BEST
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The generation of green gases from sewage sludge: A case study for H_2 from steam gasification

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Executive Summary

Neben Strom wird Wasserstoff als einer der bedeutsamsten Energieträger für eine CO_2-neutrale Gesellschaft gesehen. Wasserstoff wird vor allem in der Industrie und im Schwerverkehr von Bedeutung sein. Der heutzutage produzierte Wasserstoff ist allerdings noch nicht CO_2-neutral. Etwa 96 % des Wasserstoffs werden derzeit aus fossilen Rohstoffen hergestellt, wodurch bei einer ganzheitlichen Betrachtung der Wasserstoffnutzung die CO_2 Emissionen der Wasserstoffherstellung nicht vernachlässigt werden dürfen. Somit stellt eine, auf fossilen Energieträgern basierte, Wasserstoffbereitstellung keine langfristige Alternative dar. Derzeit ist Wasserstoff vor allem ein wichtiger Grundbaustein in der chemischen Industrie und spielt in der Mobilität derzeit noch eine untergeordnete Rolle. Die jährliche Produktion liegt bei etwa 100 Millionen Tonnen Wasserstoff pro Jahr, was etwa 2 % des jährlichen Energieverbrauchs entspricht.

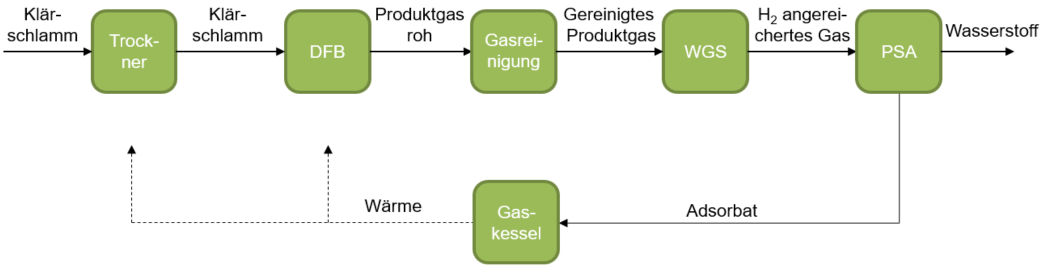
Unter dem Aspekt einer CO_2-neutralen Gesellschaft ist zurzeit vor allem die Elektrolyse von Wasser unter Verwendung von erneuerbarem Strom (Wind, Solar) als zukünftige Variante zur Wasserstoffproduktion im Gespräch. Es ist jedoch ebenso möglich Wasserstoff aus Biomasse oder Abfallstoffen herzustellen. Klärschlamm ist hier von besonderem Interesse, da dieser weltweit anfällt und verwertet werden muss. Derzeit ist in der Europäischen Union die Ausbringung in der Landwirtschaft die häufigste Verwertung von Klärschlamm, gefolgt von der thermischen Verwertung. Die landwirtschaftliche Verwertung wird aufgrund der negativen ökologischen Auswirkungen zunehmend untersagt, weshalb ein alternativer Behandlungsweg von Klärschlamm gefunden werden muss. Eine Möglichkeit um die Verwertung von Klärschlamm und die Wertschöpfung aus Klärschlamm zu erhöhen ist die Gaserzeugung und darauffolgende Produktion von H_2. Hier kann zu einem großen Teil auf Erfahrungen aus der Klärschlammverbrennung und der Kohle- (und Biomasse-)Gaserzeugung zurückgegriffen werden.

Die wesentlichen Punkte der Wasserstoffgewinnung aus der Klärschlammgaserzeugung sind im Folgenden dargestellt:

- Um das Potential der Wasserstoffgewinnung aus der Klärschlammgaserzeugung noch weiter zu verdeutlichen wurde eine mögliche Prozessanordnung detaillierter untersucht und die Ergebnisse in dieser Studie präsentiert. Die sogenannte Zweibettwirbelschicht-Gaserzeugung (Englisch: dual fluidised bed (DFB) gasification) wurde als Gaserzeugungstechnologie gewählt, da diese für anschließende Synthesen besonders geeignet ist.

- In der DFB Gaserzeugung wird Klärschlamm mit reinem Dampf vergast, wodurch ein Gas reich an Wasserstoff (30-40 Vol% im trockenen Gas) entsteht. Das Projektteam hinter dieser Studie kann dabei bereits auf mehr als 15 Jahre Erfahrung im Betrieb der Zweibettwirbelschichtgaserzeugung mit holzartiger Biomasse zurückblicken, wodurch die Umstellung auf neuartige Einsatzstoffe wie Klärschlamm erwartungsgemäß schneller erfolgen kann.

- Im Folgenden ist ein vereinfachtes Prozess-Fließschema dargestellt: Der Klärschlamm wird zunächst getrocknet und dann in einem Gaserzeuger (dual fluidised bed/DFB) zu einem wasserstoffreichen Produktgas umgesetzt. Das entstehende Gas wird gereinigt und an Wasserstoff angereichert (Wasser-Gas-Shift/WGS). Reiner Wasserstoff (99.97%) wird abgetrennt (pressure swing adsorption/PSA) und das restliche Gas wird für interne Wärmebereitstellung verwendet.



Prozess-Fließschema zur Klärschlamm-Gaserzeugung.

- Da bisher noch keine Langzeitdaten zur Klärschlammgaserzeugung vorhanden sind, wurde eine Anordnung ohne Gas-Recyclingstrom gewählt. Auf diese Weise können sich mögliche Störstoffe nicht im Gasstrom anreichern. Bereits mit diesem vereinfachten Aufbau ist es möglich aus 20 MW Klärschlamm (dies entspricht in etwa der Größe der EBS Wien) etwa 8,4 MW Wasserstoff zu produzieren. Dies bedeutet, dass etwa 14 000 Wasserstoffautos (197 Mio. km) allein mit dem Klärschlamm der EBS Wien betrieben werden können.

- Eine Evaluierung der Technology Readiness Levels (TRL) der Prozesskette zur Wasserstoffherstellung mittels Gaserzeugung aus Holz und Klärschlamm wurde ebenfalls durchgeführt. Sie zeigt, dass bei den meisten Prozessschritten auf kommerziell verfügbare Anlagen zurückgegriffen werden kann (TRL 9). Nur die Gaserzeugung aus Klärschlamm sowie nachfolgende Gasreinigung sind derzeit noch nicht ausgereift.

