





# Comparing Greenhouse Gas Emissions throughout the Biodiesel production: Steam Gasification versus CO<sub>2</sub> Gasification + Water Electrolysis for Syngas Production in the Context of Different Electricity Generation in the Czech Republic and Austria

Florian J. Müller, David Štika

**Co-operating Universities** 









Financial support by





Prague and Vienna, 2022

# Abstract

This study on biodiesel production focuses on the environmental assessment of feedstock production. Biodiesel is produced by Fischer-Tropsch synthesis, which needs CO and H<sub>2</sub> as inputs. This paper suggests two concepts based on gasification and electrolysis to produce these chemicals. One approach uses steam gasification and a comparably small electrolyzer, and the other uses  $CO_2$ gasification coupled with a bigger electrolyzer to produce syngas with the correct H<sub>2</sub>:CO ratio. The concepts are scaled to produce one metric ton of biodiesel per hour continuously, and the carbon footprint is calculated. Numbers for technological key aspects, the carbon footprint of energy production in CO<sub>2ea</sub>/kWh, and converted CO<sub>2</sub> are taken from literature and presented for the Czech Republic and Austria. The carbon footprint of water electrolysis is shown as a function of the different energy grids. Final numbers for CO2<sub>eq</sub> in kgCO<sub>2</sub>/tBiodiesel are a key performance indicator to compare the technical solutions. The investigated pathways are (a) Steam gasification +  $H_2O$ electrolysis and (b) CO<sub>2</sub> gasification + H<sub>2</sub>O-electrolysis. Both are compared against fossil diesel. For technical pathway (a), a total of 2111 kgCO<sub>2eo</sub>/tBiodiesel for Austria and 5866 kgCO<sub>2eo</sub>/tBiodiesel for the Czech Republic are found. Technical pathway (b) shows emissions of 594 kgCO<sub>2ea</sub>/tBiodiesel for Austria and 10100 kgCO<sub>2eq</sub>/tBiodiesel for the Czech Republic. These comparisons suggest pathway (b) using CO<sub>2</sub> gasification to produce biodiesel in Austria, saving 85,1% of CO2 emissions compared to fossil Diesel. In contrast, no biodiesel pathway can currently be recommended against using fossil fuels in the Czech Republic to reduce greenhouse gas emissions. In the end, thresholds for carbon intensity of electricity production are presented to demonstrate what would be necessary to achieve greenhouse gas savings using the described production methods.

# 1. Introduction

According to the Renewable Energy Directive of the European Union, having a renewable source for transportation energy is an essential target as laid out in [1]. Times of crisis in energy security highlight the need to diversify sources for such fuels by building renewable options produced locally in all union countries independently. In 2020, the EU-27 combined for a production of around 21.8 Mt/a of first-generation biodiesel, stagnating over the last decade [2]. Virgin vegetable oils make up almost 80% of biodiesel production by applying transesterification processes. The largest share of this production in 2020 is rapeseed oil (36%), followed by palm oil (30%) [3]. However, first-generation biofuels have many problems, e.g., the competition for arable land between the needs for food production and energy production [4]. Other issues are, for example, the ethical question of using biomass for transportation instead of feeding people, while there are more than 39 million people worldwide in phases 4 (emergency) or 5 (catastrophe) of food security in 2021 [5]. It is also questionable how environmentally friendly first-generation biofuels are overall due to the need for importing palm and soy oil to reach the targets set by REDII. A reliance on imports to satisfy demand comes with political dependency and a lot of emissions for transportation. E.g., Indonesia makes up the production of around 50% of the imported palm oil (4.08 Mt out of 8.2 Mt total) [3].

Second-generation biofuels use different feedstocks like residues from other industrial processes or waste, e.g., residual municipal waste, to overcome some of first-generation biofuels' issues [6]. One core objective of a seamless transition from fossil fuels to renewable energy sources is that existing infrastructure, e.g., cars and power grids, should remain useful without changes. One must produce fuel as similar as possible to the fossil option to achieve this goal. The primary route to do so is Fischer-Tropsch synthesis [6]. The feedstocks for Fischer-Tropsch synthesis can be produced using different technologies. This paper suggests and evaluates two concepts for coupling gasification with

a water electrolyzer for greenhouse gas emissions. One pathway uses steam as a reactant in gasification, while the other route utilizes  $CO_2$ .

This paper tries to answer the question of which technological solution has the smaller carbon footprint throughout the production chain while considering country-specific energy grids. Furthermore, both options shall be compared against conventional fossil fuels and investigated for their emission reduction potential. Recommendations shall be given for both countries on reducing carbon footprints in biodiesel production.

# 2. State of the art

## 2.1. Carbon footprint of fossil diesel

The carbon footprint of fossil diesel is the sum of the emissions created when burning it in a combustion engine (tank-to-wheel) and the emissions produced in the production chain before it reaches the tank (well-to-tank). The combined emissions are termed well-to-wheel.

The tank-to-wheel emissions created by burning diesel can be calculated from reaction stoichiometry. Diesel is a mixture of various hydrocarbons with a range of carbon chain lengths. About 75% are paraffin ranging from  $C_{10}H_{22}$  to  $C_{20}H_{42}$  and roughly 25% are aromatics with chemical formulas from  $C_{10}H_8$  to  $C_{20}H_{34}$  [7]. **Equation 1** shows a reaction equation representing the combustion of an average diesel molecule. The emissions from this combustion are 3.16 kgCO<sub>2</sub>/kgDiesel.

$$4 C_{12}H_{23} + 71 O_2 \rightarrow 48 CO_2 + 46 H_2O$$
 Equation 1 [8]

In addition to these emissions from combustion, the emissions in production have to be costed in as well. The main contributors to well-to-refinery emissions are gas flaring, methane venting/leaks, and energy consumption of thermal extraction methods. A global average weighted value is around  $10.3 \text{ gCO2}_{eq}/\text{MJ}$ , or about  $63 \text{ kgCO}_2/\text{kgCrude}$  [9]. In the EU, refining crude oil adds another  $5.4 \text{ gCO2}_{eq}/\text{MJ}$  for diesel [10].

Summing up these values, an estimation of the total carbon footprint of fossil diesel is in the range of  $3310 \text{ gCO2}_{eq}/\text{IDiesel}$  or  $3980 \text{ gCO2}_{eq}/\text{kgDiesel}$  [11]. The production of biofuels has to emit less than this value to decrease the carbon footprint. Therefore, this  $3980 \text{ gCO2}_{eq}/\text{kgDiesel}$  will be a benchmark for the calculated data in this study.

