electrolyser	3814	1301	3814	1271
Electricity use for r-WGS	3294	1053	3754	1071
<b>OUT</b>				
Electricity	87	67	149	77
Syngas energy	4008	1549	4486	1557
<b>Efficiency</b>	51%	54%	55%	54%

Observed, The efficiencies increase with steam injection. The steam is converted in the steam reforming reaction to CO and H<sub>2</sub>, decreasing the addition of H<sub>2</sub>.

### Adjusting syngas composition suitable for MeOH synthesis

The energy analysis for the cases where the syngas composition is adjusted to suit MeOH production can be seen in table 4.3.7-4.3.9.

Table 4.3.7: Energy balance over system for adjusting syngas suitable for MeOH synthesis, case 1

Energy [kWh]	Case 1	Case 1 +air	Case 1+steam	Case 1 +air + steam
<b>IN</b>				
Biomass in	530	530	530	530
off-gas energy	133	58.6	114.9	102.5
Electricity for electrolyser	870.42	704.16	684.6	723.72
Electricity use for r-WGS	600.7	521.8	523.4	511.3
<b>OUT</b>				
Electricity out	32	30	31	33
Syngas energy	1164.3	1028.4	1092.7	1036
<b>Efficiency</b>	56%	58%	61%	57%

Table 4.3.8: Energy balance over system for adjusting syngas suitable for MeOH synthesis, case 2

Energy [kWh]	Case 2	Case 2+air	Case 2+steam	Case 2 +air + steam
<b>IN</b>				
Biomass in	530	530	530	530
Off-gas energy	307.1	105	519.8	266
Electricity for electrolyser	2484.1	1124.7	2738.4	1193.2
Electricity use for r-WGS	1910.6	781.6	2133.9	864.7
<b>OUT</b>				
Electricity out	40	42	39	42
Syngas energy	2927.3	1384.0	3239.4	1509.7
<b>Efficiency</b>	57%	56%	55%	54%

For cases 1 and 2, the difference between FT and MeOH syngas is zero or narrow. The reason for this is the low CO<sub>2</sub> content, making no difference between production for FT or MeOH. The increased energy efficiency in syngas does not compensate for the electricity demand in the r-WGS reactor and hydrogen generation. For case 3, further addition of H<sub>2</sub> is required for syngas to be used in MeOH production.

Table 4.3.9: Energy balance over system for adjusting syngas suitable for MeOH synthesis, case 3

Energy [kWh]	Case 3	Case 3+air	Case 3+steam	Case 3 +air + steam
<b>IN</b>				
Biomass in	530	530	530	530
' Off-gas energy	321	114	403	129.2
Electricity for electrolysis	5281.2	1760.4	5868	1897.32
Electricity use for r-WGS	4553	1333	5486	1635
<b>OUT</b>				
Electricity out	87.1	66.6	149.3	76.7
Syngas energy	5267	1829	6219	2121
Hydrogen				
<b>Efficiency</b>	51%	51%	52%	52%

When hydrogen is added, the lowered CO<sub>2</sub> content in syngas increases the chemical energy in

syngas. However, the efficiency decreases due to the energy intensive electrolysis unit.

### 4.3.2 Air/steam gasification

The efficiency in the cases of air/steam gasification was calculated. These cases represent the absence of off-gas, and therefore to maintain the continuity in syngas generation, air/steam gasification is considered.

Air gasification for composition matching case 1 gasification.

Table 4.3.10: Energy balance over system, case 1

Energy [kWh]	Case 1	Case 1+air	Case 1+steam	Case 1 +air + steam
<b>IN</b>				
Biomass	530	530	530	530
Electricity in electrolysis	183	158	183	183
Electricity use for r-WGS	135	131	101	101
<b>OUT</b>				
Electricity	22.7	24	30	30
Syngas	605	590	579	579
<b>Efficiency</b>	74%	75%	75%	75%