	Biomasse DFB Gaserzeugung	**Klärschlamm DFB Gaserzeugung**
Trockner	TRL 9	TRL 9
DFB Gaserzeugung	TRL 9	TRL 3
Gasreinigung	TRL 9	?
Wasser-Gas-Shift	TRL 9	
Druckwechsel-Adsportion	TRL 9	
Gaskessel	TRL 9	
Vollständige Prozesskette	TRL 5	TRL 2

- Um das Wissen um die DFB Klärschlamm-Gaserzeugung weiter ausbauen zu können wird derzeit eine 1 MW Pilotanlage auf dem Gelände der Wien Energie errichtet. Diese Pilotanlage ist die erste ihrer Art, die sich auf die Verwendung von anspruchsvollen Brennstoffen wie Klärschlamm fokussiert. Auf der 1 MW DFB Pilotanlage können Testkampagnen unter realen, industriellen Bedingungen durchgeführt werden. Es gilt unter anderem mit Langzeitversuchen die Einflüsse verschiedenster Störstoffe (wie Chlor, Schwefel, Schwermetalle, …) auf den Gaserzeugungs-Prozess zu ermitteln, sowie die nachfolgende Gasreinigung auszulegen. Mithilfe dieser Daten wird es möglich sein die Produktion aus Wasserstoff noch näher an die Kommerzialisierung zu bringen und einen signifikanten Beitrag zur Dekarbonisierung unserer Gesellschaft beizutragen.

1 MW Pilotanlage zur DFB Klärschlamm-Gaserzeugung

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1 Production of Renewable Hydrogen

1.1 Reasons to Produce Renewable Hydrogen

Today most of the growing global energy demand is covered by fossil energy sources. Starting with the industrialisation the use and requirements of energy carriers shifted with the state of science and technology. Over the years the consumption of fuels changed from only using solids like wood and later on coal, to a simultaneous use of liquid crude oil. Nowadays a strong increase in the application of natural gas can be seen as well. Focusing on the fossil fuels (and therefore not considering the traditionally used wood) a shift from carbon to hydrogen regarding the molar ratio in the fuels can be observed. The observed start of decarbonisation can be further enhanced by substituting fossil fuels with hydrogen. [1,2]

The Paris Agreement of the United Nations Framework Convention on Climate Change collected all nations into a common cause to keep the global temperature rise below 2 °C. The United States of America have left the agreement, but based on the election of Biden/Harris a re-entry into the agreement can be expected next year [3]. The Paris Agreement promotes the use of renewable sources in industrial processes and the strongest international framework for the development of alternative sustainable technologies. [4]

Today, hydrogen is of major importance as an intermediate in refineries and chemical industry. In 2014 around 100 million tonnes of hydrogen were produced (50 % captive, 44 % by-product and 6 % merchant production), which are 12 EJ on a LHV basis (equivalent of some 2 % of the global primary energy consumption). For the future renewable hydrogen is considered as an important secondary energy carrier since it can be used as fuel, as reagent for syntheses as well as storage possibility for electricity [5,6]. At the moment around 96% of the global hydrogen production is based on fossil fuels, leading to significant CO_2 emissions [7]. Electrolysis currently produces 4 % of global H_2 (see Figure 1-2). Though at the moment electrolysis is not yet a carbon neutral alternative for H_2 production since electricity generation is also connected to significant carbon dioxide emissions due to the production from fossil fuels. Still, by producing H_2 from renewable electricity H_2 is a possible alternative to reduce greenhouse gas emissions in energy production and aid in the establishment of a decarbonised energy system [8].

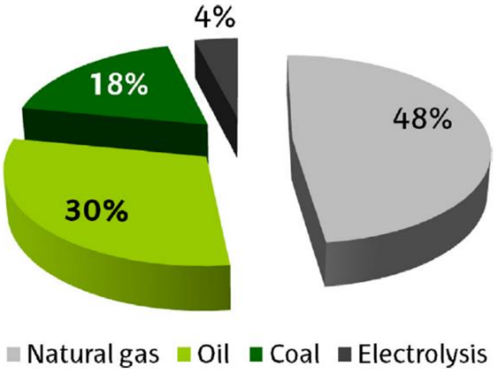

Figure 1-2: Current sources of hydrogen [6].

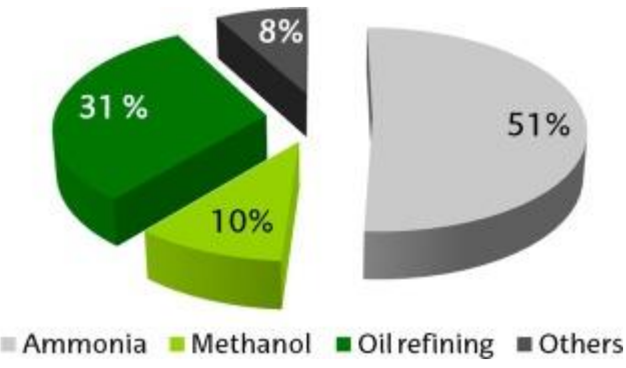

Figure 1-2: Global hydrogen consumption by sector [6].

Today's produced hydrogen is mainly consumed by four industries: ammonia production, refinery applications, methanol production, and various reduction processes (see Figure 1-2) [7]. Only 7% of global H_2 consumption are caused by other consumers. The demand for hydrogen is excepted to increase caused by an increased production of ammonia and methanol, heavier and dirtier fuels being processed in refineries as well as a higher hydrogen demand for hydro-desulphurisation processes due to more stringent environmental regulations to produce almost sulphur-free products. Additionally, the growing interest in H_2 as energy carrier will also lead to a higher H_2 demand in the future [5,9]. In general, three categories for H_2 production are available: electrochemical, biological and thermochemical methods. In theory all of these methods can also be applied on a renewable basis. For electrochemical methods it is then necessary to use electricity produced by sustainable sources of energy.