#### 2.2. Biodiesel production

#### 2.2.1. Fischer-Tropsch synthesis

A short overview of the Fischer-Tropsch synthesis (FT synthesis) is given in the following. The interested reader is advised to search for more information in [7] for a more thorough explanation.

Fischer-Tropsch synthesis makes up only a small fraction of the biofuel production in 2021 in the EU-27. A total of around 28.6 Mt/a biofuel (biodiesel, biogasoline, bio-jet kerosene) is produced in the EU-27, with current Biomass-to-Liquid Fischer-Tropsch demonstration plants amounting to less than 1MT [2][12]. The most extensive scale implementation of the Fischer-Tropsch is the commercial production of 6 MT in two plants operated by Sasol in South Africa[13]. These plants currently use coal and natural gas as fossil resources to produce synthesis gas, making the environmental benefit doubtful [14]. The Fischer-Tropsch process produces biodiesel, which can be used in regular combustion engines without changing them [15]. A scheme of the process chain starting with biomass and ending with a produced biofuel is shown in **Figure 1**.



Figure 1: Process chain of producing Fischer-Tropsch biofuels from biomass via gasification [12]

**Figure 1** shows that the needed feedstock to produce biodiesel via Fischer-Tropsch synthesis is syngas, which refers to a gas mixture of carbon monoxide and hydrogen. The chemical reactions being utilized in the depicted FT synthesis are shown in **Equation 2**, **Equation 3**, and **Equation 4**. [16]

Equation 2	$H_2 + CO \rightarrow (CH_2) + H_2O$
Equation 3	(2n+1) H <sub>2</sub> + n CO -> C <sub>n</sub> H <sub>2n+2</sub> + n H <sub>2</sub> O
Equation 4	(2n) H <sub>2</sub> + n CO -> C <sub>n</sub> H <sub>2n</sub> + n H <sub>2</sub> O

These equations show a need for a specific ratio of  $H_2$ :CO to arrive at the final product. This ratio ranges from 2.2 for a shorter molecule like  $C_{10}H_{22}$  and gets closer to 2.0 if the chain length increases. In practical applications, the ratio can be between 1.6 and 2.2 [17]. Other considerations like specifically targeted product distribution can also play into choosing this ratio. Fischer-Tropsch synthesis is a process that produces a spectrum of products. The chain growth is influenced by the  $H_2$ :CO ratio in the reactor, with higher  $H_2$ :CO ratios leading to products with shorter chain lengths on average. The distribution of products in the reactor can be described by the Anderson-Schulz-Flory distribution [14]. Calculations in this paper will be based on [18], which assumes a ratio of 2.07 for  $H_2$ :CO in the case of using a tail gas recycle loop. The product distribution to be expected is shown in **Table 1**.

Fischer-Tropsch products	wt% (Recirculation ratio of tail gas = 0.9)
CH4	1.18
Ethane and propane	2.00
Naphtha	9.54
Middle distillate ≈ biodiesel	14.98
Wax	15.71
Fischer-Tropsch H2O	56.58

Table 1: Product distribution from Fischer-Tropsch synthesis

#### 2.2.2. Carbon monoxide production

Carbon monoxide is produced by reforming or partially oxidizing various hydrocarbon feedstocks such as natural gas, mineral oil fractions, or coal [19]. Gasification is the most consistent and energy-efficient of such conversion technologies [20]. Globally in 2020, the most used feedstock for gasification was coal at 62.1%. Petroleum, natural gas, and biomass/waste comprise the rest of global production, contributing similarly [21]. It isn't easy to give numbers for emitted  $tCO_{2eq}/tCO$  for these processes since this heavily depends on the actual process setup and the system boundaries. A lower emission boundary can be given by assuming that every molecule of CO produced will be converted to  $CO_2$  and end up in the atmosphere. This lower boundary uses a process that is 100% efficient with zero losses or energy demand, which is highly unrealistic. This means the lower boundary for emissions using coal, natural gas, or petroleum as a gasification feedstock is 1.57

 $tCO_2/tCO$  even before considering the process's energy consumption. This means a significantly sized carbon footprint is the best-case scenario for such pathways.

Biomass-to-Liquids concepts fulfill the need for CO by gasifying the renewable feedstock biomass [12]. Using the same assumption of every molecule of CO being converted to  $CO_2$  later on, these processes have lower limits of being carbon neutral, meaning their carbon footprint is 0 t $CO_2$ /tCO. In practical application, energy demands and inefficient processes increase this footprint, but it is hard to find overall representative numbers.

## 2.2.3. Hydrogen production

Hydrogen is industrially produced almost exclusively from fossil resources. In 2019 around 76% of the annual hydrogen production used natural gas as a feedstock, while coal produced another 23%. 1-2% of the global output has come from electrolysis. Hydrogen from biomass plays an insignificant role globally at present times. Hydrogen produced from natural gas or coal is called "gray hydrogen" and has a significant carbon footprint. About 10  $tCO_2/tH_2$  are produced for steam-methane reforming (SMR). Coal gasification releases even more  $CO_2$  at around 19  $tCO_2/tH_2$ . These routes alone combine for about the same emissions as the annual emissions of Indonesia and the United Kingdom. [22]

The carbon footprint of SMR and coal gasification can be lowered by applying carbon capture methods to produce so-called "blue hydrogen". This captured  $CO_2$  is in an idealized scenario stored safely indefinitely underground afterward, reducing the carbon dioxide emissions of these processes. Some concepts only aim to capture the  $CO_2$  from the reforming process, while others also consider the capture of  $CO_2$  on the flue gas side. Still, blue hydrogen production's total global warming potential is not much better than gray hydrogen. This is due to methane leakages, less-than-perfect capture efficiency, and added energy input for carbon capture. A recent study found blue hydrogen has only 9-12% less carbon dioxide equivalents than gray hydrogen. Therefore although the  $CO_2$  emissions of such a process might be significantly lowered, it appears very difficult to justify on climate grounds. [23]

While hydrogen production via electrolysis comprised around 2% of the global output in 2019, less than 0.1% of dedicated hydrogen production came from water electrolysis. Nearly all global output came as a side product of Chlor-alkali electrolysis. [22] The market share of water electrolysis is expected to grow in the future for several reasons. The expected drivers of this development are technical improvements of electrolyzers, a predicted decline of the levelized cost of energy, and an increase in taxation for carbon-intensive processes. [24]

The impact of water electrolysis on greenhouse gas emissions is highly dependent on electricity production. **Figure 2** shows the strong correlation between electricity production resources and the carbon intensity in  $tCO_2/tH_2$  for water electrolysis. If fossil fuels power the electricity grid, producing hydrogen via electrolysis emits more  $CO_2$  than using the fossil fuels directly for hydrogen production. On the contrary, if there is enough renewable or nuclear energy available to power the electrolyzer, the emissions for this technology drop to zero. This dependency on the energy grid is the basis for the comparison case in this paper.