Table 4.3.11: Energy balance over system, case 2

Energy [kWh]	Case 2	Case 2+air	Case 2+steam	Case 2 +air + steam
<b>IN</b>				
Biomass	530	530	530	530
Electricity in electrolysis	101	101	101	95
Electricity use for r-WGS	85	130	130	14
<b>OUT</b>				
Electricity	56	24	24	33
Syngas	559	586	586	484
<b>Efficiency</b>	86%	80%	80%	81%

Table 4.3.12: Energy balance over system, case 3

Energy [kWh]	Case 3	Case 3+air	Case 3+steam	Case 3 +air + steam
<b>IN</b>				
Biomass	530	530	530	530
Electricity in electrolysis	0	158	0	0
Electricity use for r-WGS	157	131	157	157
<b>OUT</b>				
Electricity	55	24	55	55
Syngas	433	590	433	433
<b>Efficiency</b>	71%	75%	71%	71%

For case 3 (except for case 3+air), no additional  $H_2$  is available since pure air is used. Since the gasification reactor is autothermal, no additional heat is supplied. The only energy supplied is to r-WGS. It is observed that the efficiencies for air gasification are high. High nitrogen content in the gasifying agents decreases the efficiencies. The nitrogen acts as diluent and takes away thermal energy with it.

### Adjusting syngas conditions suitable for FT process

Air gasification was also used to produce syngas for being used in FT. The result of energy balance is presented in table 4.3.13- 4.3.15.

Table 4.3.13: Energy balance over system for adjusting syngas for FT synthesis, case 1

Energy [kWh]	Case 1	Case 1+air	Case 1+steam	Case 1 +air + steam
<b>IN</b>				
Biomass	530	530	530	530
Electricity for Electrolysis	328	341	246	246
Electricity use for r-WGS	346.1	372.1	315.3	315.3
<b>OUT</b>				
Electricity	22.7	24	30	30
syngas	817	830.5	793.6	793.6
<b>Efficiency</b>	70%	69%	75%	75%

Table 4.3.14: Energy balance over system for adjusting syngas for FT synthesis, case 2

Energy [kWh]	Case 2	Case 2+air	Case 2+steam	Case 2 +air + steam
<b>IN</b>				
Biomass	530	530	530	530
Electricity for electrolysis	328	328	328	284
Electricity use for r-WGS	316.75	372.1	372.1	328.3
<b>OUT</b>				
Electricity	56	24	24	33
Syngas	791	830.5	830.5	797.6
<b>Efficiency</b>	72%	69%	69%	73%

Table 4.3.15: Energy balance over system for FT syngas, case 3

Energy [kWh]	Case 3	Case 3+air	Case 3+steam	Case 3 +air + steam
<b>IN</b>				
Biomass	530	530	530	530
Electricity for Electrolysis	334	341	334	334
Electricity use for r-WGS	522.6	522.6	522.6	311.7
<b>OUT</b>				
Electricity	55	55	55	53
Syngas	799	830	799	799
<b>Efficiency</b>	62%	64%	62%	72%

For air gasification, the efficiencies decrease in the syngas production for the FT process. The same trend was observed in off-gas gasification. The high energy demand for electrolysis units exceeds the increased energy in produced syngas.

### Adjusting syngas conditions for MeOH synthesis

Energy balance calculations for air gasification of syngas production for MeOH process were conducted, and results are presented in table 4.3.16- 4.3.18.



Table 4.3.16: Energy balance over system for adjusting syngas to suit MeOH synthesis, case 1

Energy [kWh]	Case 1	Case 1+air	Case 1+steam	Case 1 +air + steam
<b>IN</b>				
Biomass	530	530	530	530
Electricity for Electrolysis	366	341	342	342
Electricity use for r-WGS	369.7	372.1	411.3	411.3
<b>OUT</b>				
Electricity	22.7	24	30	30
Syngas	840.4	830.5	889.6	889.6
<b>Efficiency</b>	68%	69%	72%	72%

Table 4.3.17: Energy balance over system for adjusting syngas to suit MeOH synthesis, case 2

Energy [kWh]	Case 2	Case 2+air	Case 2 +steam	Case 2 +air + steam
<b>IN</b>				
Biomass	530	530	530	530
Electricity for Electrolysis	341	341	341	328
Electricity use for r-WGS	458	372	372	391
<b>OUT</b>				
Electricity	56	24	24	33
Syngas	932	831	831	860
<b>Efficiency</b>	74%	69%	69%	71%