Thermochemical routes using fossil fuels are the current state of the art applied for industrial H_2 production. However, thermochemical routes can also be realised with biomass as fuel, making the produced H_2 renewable. Thermochemical routes summarise the production of H_2 from hydrocarbons like fossil fuels and biomass and include conversion technologies like reforming, gasification and pyrolysis. During these processes a so-called product gas is obtained, with CO and H_2 being the major products. From this product gas H_2 can be separated in downstream processes to obtain pure H_2.

Hydrogen is also seen as a possible candidate for long-term electricity storage. The share of renewables is expected to rise in the next years [10] leading to challenges for the system integration of renewable energy. At the moment the share of renewables is not yet high enough to cause problems in meeting electricity demand [10]. Though, further increasing the share of variable renewable energy will make long term storage of energy relevant [11]. Hydrogen production via electrolysis (see Subsection 1.2.4) will be one possible approach to further stabilise the energy grid during times of electricity production surpluses.

1.2 Commercial H_2 Production Technologies

This section summarises the main industrial production technologies for H_2: steam reforming (SR) of natural gas, partial oxidation, coal gasification, and electrolysis.

1.2.1 Steam Reforming

SR describes the reaction of methane with steam to Co and H_2 in the presence of a catalyst, see Equation 1.

$$\mathbf{CH_4 + H_2O \leftrightarrow CO + 3\,H_2 \qquad \Delta H = +203\ kJ \cdot mol^{-1}} \tag*{Equation 1}$$

SR is a highly endothermic reaction. After SR the product gas is led into a Water gas shift (WGS) unit (see subsection 2.3.1). A typical process chain with the main process steps for SR of methane to produce hydrogen is shown in Figure 1-3.

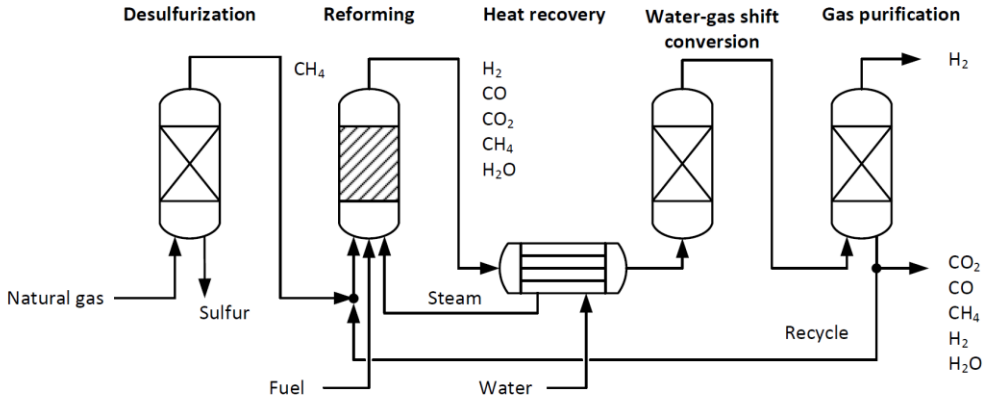

Figure 1-3: Hydrogen production using the SR process with its process steps. [12]

Before SR the natural gas is desulfurized. SR is typically operated at temperatures between 500 and 900 °C. Since the reaction is endothermic, external heating is needed to maintain the temperature. The pressure is typically maintained at 20 bar and the steam to carbon ratio. Referring to the overstoichiometricly needed steam, ranges from 2.5 to 3. Nickel-based catalysts are usually employed due to their sufficient activity and comparably low cost. After SR the obtained gas passes a WGS conversion and finally a H_2 purification step. [5]

SR plants are mainly used to cover the demand of refineries and ammonia plants and can reach efficiencies up to 85 % for plant sizes of 150-300 MW [13,14]. For other industries, like glass, food, metal, and petrochemicals smaller size plants are needed due to the lower H_2 demand. This leads to the construction of small-scale SR plants since in most cases on-site production is more economically feasible to delivery by trucks [15]. Due to the smaller size (0.15-15 MW) the efficiency of these plants is around 50 % [14].

1.2.2 Partial Oxidation

Non-catalytic partial oxidation (POX), autothermal reforming (ATR), and catalytic partial oxidation (CPO) of hydrocarbon containing fuel all describe the same reaction, shown for the example of methane in Equation 2.

$$\mathbf{CH_4 + \frac{1}{2}O_2 \leftrightarrow CO + 2\,H_2 \qquad \Delta H = -36\,kJ \cdot mol^{-1}} \qquad \textbf{Equation 2}$$

Partial oxidation technologies are applied in a wide scale range. Additionally, it is possible to construct larger single-train units compared to SR.

POX describes the non-catalysed reaction of methane or liquid hydrocarbons with O_2 at high temperatures and high pressure to produce product gas. ATR describes the reaction of methane or liquid hydrocarbons with both steam and O_2 at high temperatures and high pressures to obtain product gas. The reactions occurring during ATR are exothermic and catalysts are used to obtain a higher H_2 yield. CPO uses a solid catalyst for heterogenous reactions of methane or liquid hydrocarbons with O_2 and steam at high space velocities to produce product gas [5]. The different partial oxidation processes are compared in Figure 1-4 also including the necessary unit operations when focusing on H_2 production for all these technologies.

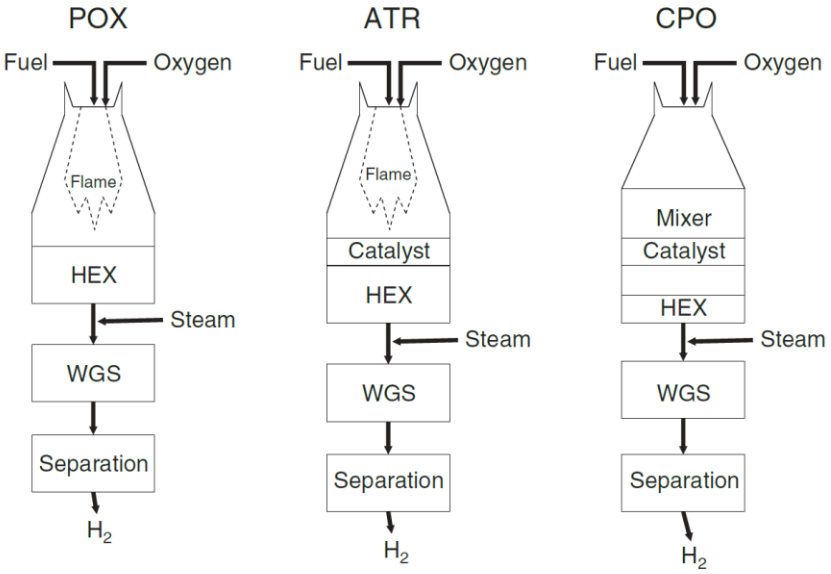

Figure 1-4: Schematic representation of non-catalytic partial oxidation (POX), autothermal reforming (ATR), and catalytic partial oxidation (CPO) reformers. Heat exchanger (HEX). [5]