*Figure 2: The carbon footprint of various H*<sup>2</sup> *production pathways* [22]

In Biomass-to-Liquid concepts, hydrogen is often produced together with CO in a gasification process. There are many process configurations and differences between gasification routes, and the interested reader is advised to find more information in [25]. One study, which compared different methods of producing hydrogen, found a negative carbon footprint of  $-0.43 \text{ kgCO2}_{eq}/\text{kgH}_2$  for the production of H<sub>2</sub> from biomass[26]. Biomass utilization is described as carbon neutral in this paper. The negative carbon footprint comes from surplus electricity production within the defined process, which helps decarbonize the Spanish power grid.

## 2.2.4. Gasification at TUW

A short overview of gasification at Technische Universität Wien (TUW) is presented hereafter, although the focus of this paper is not on the technological aspects of such technologies. The interested reader is advised to find more such information, e.g., in [25]. The gasification process described hereafter represents how gasification is performed and researched at TUW. The process routes described in 4.1 use gasification processes that are set up identical or similar to the process design described here.

Biomass gasification is a technology that allows producing  $H_2$  and CO simultaneously in one reactor. This is possible in different reactor types, the most widespread being fixed-bed, fluidized-bed, and entrained flow reactors. [27] Biomass gasification at TUW has been researched extensively with a focus on fluidized-bed technology. In such a reactor, the solid feedstocks are converted at temperatures between 750-950°C. **Figure 3** shows a basic concept of a circulating fluidized-bed (CFB) reactor used by TUW.



Figure 3: Reactor concept circulating fluidized-bed gasification [28]

This system uses two connected reactors; both operated in fluidized bed mode. The gasification reactor (blue) is operated at temperatures between 750-950 °C and atmospheric pressure. Different biomasses can be supplied as fuel. Steam or  $CO_2$  can be used as a reaction partner, often called a gasification agent. Steam and  $CO_2$  have two primary purposes in this reactor concept, namely (a) fluidizing the bed material and smaller particles in the reactor to form a fluidized bed and (b) reacting with the biomass and its derivatives via multiple gas-solid or gas-gas reactions to form the product gas. This product gas is called synthesis gas or, in short, syngas. Some of these reactions are given in **Table 2.** 

Reaction name	Heterogeneous reactions (gas-solid)	Enthalpy	
Water-gas reaction	$C + H_2O \rightarrow CO + H_2$	Endothermic	Eq. 1
Boudouard reaction	$C + CO_2 \rightarrow 2 CO$	Endothermic	Eq. 2
Hydrogenated gasification	$C + 2 H_2 \rightarrow CH_4$	Slightly exothermic	Eq. 3
	Homogeneous reactions (gas-gas)		
Reverse water-gas shift reaction (RWGS)	$CO_2 + H_2 \leftrightarrow CO + H_2O$	Endothermic	Eq. 4
Methanation	$CO + 3 H_2 \leftrightarrow CH_4 + H_2O$	Exothermic	Eq. 5
Steam reforming	$C_xH_y + x H_2O \rightarrow x CO + (x + \frac{y}{2}) H_2$	Endothermic	Eq. 6
Dry reforming	$C_x H_y + x CO_2 \rightarrow 2x CO + \frac{y}{2} H_2$	Endothermic	Eq. 7

Table 2: Relevant gasification reactions[28]

This process is adjustable in various ways to produce different syngas compositions. One essential option to tune the  $H_2$ :CO ratio is the choice of gasification agent. The same reactor setup produces syngas with an  $H_2$ :CO ratio of 1.49 for steam as a gasification agent and a significantly lower 0.36 for CO<sub>2</sub> as a gasification agent[28]. Both ratios are below the target ratio of 2.07, described in 2.1, therefore demanding additional hydrogen production. Using CO<sub>2</sub> as a gasification agent and converting it to CO leads to negative emissions in the gasification process.

# 3. Methodology

The key performance indicator this paper uses to compare both suggested technical pathways is the specific carbon footprint of Biodiesel production  $f_{fuel}$  in gCO2<sub>eq</sub>/kgBiodiesel. This value combines multiple factors and can be calculated using **Equation 5**.

$$\frac{m_{CO2,product} - m_{CO2,educt} + \Delta E * f_{Elec}}{m_{fuel}} = f_{fuel}$$
 Equation 5

Gasification processes produce a range of products, among which there is also CO<sub>2</sub>, referred to as  $m_{CO2,product}$  in **Equation 5.** The amount of CO<sub>2</sub> varies between different process setups. In the case of steam gasification, the CO<sub>2</sub> comes exclusively from biogenic sources and is therefore not counted as CO<sub>2</sub> emission but rather as carbon neutral in the base case scenario. In CO<sub>2</sub> gasification, the emitted CO<sub>2</sub> is either from biomass or residual unconverted CO<sub>2</sub> fed into the reactor as a gasification agent. The source of this gasification agent, CO<sub>2</sub>, is assumed to be renewable in this work, such as direct air capture or biomass combustion. This makes the emission from CO<sub>2</sub> which didn't react carbon neutral.

In CO<sub>2</sub> gasification, external CO2 is utilized and converted to products, acting as a CO<sub>2</sub> sink. This amount of CO<sub>2</sub> is referred to as  $m_{CO2,educt}$  and given as a credit in **Equation 5**, opening the door for carbon-negative production. It is hard to distinguish between biogenic carbon from biomass and carbon from other sources as gasification agent. The literature found that 26-45 % of the supplied CO<sub>2</sub> was converted [28]. For carbon footprint calculation, the supplied CO<sub>2</sub> is multiplied by the average value of 26-45 % (35.5 %), which is used as CO<sub>2</sub> credit.