Table 4.3.18: Energy balance over system for adjusting syngas to suit MeOH synthesis, case 3

Energy [kWh]	Case 3	Case 3+air	Case 3+steam	Case 3 +air + steam
<b>IN</b>				
Biomass	530	530	530	530
Electricity for Electrolysis	398	341	398	398
Electricity use for r-WGS	570.2	570.2	570.2	342.08
<b>OUT</b>				
Electricity	55	51	55	51
Syngas	846.1	822	846.1	846.1
<b>Efficiency</b>	60%	69%	60%	60%

The difference in efficiencies between cases for adjusting syngas for FT and MeOH synthesis via air gasification is not significant, especially for case 2 and case 3. The low CO<sub>2</sub> content in the syngas is the explanation for this.

Air gasification has a higher efficiency compared to off-gas gasification. Fewer requirements for additional hydrogen, which is the main contributor to electricity demand, is the explanation for this. As observed in the compositions discussed previously, oxygen in gasifying agent promotes biomass conversion to CO and H<sub>2</sub>.

## **4.4 Overall evaluation of process**

The proposed integration of gasification process with EAF by utilising the energy in EAF off-gas for gasification results in increased efficiency, regardless of off-gas composition. By utilising the off-gas emissions in the process, high-value products can be formed. The carbon utilisation results in decreased direct CO<sub>2</sub> emissions. The emissions can be further reduced by producing syngas for FT or MeOH production. When the gasifier was modelled with air as a gasifying agent, the efficiencies increase further. The main reason for this is the lowered H<sub>2</sub> demand for adjusting syngas composition. Overall, the integration of gasification with EAF process is beneficial when it comes to technical feasibility.

A possible outlook for off-gas gasification is to include the effect of dust on the gasification reactions. As mentioned in the literature review, EAF dust and slag can be used as catalysts in the gasification process. The prospect of this is to increase the efficiencies further and increase carbon conversion. To evaluate this, experimental investigations are required.

# Chapter 5

## Conclusions

The world's GHG are increasing and rapidly becoming a concern. The steel sector is responsible for 7% of the emissions. Via EAF, one-quarter of the world's steel is produced. The steel recycling process emits around 500 kg CO<sub>2</sub> per produced ton of steel. A possibility to decrease the emissions in the EAF process is through integrating it with biomass gasification followed by a carbon dioxide utilisation process (through r-WGS).

The project's outcomes indicates the technical feasibility of integrating the gasification process with the EAF process by utilising the EAF off-gas as gasifying agent and for providing the energy for the gasification reactions. From the EAF off-gases, it is possible to create high-value products. By coupling the gasification process and r-WGS to EAF process, the system's energy efficiency increases, the direct emissions decrease via the carbon utilisation increases.

The carbon utilisation and system efficiencies in the proposed process are sensitive to off-gas composition. Case 1, average composition, shows high carbon conversion and energy efficiency with respect to the reference case. The same is for case 2. Case 3 shows the lowest carbon utilisation. The reason for this is the high CO<sub>2</sub> emissions in the off-gas. A problem with off-gases from EAF process is the fluctuations in composition, giving different syngas composition.

The efficiencies decrease when syngas is produced to be used in FT and MeOH production. The explanation is the high energy demand in electrolysis used for H<sub>2</sub> production. However, the efficiencies remain higher than the reference case (case without adding the gasifier). While the energy efficiencies decrease, carbon utilisation increases.

When EAF off-gas is unavailable, air can be used as gasifying agent. In this study, it was desirable to have similar producer gas compositions while shifting between off-gas and air gasification. However, it is difficult to obtain similar producer gas compositions between off-gas and air gasification when the off-gas composition is similar to case 2 and 3. If air infiltration is considered, all the cases 1-3 can achieve similar compositions of producer gas while shifting between off-gas and air gasification. The effect of EAF dust (that comes along with EAF off-gas) on the gasification reactions can be considered for future research.

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