Compared to SR the POX reaction is slightly exothermic. The difference in these technologies is the way in which heat is provided. For CPO and ATR, part of the fuel is oxidised inside the reactor to obtain the heat necessary to cover the energy necessary for the endothermic SR reaction occurring over the same catalyst bed. POX has the advantage that it produces a product gas with a favourable H_2:CO ratio for downstream syntheses. Downstream of the POX, ATR or CPO reactors a WGS unit and a separation unit are used to obtain pure H_2. [5]

1.2.3 Coal Gasification

The gasification of coal is a well-established technology converting coal with steam an O_2 to a product gas consisting of CO, H_2, CO_2, higher hydrocarbons and impurities like H_2S and NH_3. Equation 3 summarises the reactions of the coal with both O_2 and H_2O to the most desired products H_2 and CO.

$$3\,C + O_2 + H_2O \leftrightarrow H_2 + 3CO \qquad \Delta H = -91\,kJ \cdot mol^{-1} \qquad \textbf{Equation 3}$$

A more extensive description of the reactions occurring during gasification will be given in Section 1.3.

During coal gasification some of the coal is combusted with O_2 to provide the heat necessary for the endothermic gasification reactions. This internal delivery of heat is termed autothermal gasification. Apart from O_2 also steam and CO_2 can be added to enhance gasification reactions [5]. If pure O_2 is used as gasification agent coal gasification can also be seen as POX of a solid fuel. A schematic flow diagram of coal gasification is shown in Figure 1-5. Additionally, several possible applications of coal gasification are given. Most of the times coal gasification is rather used for the production of chemicals like ammonia and methanol and not so much for the production of pure H_2.

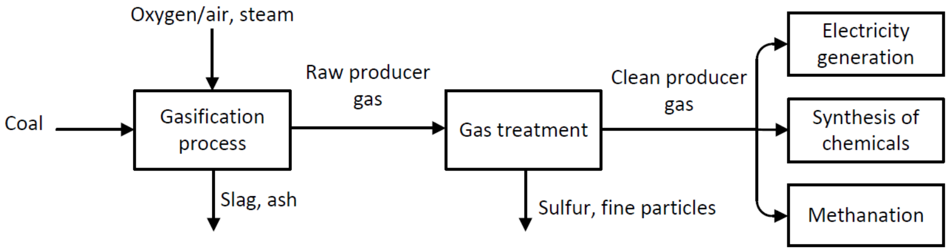

Figure 1-5: Basic process steps of coal gasification and its main applications [12].

1.2.4 Electrolysis

Electrolysis of water is another possibility to produce H_2. The reaction occurring during electrolysis of water is shown in Equation 4.

$$H_2O \leftrightarrow \frac{1}{2} O_2 + H_2 \qquad \Delta H = +286\,kJ \cdot mol^{-1} \qquad \textbf{Equation 4}$$

If the electricity used for electrolysis originated from renewable sources, electrolysis could be a promising technology to produce carbon-neutral H_2 in the future. Though at the moment electrolysis only plays a minor role compared to SR of fossil resources [5].

Several electrolyser technologies are available with operating pressures ranging from atmospheric to 1 MPa pressure. Several different electrolytes can be used therefore subdividing electrolysers in alkaline, proton exchange membrane (PEM) and solid oxide electrolysis cells [16]. The main process steps of hydrogen production as well as other power-to-gas applications using electrolysis are shown in Figure 1-6. On advantage is that electrolysers directly produce high-purity H_2 and only drying and compression is necessary to produce merchant quality. Depending on the size and type of the plant efficiencies of 52-85% are reachable with industrial electrolyses [16].

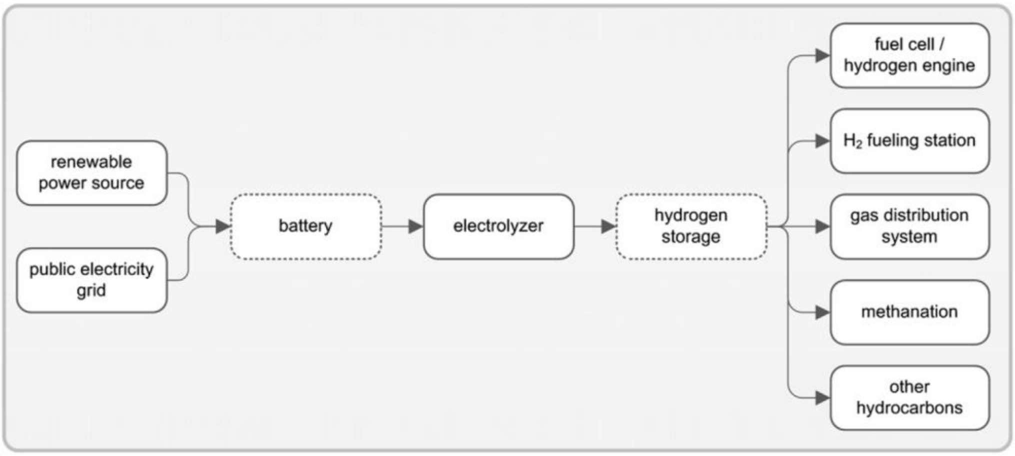

Figure 1-6: Process chain of hydrogen production based on electrolysis [16].