The final part of the calculated carbon footprint is the carbon footprint of the electricity generation. In **Equation 5**, the total amount of energy demand within the process is called  $\Delta E$ , and the factor  $f_{Elec}$  is the carbon intensity of electricity generation. Primary energy sources directly affect the carbon intensity of the power grid. Austria and the Czech Republic have different electricity generation mixes; therefore, this value  $f_{Elec}$  is country-specific. The newest available country reports from the International Energy Agency (IEA) give values of 160 gCO2<sub>eq</sub>/kWh for Austria (2017) and 406 gCO2<sub>eq</sub>/kWh for the Czech Republic (2019). [29][30] **Figure 4** shows the carbon intensity in both countries from 2000-2021.



Figure 4: Carbon footprint of electricity production in Austria and the Czech Republic[31]

The electricity grid in both countries is vastly different, as depicted in **Figure 4**. Austria's primary sources of electricity are renewable (79.4% in 2021), with hydro (60%) and wind (9.8% in 2021) power contributing the most. The two most significant primary sources in the Czech Republic are coal (39.9% in 2021) and nuclear (36.9% in 2021). Counting nuclear as a renewable energy source, the Czech Republic produced 49.9% of its electricity generation in 2021 from clean sources. As a result of this imbalance in renewable energy production, 1 kWh of electricity in Austria has a carbon footprint of 144.4 gCO2eq/kWh, while the production of the same 1 kWh of electricity has a carbon footprint

of 401.3 gCO2eq/kWh in the Czech Republic. These values are used as a calculation basis in the rest of this paper. [31]

Four scenarios for calculating total carbon footprints are given. They differ only in two calculation aspects, while technical changes and necessities are disregarded for everything except scenario 1 (TOTAL 1).

The first difference is concerning the fuel, which is used for gasification. The first and primary option is using biomass as fuel. When looking at the whole cycle of plant growth and process, there is a solid argument for not counting  $CO_2$  from renewable sources as an emission to penalize (carbon neutral). This also includes the combustion of the biodiesel, therefore defining well-to-tank emissions as equivalent to well-to-wheel emissions for these cases. (TOTAL 1 and 2) If the used fuel would be fossil in origin, all combustion emissions (combustion reactor in gasification and purge gas combustion in Fischer-Tropsch) and any  $CO_2$  generated in the gasification reactor would have to be counted as emissions. (TOTAL 3 and 4)

The second difference between the four presented cases concerns the energy supply of the gasification reactor. Gasification technology, as applied at TUW, utilizes a combustion reactor to harvest thermal power from fuel combustion (TOTAL 1 and 3). A theoretical case is also presented here, where the necessary reaction heat would be supplied by the national power grid instead (TOTAL 2 and 4). Such a technical change would not be an easy transition and drastically change the reactor setup. Because of that reason, these values have a lot of uncertainty and are only meant as a guideline.

For the case with biomass as a fuel and energy production by burning biomass (TOTAL 1), a short analysis is also conducted, varying the carbon intensity of electricity production. Thresholds for change in the best available technology are identified and presented in **Table 10**.

The carbon footprint of the produced biodiesels is also compared to the carbon footprint of fossil diesel. This footprint is  $3980 \text{ gCO2}_{eq}/\text{kgDiesel}$  and is explained in 2.1.

# 4. Results

## 4.1. Process scaling

Two concepts based on gasification and a water electrolyzer are suggested and scaled to produce 1t of biodiesel per hour. Technical pathway (a) uses steam gasification, while technical pathway (b) uses  $CO_2$  gasification. There is a gap between gasification's hydrogen supply and the Fischer-Tropsch plant's hydrogen demand. Water electrolysis is used to cover that gap. Energy consumption of the electrolyzer will be derived from this model and literature. This energy consumption is then translated into greenhouse gas emissions according to the power grid's carbon footprint. This emission equivalent is compared to the negative emissions generated using  $CO_2$  as a feedstock in the gasification process. A recommendation will be given, stating which technology produces less greenhouse gas emissions in Austria and the Czech Republic.

#### 4.1.1. Fischer-Tropsch synthesis

The technical implementation of the Fischer-Tropsch synthesis follows [18]. Herein various cases are presented and compared against each other. This paper chooses the case of using a recirculation for the tail gas with a recirculation ratio of 0.9. Reasons for this are the good performance and  $H_2$ :CO ratio of close to 2.0, which makes comparison easier with other Fischer-Tropsch setups. The exact value used as the ratio here is 2.07, which is given as a molar ratio. In **Table 3**, the relevant values from this paper are presented and scaled to produce 1 tBiodiesel/h.

#### Table 3: Process parameters of Fischer-Tropsch synthesis

	Mass flowMass flowtaken or calculated from [18]scaled to 1 tBiodies					
	kg/h	kg/h				
	Feed					
H <sub>2</sub>	15.01	909.7				
со	100.1	6068.5				
	Main products					
Naphtha	10.5	636.4				
Diesel	16.5	1000				
Wax	17.3	1048.5				
Emission from tail gas combustion						
CO <sub>2</sub>	<b>CO</b> <sub>2</sub> 21.6 1308.0					
	Power, taken or calculated from [18] Power scaled to 1t/h Biodiesel					
	kW	MW				
Primary power demand, FT-plant	66.3	4.0				
Thermal power tail gas combustion	100.2	6.1				
Electrical power tail gas combustion	35.1	2.1				
Secondary power demand, FT-plant discounted	31.21	1.89				

The total power demand presented here includes syngas compression, syngas cooling, condenser, tail gas recirculation, and pumps. The purge gas is assumed to be combusted in a gas turbine, for which an efficiency of  $\eta_{el}$ =35% is supposed to produce electric power. This electric power is used to partly cover the power demand of the FT plant [32]. The corresponding flow and energy rates are given in **Table 4**.

PURGE GAS	vol%	Nm³/h	kg/h	MJ/kg	MW <sub>th</sub>	MW <sub>el</sub>
СО	11.7	367.3	453.0	10.1	1.3	0.4
H <sub>2</sub>	21.9	687.5	61.0	120.0	2.0	0.7
CO2	60.1	1886.8	3656.3	0	0	0
H <sub>2</sub> O	0.2	6.3	5.0	0	0	0
CH₄	3.6	113.0	79.8	50.0	1.1	0.4
C₂H <sub>6</sub>	1.3	40.8	54.0	47.8	0.7	0.3
C₃H <sub>8</sub>	1.2	37.7	73.1	46.4	0.9	0.3
TOTAL	100	3139.4	4382.3		6.1	2.1

#### Table 4: Purge gas from Fischer-Tropsch synthesis [18]

#### 4.1.2. Pathway a: Steam gasification + electrolysis

Steam gasification is the more established process route researched at TUW, which has already been implemented on a larger scale. One example is the 8 MWth combined heat and power plant, which was realized in Güssing in 2002 [33]. In this paper,  $H_2O$  gasification is combined with an electrolyzer and scaled appropriately to produce the feedstocks for the Fischer-Tropsch plant, as described in

**Table 3**. The 6068.5 kg/h CO is produced entirely within the steam gasification plant. The 909.7 kg/h  $H_2$  is produced partly in the same gasification step, and the electrolyzer is used to make up for missing  $H_2$  to reach the target specification. The overall chain is depicted in **Figure 5**.



Figure 5: Process chain of producing Fischer-Tropsch diesel from biomass via steam gasification and electrolysis, adapted from [16]; DFB=dual fluidized bed; SBCR=slurry bubble column reactor

The process parameters of steam gasification are derived from [34], and the process setup is as described in 2.2.4. The primary feeds into the reactor are biomass and steam. Air is used to combust some biomass, which delivers the heat for the endothermic gasification reactions.

	Values taken or calculated Values scaled to 1 from [34] tBiodiesel/b			
	kg/h	kg/h		
	Feed			
Softwood	18.8	13205.6		
Steam	16.9	11885.00		
Main Products				
H <sub>2</sub>	0.916	642.5		
СО	8.65	6068.5		
CO <sub>2</sub>	9.41	6598.5		
Combustion reactor				
Softwood as fuel in MW	0.046	32.3		
Softwood as fuel in kg/h	9.50	6675.4		
CO <sub>2</sub> in flue gas in kg/h	16.10	11316.5		

Table 5: Process parameters of steam gasification

The technical implementation of the electrolyzer is not defined in detail. The best commercial-scale electrolyzers use proton-exchange membrane (PEM) technology to reach energy efficiencies of ~70%, which is therefore used as estimation here [35]. The scaling of the electrolyzer is based on the

gap between the FT-plant's  $H_2$  demand and the steam gasification plant's  $H_2$  supply. The scaled values are presented in **Table 6**.

Table 6: Electrolyzer as needed to support steam gasification

Feed					
H <sub>2</sub> O Kg/h 2388.1					
	Products				
H <sub>2</sub>	Kg/h	267.2			
<b>O</b> <sub>2</sub>	Kg/h	2121.0			
Energy demand					
Hydrogen energy content	MJ/kg	120			
Electrolyzer efficiency [35]	%	70			
Power demand	MW	12.73			

## 4.1.3. Pathway b: CO<sub>2</sub> gasification + electrolysis

 $CO_2$  gasification is a newer concept and not yet well optimized. Therefore, the current assumptions have room for improvement in key performance areas like carbon conversion rate and product gas composition. The main advantage of  $CO_2$  gasification is using  $CO_2$  as a feedstock and therefore taking it out of the carbon economy, acting as a  $CO_2$  sink in the process.

CO is the main product in  $CO_2$  gasification, while  $H_2$  production is far less than in steam gasification. Therefore, the gasification unit is again used to fulfill the 6068.5 kg/h CO demand from the FT plant, while the electrolyzer is scaled to cover the gap to meet the 909.7 kg/h  $H_2$  demand. The overall process chain is shown in **Figure 6**.



Figure 6: Process chain of producing Fischer-Tropsch diesel from biomass via CO<sub>2</sub> gasification and electrolysis, adapted from [16]

DFB= dual fluidized bed; SBCR=slurry bubble column reactor

Literature data for  $CO_2$  gasification is taken from [28] and scaled to match the FT-plant's feed demands. The respective data is presented in **Table 7**.

#### Table 7: Process parameters of CO<sub>2</sub> gasification

	Values taken or calculated from [28]	Values scaled to 1 tBiodiesel/h			
	kg/h	kg/h			
	Feed				
Softwood	17.2	6285.6			
CO2	36.5	13377.5			
Main Products					
H <sub>2</sub>	0.471	172.4			
СО	16.6	6068.5			
CO <sub>2</sub>	26.7	9785.9			
Combustion reactor					
Softwood as fuel in MW	0.059	16.9			
Softwood as fuel in kg/h	12.2	3486.6			
CO <sub>2</sub> in flue gas in kg/h	21.2	6042.2			

The electrolyzer must be scaled to match the demand gap between FT plant demand and  $CO_2$  gasification supply. Since less H<sub>2</sub> is produced in  $CO_2$  gasification, the electrolyzer is comparably bigger than in steam gasification. Values for the electrolyzer are presented in **Table 8**.

Table 8: Electrolyzer as needed to support CO<sub>2</sub> gasification

Feed			
H <sub>2</sub> O	Kg/h	6588.9	
	Products		
H <sub>2</sub>	Kg/h	737.3	
O <sub>2</sub>	Kg/h	5851.7	
	Energy demand		
Hydrogen energy content	MJ/kg	120	
Electrolyzer efficiency[35]	%	70	
Power demand	MW	35.11	

#### 4.2. Carbon footprint calculation

In chapter 4.1, both process routes were presented and scaled appropriately. In the following chapter, **equation 5** calculates specific carbon footprints in  $kgCO2_{eq}/tBiodiesel$  for both pathways. The results are shown in **Table 9**. The differences and calculation of the four scenarios (TOTAL 1-4) are also explained in section 3 Methodology.