1.2.5 Methane Pyrolysis

Methane pyrolysis is a process historically used for ethyne and C_2 production in general. Fundamental research in methane pyrolysis has already been performed since the early 1900s [17–19]. In the last years this research field has piqued new interest as a technology to produce CO_2 emission-free H_2 from methane (see Equation 5).

$$\mathbf{CH_4 \leftrightarrow \ C + 2\,H_2 \qquad \Delta H = \ +75\ kJ \cdot mol^{-1}} \qquad \textbf{Equation 5}$$

A typical process flow chart of a methane pyrolysis plant is depicted in Figure 1-7. Methane (Natural Gas) is enters the methane pyrolysis where it reacts to C and H_2. The carbon is deposited during this step which can pose problems regarding blocking of the reactor by carbon particles [20]. Blocking of the reactor can be inhibited by using a packed bed bubble column with liquid tin and temperatures of around 1175 °C. H_2 yields of up to 78% are reachable, therefore a pressure swing adsorption reactor is necessary to remove unreacted methane from the gas stream and recycle it back into the methane pyrolyzing reactor. The carbon obtained during methane pyrolysis has a grain size of 40-100 nm and agglomerates of a size of 15-20 µm. The agglomerates coat the liquid tin and do not dilute it. This carbon can be used for paint particles or as tire additives as one example. With methane pyrolysis a H_2 efficiency of 55% can be reached, which is a similar efficiency to steam gasification. [21]

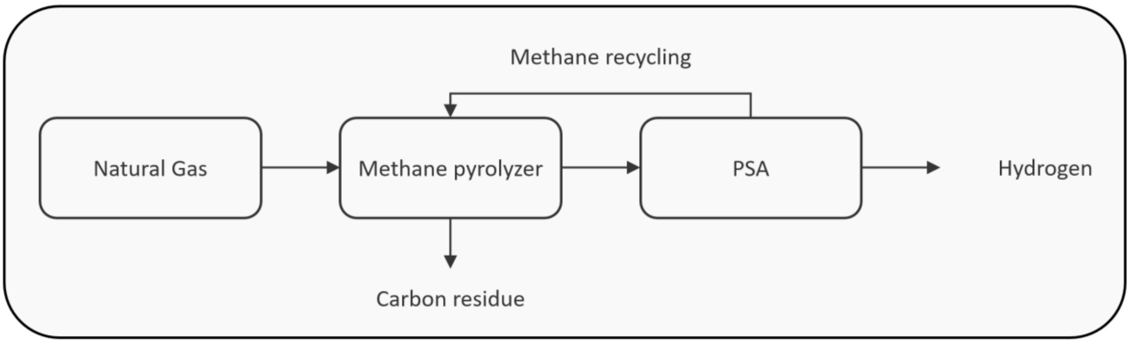

Figure 1-7: Process chain of a methane pyrolysis unit for hydrogen production

1.3 Gasification Fundamentals

Gasification describes the thermochemical conversion of a carbonaceous fuel with a gasification agent into product gas (often also called producer gas or wood gas if wooded fuel is used). The general process layout for H_2 production from gasification is shown in Figure 1-8

Figure 1-8: General process layout for hydrogen production via gasification.

The gas cleaning and upgrading positioned after gasification is needed to remove bulk CO and CO_2 as well as several impurities like H_2S, NH_3, HCl and tar. The removal of benzene, toluene, ethylbenzene and xylene (BTEX) is normally not necessary since the H_2 separation equipment is able to remove them as well.

Various biomasses and coals are depicted in a C-H-O-diagram shown in Figure 1-9. Within gasification there are several different approaches or pathways for the conversion from fuel towards product gas. Each of these pathways is indicated by a letter (a-e) and marked with arrows. The addition of steam as gasification agent is common, since on the one hand it has a positive stoichiometric effect but on the other hand also enhances char gasification and temperature moderation in the reactor. [22]

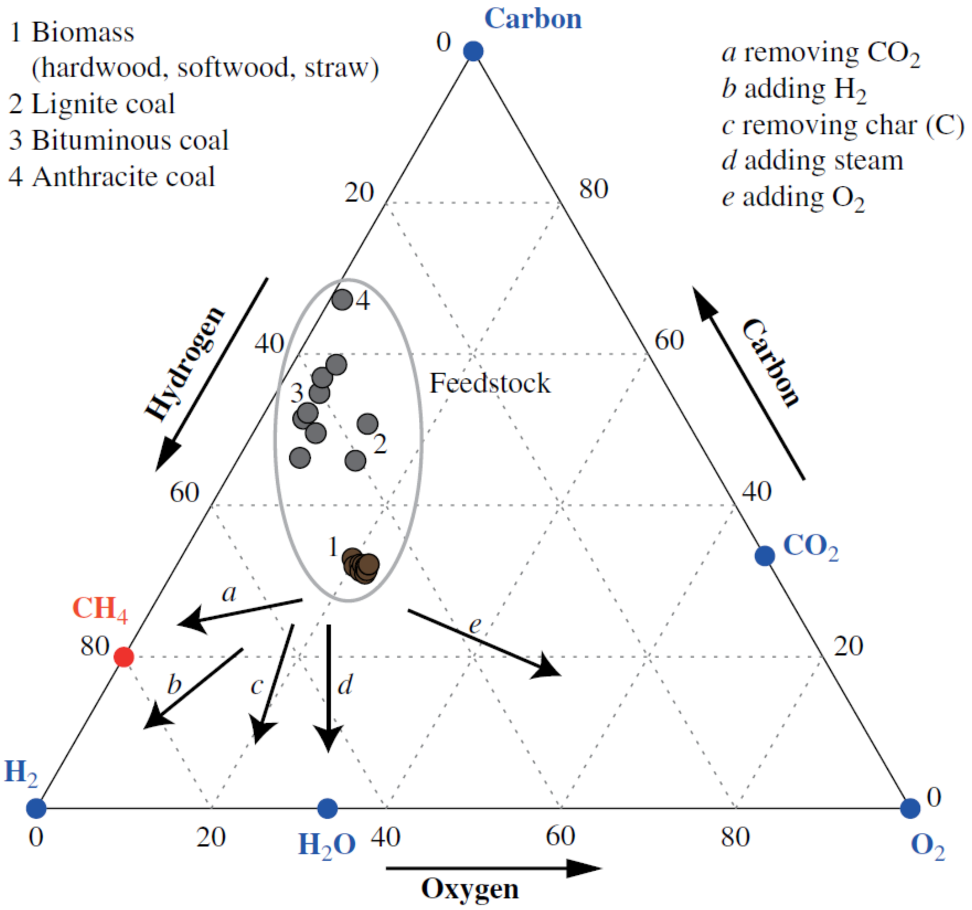

Figure 1-9: C-H-O-diagram for coal and biomass and possible gasification pathways [22].

The gasification of biomass opens up a wide array of possible applications of the product gas and several different gasification technologies are available for biomass. The different gasification technologies mainly differ in the used gasification agent and, connected to the gasification agent, the way of heat supply. Since gasification is an overall endothermic process heat has to be either supplied internally or externally, which are called autothermal and allothermal gasification, respectively. Autothermal gasification is realised by full combustion of some of the fuel used in gasification. Gasification processes can also be categorised by the reactor design, namely fixed bed, fluidised bed and entrained flow reactors.

During gasification several steps are occurring [5,23]:

- Evaporation of moisture at temperatures up to 150 °C
- Pyrolysis, therefore releasing of volatiles (H_2, CO, CO_2, CH_4, tar, etc.) between 200 and 650 °C
- Reaction of volatiles in the gas phase between 700 and 1 000 °C
- Heterogeneous reaction of char between 700 and 1 000 °C

During gasification a variety of homogeneous (Equation 6 - Equation 10) and heterogenous (Equation 11 - Equation 17) reactions occur [5,23]. Looking at the reactions, air, O_2, H_2, CO_2 and H_2 can be identified as possible gasification agents. The list of equations given is not exclusive but only summarises the most important reactions. Though other reactions like pyrolysis or volatiles reaction after their release are also of significance during gasification processes.

Heterogeneous gasification reactions:

$$\mathbf{C + O_2 \leftrightarrow CO_2 \qquad \Delta H = -394\ kJ \cdot mol^{-1}} \qquad \textbf{Equation 6}$$

$$\mathbf{C + \frac{1}{2} O_2 \leftrightarrow CO \qquad \Delta H = -111\ kJ \cdot mol^{-1}} \qquad \textbf{Equation 7}$$

$$\mathbf{C + H_2O \leftrightarrow CO + H_2 \qquad \Delta H = +119\ kJ \cdot mol^{-1}} \qquad \textbf{Equation 8}$$

$$\mathbf{C + CO_2 \leftrightarrow 2\ CO \qquad \Delta H = +160\ kJ \cdot mol^{-1}} \qquad \textbf{Equation 9}$$

$$\mathbf{C + 2\ H_2 \leftrightarrow CH_4 \qquad \Delta H = -88\ kJ \cdot mol^{-1}} \qquad \textbf{Equation 10}$$

Homogeneous gasification reactions:

$$\mathbf{CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H = -41\ kJ \cdot mol^{-1}} \qquad \textbf{Equation 11}$$

$$\mathbf{CO + 3\ H_2 \leftrightarrow CH_4 + H_2O \qquad \Delta H = -203\ kJ \cdot mol^{-1}} \qquad \textbf{Equation 12}$$

$$\mathbf{CO_2 + 4\ H_2 \leftrightarrow CH_4 + 2\ H_2O \qquad \Delta H = -162\ kJ \cdot mol^{-1}} \qquad \textbf{Equation 13}$$

$$\mathbf{CO + \frac{1}{2} O_2 \leftrightarrow CO_2 \qquad \Delta H = -283\ kJ \cdot mol^{-1}} \qquad \textbf{Equation 14}$$

$$\mathbf{H_2 + \frac{1}{2} O_2 \leftrightarrow H_2O \qquad \Delta H = -242\ kJ \cdot mol^{-1}} \qquad \textbf{Equation 15}$$

$$\mathbf{2\ CO + 2\ H_2 \leftrightarrow CH_4 + CO_2 \qquad \Delta H = -244\ kJ \cdot mol^{-1}} \qquad \textbf{Equation 16}$$

$$\mathbf{CO_2 + 2\ H_2O \leftrightarrow CH_4 + 2\ O_2 \qquad \Delta H = +790\ kJ \cdot mol^{-1}} \qquad \textbf{Equation 17}$$

Not all gasification agents are suitable for autothermal gasification. Normally only air, pure O_2, or a mixture of O_2 and steam are used supplying the necessary heat by partial combustion of the fuel. When using air as the gasification agent the resulting product gas is diluted by N_2 leading to a relatively low lower heating value of around 3 to 6.5 MJ·m^{-3} with N_2 contents between 42 and 60% [23]. For allothermal gasification, steam, CO_2 or a mixture of both is used as gasification agent. In this case heat has to be supplied from the outside. This can be realised by a heat pipe or a circulating bed material. Examples for gasification technologies using a circulating bed material are the dual fluidised bed (DFB) steam gasification or the sorption enhanced reforming (SER) process.

1.4 Dual Fluidised Bed Steam Gasification

The basic principle of DFB steam gasification, which was mainly developed at TU Wien, Austria, is the separation of the gasification process into two separated zones, namely the gasification reactor and the combustion reactor. The basic principle of the DFB steam gasification technology is depicted in Figure 1-10.The fuel is fed into the gasification reactor where it is gasified with steam as gasification agent. The gasification reactor is operated as a fluidised bed. The bed material as well as part of the char that is produced during gasification is transported to the combustion reactor where the char is combusted with air, heating up the bed material. The combustion reactor is operated as a fast-fluidised bed. The heated-up bed material is transported back to the gasification reactor supplying the heat necessary for the endothermic gasification reactions. Fluidised loop seals separate the gas streams between the combustion and gasification reactor. It is therefore possible to obtain a nearly N_2 free product fast with a heating value above 12 MJ·m^{-3} [23,24].