Table 9: Carbon footprint parts and total for the production of 1 ton of Biodiesel

\*If a biogenic or renewable source is used as fuel, this value is 0

\*\*Alternative way of supplying gasification reactor with energy; national power grid instead of biomass combustion; not technically demonstrated with this/similar reactor design in scale

All values for producing 1t Biodiesel/h		Austria Czech I		Republic		
Symbol in Equation 5	Description	Unit	H <sub>2</sub> O gasification + electrolysis	CO <sub>2</sub> gasification + electrolysis	H <sub>2</sub> O gasification + electrolysis	CO <sub>2</sub> gasification + electrolysis
	CO <sub>2</sub> emission from gasification reactor*	kgCO₂/ tBiodiesel	6599*	1157*	6599*	1157*
mCO <sub>2,product</sub>	CO <sub>2</sub> emission from combustion reactor*	kgCO <sub>2</sub> / tBiodiesel	11317*	7743*	11317*	7743*
	CO <sub>2</sub> emission from tail gas combustion*	kgCO <sub>2</sub> / tBiodiesel	1308*	1308*	1308*	1308*
mCO <sub>2,educt</sub>	CO <sub>2</sub> feed converted in gasification reactor	kgCO <sub>2</sub> / tBiodiesel	0	4749	0	4749
ΔE*f <sub>elec</sub>	Carbon footprint energy for electrolysis	kgCO <sub>2eq</sub> / tBiodiesel	1838	5070	5107	14089
	Carbon footprint energy for FT plant	kgCO <sub>2eq</sub> / tBiodiesel	273	273	759	759
	Carbon footprint energy for gasification reactor**	kgCO <sub>2eq</sub> / tBiodiesel	4659**	3118**	12948**	8666**
TOTAL 1 biogenic fuel ( gasification biomass comb	*=0) heated by ustion	kgCO <sub>2eq</sub> / tBiodiesel	2111	594	5866	10100
TOTAL 2 biogenic fuel ( gasification he grid (+**)	*=0) eated by energy	kgCO <sub>2eq</sub> / tBiodiesel	6770	3712	18813	18766
TOTAL 3 Fossil fuel (*≠0 gasification biomass	)) heated by	kgCO <sub>2eq</sub> / tBiodiesel	24494	13962	28249	23468
TOTAL 4 Fossil fuel (*≠0 gasification he grid (+**)	)) eated by energy	kgCO <sub>2eq</sub> / tBiodiesel	17836	9338	29880	24391
FOSSIL Diesel   Well-to-Whee	[11] I-emission	kgCO <sub>2eq</sub> / tDiesel	3980			

# 5. Discussion

The results presented in 4.2 show sizeable differences in carbon footprint for biodiesel production between Austria and the Czech Republic. For better visualization, they are shown in **Figure 7**.



TOTAL 1=biogenic fuel + fuel as an energy source in gasification TOTAL 2=biogenic fuel + energy grid as an energy source in gasification TOTAL 3=fossil fuel + fuel as an energy source in gasification TOTAL 4=fossil fuel + energy grid as an energy source in gasification

For TOTAL 1 and TOTAL 2, which use biomass as emission-neutral fuel, the carbon footprint is only energy-related. The dominating factor in TOTAL 1 is the emission caused by electrolysis by a considerable margin. The power demand of the Fischer-Tropsch synthesis is small in comparison, which holds for all comparison cases. If the gasification reactor were to be powered by the national

energy grids, this would add another significant share to the total carbon footprint, as depicted in TOTAL 2. TOTAL 3 and TOTAL 4 show that the direct emissions significantly add to the entire footprint in both scenarios if the used fuel is fossil.

A comparison of the countries shows that the same plant has a smaller carbon footprint in Austria than in the Czech Republic. Technical parameters are not varied for the country comparison; therefore, the differences come directly from different energy grids. The power grid in Austria has a drastically smaller carbon footprint, lowering all emissions caused by external energy usage.

This paper's most crucial comparison and research question is the comparison between technological pathways. The total values for calculation method TOTAL 1-4 vary, but the following statements hold for all of them. Comparing (a) steam gasification + electrolysis or (b) CO<sub>2</sub> gasification + electrolysis reveals different results in Austria and the Czech Republic. Technological pathway (b) has a higher energy demand than pathway (a). The electrolysis unit must be built much bigger (35.11 vs. 12.73 MW) for CO<sub>2</sub> gasification because there is a more significant gap between the FT plant's hydrogen demand and the gasification plant's supply. This considerable energy demand is scaled by the different carbon footprints of energy grids in both countries, creating a significant footprint in the Czech Republic while profiting from Austria's relatively clean grid to stay smaller. Technological pathway (b) tries to compensate for this disadvantage by utilizing CO<sub>2</sub> and reintegrating it into the carbon economy. This value is the same for Austria and the Czech Republic since it is derived from technological design only. Adding these disadvantages and advantages together shows a different result for Austria and the Czech Republic.

In Austria, the  $CO_2$  credit from utilizing it in pathway (b) outweighs the additional emissions from the electrolysis unit. This case displays very low emissions of 594 kg $CO2_{eq}$ /tBiodiesel (TOTAL 1), proving that this technology has vast potential for  $CO_2$  savings (-85.1% compared to fossil). The comparison of biodiesel production against fossil fuel is favorable in Austria for  $CO_2$  gasification and steam gasification. Therefore, producing biofuels (and waxes) via  $CO_2$  gasification + electrolysis + Fischer-Tropsch plant is the best solution in Austria regarding the carbon intensity of the production chain.

On the contrary, in the Czech Republic, the  $CO_2$  savings from utilization in pathway (b) are outgained by the additional emissions caused by the large electrolysis unit. However, both paths have more significant carbon footprints under current assumptions than fossil fuels. This is a testament to how carbon-intensive the Czech electricity grid currently is. Therefore, under present conditions, none of the investigated biofuel production routes can be recommended in the Czech Republic. That will change if the Czech Republic decarbonizes its power grid significantly. Currently, the Czech power grid has a carbon footprint of 401.3 g $CO2_{eq}$ /kWh. Decarbonization of the power grid would lead to significant changes in this evaluation. A sensitivity analysis for varying carbon intensity of electricity production is shown in **Figure 8**. Technological advancement will increase electrolyzer efficiencies going forward. Therefore, this analysis is presented for the current commercially available electrolyzers with efficiencies of 70% and currently researched electrolyzers in the range of 90%.



Figure 8: Well-to-wheel carbon footprint against carbon intensity of electricity generation

Thresholds for such changes are for clearer visibility, also shown in **Table 10**. If such decarbonization steps could be achieved, biofuel production could also be recommended in the Czech Republic or any other country with a power grid carbon footprint below these levels.