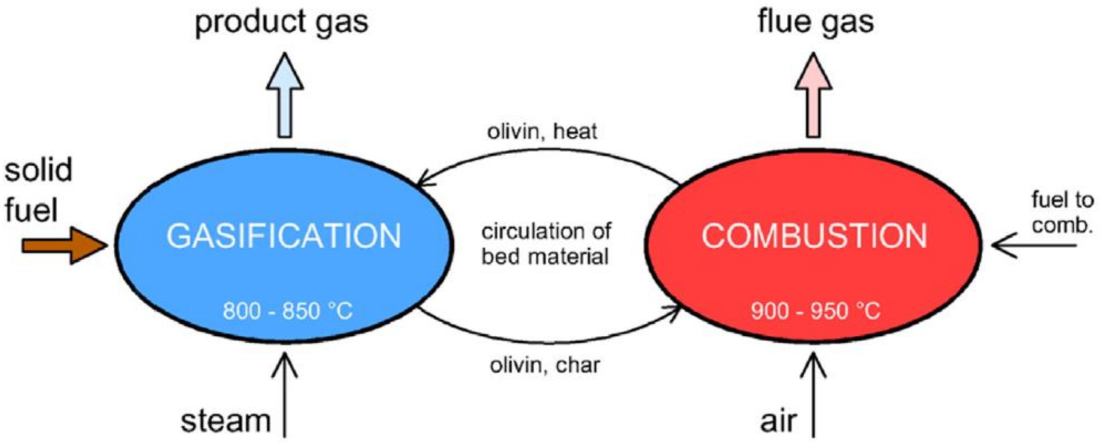

Figure 1-10: Principle of DFB steam gasification of biomass [25].

The gasification reactor is operated with comparably low gas velocities to increase the residence time and promote gasification reactions. Though, different concepts for DFB gasification plants are available as well. ECN proposed a DFB system with a circulating bed gasification reactor and a bubbling fluidised bed combustion reactor. A detailed overview of DFB gasification concepts was given by Corella et al. [26].

For DFB steam gasification olivine is normally used as bed material in industrial scale [27]. Olivine acts as a heat carrier to transport heat from the combustion to the gasification reactor. It additionally acts as a catalyst to promote gasification reactions such as SR of hydrocarbons (lighter hydrocarbons and tar) and the WGS reaction [28,29].Commercial plants using olivine as bed material and woody biomass as fuel can reach H_2 contents in the product gas of around 40% [27]. A typical product gas composition for woody biomass gasification with olivine bed material is summarised in Table 1-1. It can be seen that a H_2:CO ratio between 1.5:1 and 2:1 can be reached. This ratio is favourable for several synthesis reactions like mixed alcohol or Fischer Tropsch (FT) synthesis [30].

Table 1-1: Typical product gas composition of the DFB gasification [23].

Components	Values	Units
H_2	0.35-0.45	$m^3\ m^{-3}$
CO	0.22-0.25	$m^3\ m^{-3}$
CO_2	0.20-0.25	$m^3\ m^{-3}$
CH_4	about 0.10	$m^3\ m^{-3}$
C_2H_4	0.02-0.03	$m^3\ m^{-3}$
Tar (incl. BTEX)	20-30	$g\ m^{-3}$

The DFB steam gasification technology was first realised in demonstration scale in Güssing, Austria. The plant provided heat and power for a total of about 15 years [31] and it was possible to obtain valuable scientific and industrial knowledge to further develop the technology. Several other commercial plants based on the same technology were erected over the years [23,32].

A simplified flowchart of the CHP plant in Güssing, Austria is depicted in Figure 1-11. After the gasification reactor the gas is cooled down below 200 °C and passes a filter to separate fly char from the gas stream. The next step in gas cleaning is a rapeseed methyl ester (RME) scrubber which is used to condensate H_2O and remove condensable tar from the product gas. The resulting emulsion of tar and bio-oil is led into the combustion chamber where it is combusted to supply additional heat for the process. After the scrubber the product gas is led into a gas engine to produce electricity and district heat.

The flue gas from the combustion reactor is cooled down as well and filtered to remove the fine ash fraction. The heat obtained from the flue gas stream is either utilised internally for steam generation or as district heat.

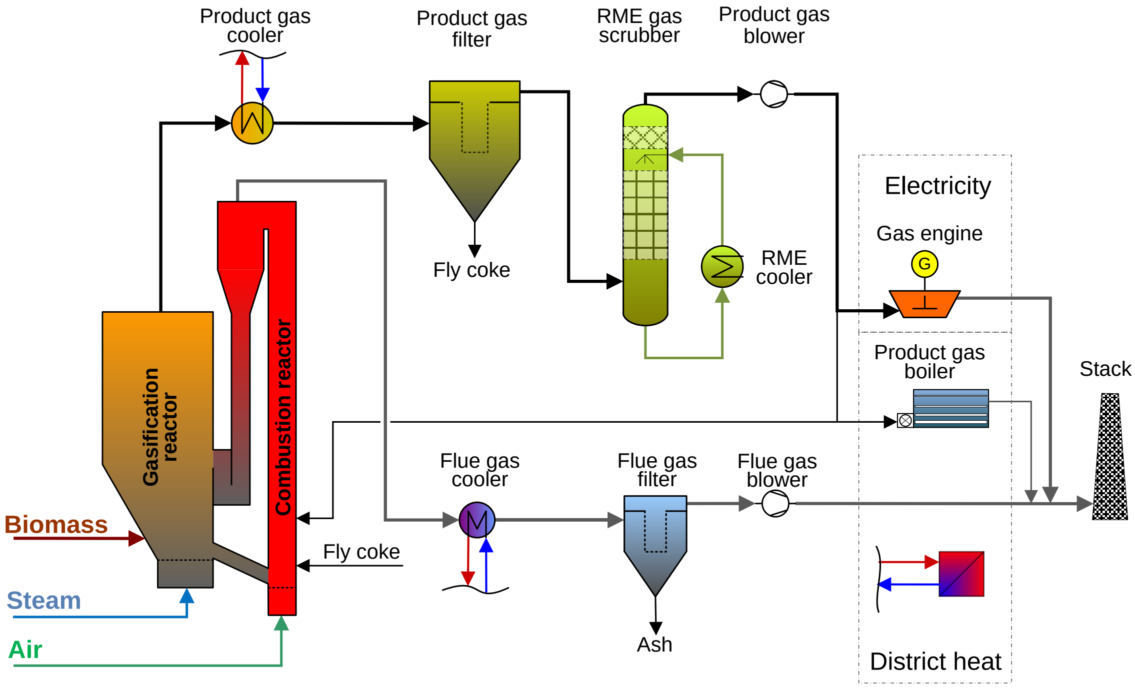

Figure 1-11: Flowchart of the commercial DFB plant in Güssing, Austria. Based on [24].