Table 10: Sensitivity of biodiesel production carbon footprint against carbon intensity of electricity production and electrolyzer efficiency

	70% electrolyzer efficiency		90% electrolyzer efficiency	
	Thresholds for power grid	Carbon footprint of biodiesel production	Thresholds for power grid	Carbon footprint of biodiesel production
	gCO2 <sub>eq</sub> /kWh	kgCO2 <sub>eq</sub> /tBiodiesel	gCO2 <sub>eq</sub> /kWh	kgCO2 <sub>eq</sub> /tBiodiesel
Steam gasification has a smaller footprint than fossil fuel	272	3976	338	3985
CO <sub>2</sub> gasification has a smaller footprint than H <sub>2</sub> O gasification	212	3095	273	3218
CO <sub>2</sub> gasification reaches carbon neutral production	128	0	163	0
Theoretical maximum with perfectly clean power grid	0	-4749	0	-4749

# 6. Summary and Outlook

This paper presented two different routes to produce Biodiesel via gasification, electrolysis, and Fischer-Tropsch synthesis. The first route (a) produced carbon monoxide by steam gasification of biomass and hydrogen by steam gasification plus a small electrolyzer. The second route (b) produced carbon monoxide by CO<sub>2</sub> gasification of biomass and hydrogen by CO<sub>2</sub> gasification plus a larger electrolyzer. Direct emissions from these processes and indirect emissions from the power grids in Austria and the Czech Republic were presented. Based on this, the carbon footprints for both process routes were calculated and evaluated. The key findings of this paper were the following:

- Electricity produced in the Czech Republic has a much larger carbon footprint than in Austria (401.3 vs. 144.4 gCO2<sub>eq</sub>/kWh). This increases the carbon footprint of energy-intensive processes like electrolysis in the Czech Republic significantly, even if there is no CO<sub>2</sub> produced directly.
- An electrolyzer was needed to adjust the syngas produced via steam gasification and CO<sub>2</sub> gasification. The electrolyzer for CO<sub>2</sub> gasification was significantly larger (35.11 vs. 12.73 MW).
- It is possible to utilize CO<sub>2</sub> via CO<sub>2</sub> gasification to produce renewable fuels.
  4.75 tCO<sub>2</sub>/tBiodiesel was converted in the production chain. The most important products were biodiesel, waxes, and naphtha.
- In Austria, the CO<sub>2</sub> gasification + electrolysis production route is more carbon efficient than steam gasification + electrolysis. It is possible to produce biofuels with a very low well-towheel carbon footprint of 594 kgCO2<sub>eq</sub>/tBiodiesel. Both pathways had a smaller carbon footprint than fossil fuels. Steam gasification saved 47% and CO<sub>2</sub> gasification even 85,1% of the emissions created by using fossil Diesel.
- In the Czech Republic, none of the presented pathways currently produces biofuel with a smaller carbon footprint than conventional fossil fuel. If the power grid was decarbonized from its current 401.3 gCO2<sub>eq</sub>/kWh, at 272 gCO2<sub>eq</sub>/kWh H<sub>2</sub>O gasification + electrolyzer would break even with fossil fuels. Lowering this footprint to 212 gCO2<sub>eq</sub>/kWh would lead to CO<sub>2</sub> gasification having a smaller carbon footprint than steam gasification. At 128 gCO2<sub>eq</sub>/kWh or below, negative carbon emissions from biofuel production would be possible with CO<sub>2</sub> gasification.

The last point demonstrates that accurately estimating future energy production carbon intensity is essential for long-term technology implementation planning. If the carbon footprint of the power grids continues to decrease, both gasification pathways get more attractive. CO<sub>2</sub> gasification in the currently described state profits more from such a decrease and bears the potential of carbon-negative production at sufficiently low energy grid carbon footprints.

Additional thought must be given to technological advancements in gasification processes and electrolyzers. Fischer-Tropsch synthesis is a relatively mature technology that does not contribute much to the overall process carbon footprint. Electrolyzers are currently reaching around 70% efficiency commercially, with the first scientific papers describing 95+% efficiency. Therefore, in this area, there is significant potential for improvement. CO<sub>2</sub> gasification is a relatively young research area. The values expressed in this paper correspond to around 26% to 45% utilization of CO<sub>2</sub>. Thermodynamic equilibrium for the Boudouard reaction would allow close to a 90% conversion rate at these temperatures, meaning this technology has significant potential for improvement.

Two recommendations can be given to policymakers building on this research. First, it is crucial to decarbonize electricity production. A transition from coal and gas-fired power plants to clean technology like hydro, wind, and solar energy is critical to enable technological progress building on

the usage of hydrogen. Second, when choosing which technology to invest in,  $CO_2$  gasification seems the most promising technology if the electricity production is clean enough. This technology is not yet proven to use on a large scale. Investments in research on this technology are necessary to make such production possible within a reasonable time. According to this research, a combination of renewable electricity production and  $CO_2$  gasification would effectively help decarbonize the transport sector.

## Literature

- EU, "Directive (EU) 2018/2001 of the European Parliament and of the Council on the promotion of the use of energy from renewable sources," *Off. J. Eur. Union*, vol. 2018, no. L 328, pp. 82–209, 2018.
- [2] "Eurostat Data Explorer." https://appsso.eurostat.ec.europa.eu/nui/submitViewTableAction.do (accessed May 06, 2022).
- [3] S. Rangaraju, "Briefing: 10 years of EU fuels policy increased EU's reliance on unsustainable biofuels," *Transp. Environ.*, no. June, pp. 1–20, 2021.
- [4] A. Mohr and S. Raman, "Lessons from first generation biofuels and implications for the sustainability appraisal of second generation biofuels," *Effic. Sustain. Biofuel Prod. Environ. Land-Use Res.*, vol. 63, pp. 281–310, 2015, doi: 10.1016/j.enpol.2013.08.033.
- [5] L. Antonaci et al., "Food Security Information Network."
- [6] H. L. Raghavendra, S. Mishra, S. P. Upashe, and J. F. Floriano, "Research and Production of Second-Generation Biofuels," *Bioprocess. Biomol. Prod.*, no. November, pp. 383–400, 2019, doi: 10.1002/9781119434436.ch18.
- [7] "www.ChemistryIsLife.com The Chemistry of Diesel Fuel." https://www.chemistryislife.com/the-chemistry-of-dies (accessed Jun. 15, 2022).
- [8] "Equations of Diesel You Must Know |." https://www.fueltek.co.uk/equations-of-diesel-youmust-know/ (accessed Jun. 15, 2022).
- [9] M. S. Masnadi *et al.*, "Global carbon intensity of crude oil production," *Science (80-. ).*, vol. 361, no. 6405, pp. 851–853, 2018, doi: 10.1126/science.aar6859.
- [10] V. Gordillo, N. Rankovic, and A. F. N. Abdul-Manan, "Customizing CO2 allocation using a new non-iterative method to reflect operational constraints in complex EU refineries," *Int. J. Life Cycle Assess.*, vol. 23, no. 8, pp. 1527–1541, 2018, doi: 10.1007/s11367-017-1380-1.
- [11] "Producing gasoline and diesel emits more CO2 than we thought Innovation Origins." https://innovationorigins.com/en/producing-gasoline-and-diesel-emits-more-co2-than-we-thought/ (accessed Jun. 15, 2022).
- [12] European Technology and Innovation Platform, "Fischer-Tropsch synthesis," 2021.
- [13] SASOL, "The Fischer-Tropsch process\_generating synthetic fuels\_sasol.pdf." 2011.
- [14] A. de Klerk, Biogas from Waste and Renewable Resources Beyond Oil and Gas : The Methanol Economy Catalysis for Sustainable Energy Production Planning and Integration of Refinery and Petrochemical Operations Hydrogen and Fuel Cells. 2011.
- [15] X. Pan, "Biodiesel instead of fossil fuels in Diesel vehicles," 2021.
- [16] H. Gruber *et al.*, "Fischer-Tropsch products from biomass-derived syngas and renewable hydrogen," *Biomass Convers. Biorefinery*, vol. 11, no. 6, pp. 2281–2292, 2021, doi: 10.1007/s13399-019-00459-5.
- [17] M. Ostadi, E. Rytter, and M. Hillestad, "Boosting carbon efficiency of the biomass to liquid process with hydrogen from power: The effect of H2/CO ratio to the Fischer-Tropsch reactors on the production and power consumption," *Biomass and Bioenergy*, vol. 127, no. October 2018, p. 105282, 2019, doi: 10.1016/j.biombioe.2019.105282.
- [18] S. Pratschner, M. Hammerschmid, F. J. Müller, S. Müller, and F. Winter, "Simulation of a Pilot

Scale Power-to-Liquid Plant Producing Synthetic Fuel and Wax by Combining Fischer–Tropsch Synthesis and SOEC," *Energies*, vol. 15, no. 11, p. 4134, 2022, doi: 10.3390/en15114134.

- [19] "Carbon monoxide | Linde Engineering." https://www.linde-engineering.com/en/processplants/hydrogen\_and\_synthesis\_gas\_plants/gas\_products/carbon\_monoxide/index.html (accessed May 09, 2022).
- [20] "Carbon Monoxide Market Size & Share | Global Report [2028]." https://www.fortunebusinessinsights.com/carbon-monoxide-market-105343 (accessed May 09, 2022).
- [21] "Gasification Market Size, Growth | Global Industry Trends [2028]." https://www.fortunebusinessinsights.com/gasification-market-103487 (accessed May 09, 2022).
- [22] International Energy Agency, "The Future of Hydrogen: Seizing today's opportunities," *IEA Publ.*, no. June, p. 203, 2019.
- [23] R. W. Howarth and M. Z. Jacobson, "How green is blue hydrogen?," *Energy Sci. Eng.*, vol. 9, no. 10, pp. 1676–1687, 2021, doi: 10.1002/ese3.956.
- [24] M. Holst, S. Aschbrenner, T. Smolinka, C. Voglstätter, and G. Grimm, "Cost Forecast for Low Temperature Electrolysis - Technology Driven Bottom-up Prognosis for PEM and Alkaline Water Electrolysis Systems," p. 79, 2021.
- [25] J. Speight, Handbook of Gasification Technology Science, Processes and Applications, 1st Editio. New Jersey: Scrivener Publishing LLC and John Wiley & Sons, Inc, 2020.
- [26] A. Valente, D. Iribarren, and J. Dufour, "Prospective carbon footprint comparison of hydrogen options," *Sci. Total Environ.*, vol. 728, p. 138212, 2020, doi: 10.1016/j.scitotenv.2020.138212.
- [27] I. E. A. B. Task, "Gasification applications in existing infrastructures for production of sustainable value-added products production of sustainable value-added products," no. December, 2021.
- [28] A. M. Mauerhofer *et al.*, "Conversion of CO2 during the DFB biomass gasification process," *Biomass Convers. Biorefinery*, vol. 11, no. 1, pp. 15–27, 2021, doi: 10.1007/s13399-020-00822x.
- [29] IEA, "Austria 2020. Energy Policy Review," *Int. Energy Agency*, vol. 4, no. 1, pp. 1–14, 2020, [Online]. Available: https://www.iea.org/reports/austria-2020.
- [30] International Energy Agency, "Turkey 2021 Energy Policy Review," *lea*, pp. 17–27, 2021.
- [31] "Ember | Coal to clean energy policy." https://ember-climate.org/ (accessed Jun. 22, 2022).
- [32] "Gas Turbines for Power Generation Introduction." https://www.wartsila.com/energy/learnmore/technical-comparisons/gas-turbine-for-power-generation-introduction (accessed Jun. 14, 2022).
- [33] H. Hofbauer, R. Rauch, K. Bosch, R. Koch, and C. Aichernig, "Biomass CHP Plant Güssing A Success Story," *Expert Meet. Pyrolysis Gasif. Biomass Waste*, pp. 527–536, 2003, [Online]. Available: http://members.aon.at/biomasse/strassbourg.pdf.
- [34] J. Fuchs, J. C. Schmid, S. Müller, and H. Hofbauer, "Dual fluidized bed gasification of biomass with selective carbon dioxide removal and limestone as bed material: A review," *Renew. Sustain. Energy Rev.*, vol. 107, no. November 2018, pp. 212–231, 2019, doi: 10.1016/j.rser.2019.03.013.

[35] Z. Yan, J. L. Hitt, J. A. Turner, and T. E. Mallouk, "Renewable electricity storage using electrolysis," *Proc. Natl. Acad. Sci. U. S. A.*, vol. 117, no. 23, pp. 12558–12563, 2020, doi: 10.1073/pnas.1821686116.