Most of the commercial plants built so far are not in operation at the moment caused by changes in ownership or decisions to stop commercial operation. Today, the plant in Nong Bua District, Thailand is the state-of-the-art of commercial DFB gasification as it successfully operates with local woodchips as fuel in long-term experimental campaigns [27]. The Nong Bua plant in Thailand was commissioned in 2017 and is based on the DFB steam gasification plant design of Güssing. Several process steps (e.g. gasifier design, tar scrubber design) were improved compared to the original design. The Nong Bua plant can be operated with a variety of fuels including various agricultural residues and municipal organic solid wastes with 1 MW_{el} output.

Hofbauer et al. [33] performed a feasibility study investigating the potential to substitute all fossil fuels in Austrian agriculture by FT diesel and synthetic natural gas (SNG) produced from product gas. They determined a need for ten 100 MW plants in Austria. It was concluded that FT diesel and SNG are economically feasible with subsidies or the introduction of a CO_2 tax on fossil sources. To further evaluate the process a “Reallabor” with 5 MW fuel input is proposed before rollout in Austria.

Furthermore, a 1 MW fuel input DFB steam gasification pilot plant is currently erected at the industrial site of Wien Energie GmbH at Simmeringer Haide, Austria. The plant will be operated in experimental campaigns of up to 1000 h. The major focus lies on alternative residuals as fuel input and downstream synthesis to FT products rather than heat and power production. Further information on this plant is given in Chapter 5.

1.4.1 Sorption Enhanced Reforming

SER is another technology also utilising the same reactor design as DFB steam gasification. During SER operation higher H_2 contents are achievable in the product gas which is realised by an active removal of CO_2 from the reactive zone in the gasifier. This removal of CO_2 shifts the WGS equilibrium towards higher H_2 contents. It is therefore possible to reach H_2 contents of about 75% in the product gas. The principle of SER is depicted in Figure 1-12. SER also uses a circulating bed material, which is limestone ($CaCO_3$).

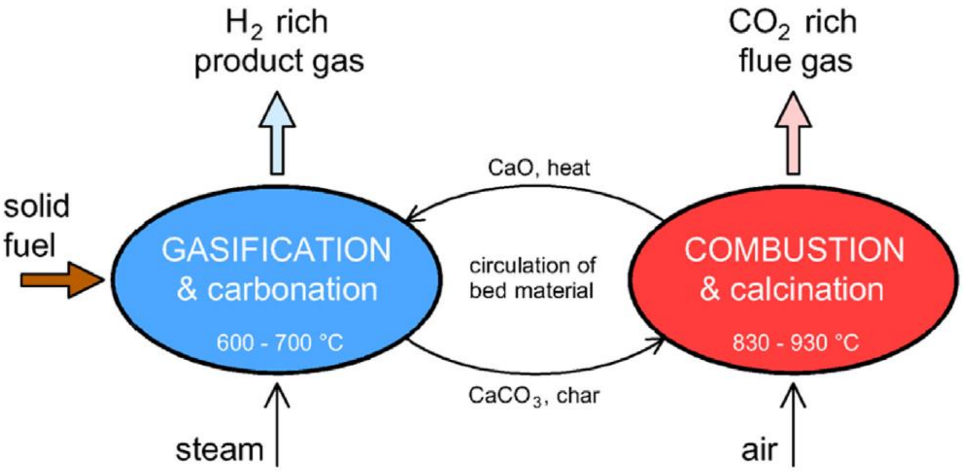

Figure 1-12: Principle of SER process based on biomass [25].

The limestone acts as a CO_2 carrier leading to the removal of CO_2 from the product gas. The bed material enters the gasification reactor as CaO and reacts with CO_2 to $CaCO_3$ (Equation 18).

$$\mathbf{CaO + CO_2 \leftrightarrow CaCO_3} \qquad \Delta\mathbf{H} = -\mathbf{178\,kJ \cdot mol^{-1}} \qquad \textbf{Equation 18}$$

The gasification reactor is operated at 650-700°C. The $CaCO_3$ formed in the gasification reactor is transported back to the combustion reactor where it reacts back to CaO and releases CO_2 at around 900°C.

$CaCO_3$ also is a suitable bed material for conventional DFB steam gasification since it leads to higher H_2 contents and lower tar contents compared to olivine, due to its higher catalytic activity [34]. Though its lower mechanical stability compared to olivine leads to more abrasion of the bed material causing higher bed material losses as well as higher dust contents in the product gas.

At this point SER was studied on three different plants. Experiments were performed by TU Wien at a 100 kW (fuel) DFB gasifier, the University of Stuttgart at a 200 kW (fuel) DFB gasifier, and the commercial biomass steam gasification plant in Güssing, Austria. All of these plants are based on the DFB steam gasification technology [35–39]. The product gas composition measured for these experiments is summarized in Table 1-2.

Table 1-2: Typical product gas composition of the SER process [35–39].

Components	**Values**	**Units**
H_2	0.73	$m^3\ m^{-3}$
CO	0.08	$m^3\ m^{-3}$
CO_2	0.06	$m^3\ m^{-3}$
CH_4	0.11	$m^3\ m^{-3}$
C_xH_y	0.02	$m^3\ m^{-3}$
Tar (excl. BTEX)	~10	$g\ m^{-3}$

2 Green Product Gas Utilization

Product gas from gasification can be used for a variety of applications, highly varying in complexity and value, on one hand depending on the used fuel, and on the other hand depending on the pursued product. Typical biogenic fuels, already used in commercial scale DFB steam gasification plants are woody biomass and biogenic residues. Depending on their properties also waste fractions and sewage sludge are suitable fuels for gasification. The product gas can be utilised directly for heat and/or power generation. In addition, the product gas can be upgraded to be subjected to syntheses to produce gaseous and liquid products. In general, synthesis processes require a higher product gas quality, so the product gas has to be cleaned and conditioned to fulfil the higher requirements. The possible fuels and products for gasification are summarised in Figure 2-1 and will be further elaborated in this chapter. Surplus energy in the form of hydrogen (via electrolysis using surplus electricity) can optionally be used to enhance various syntheses.

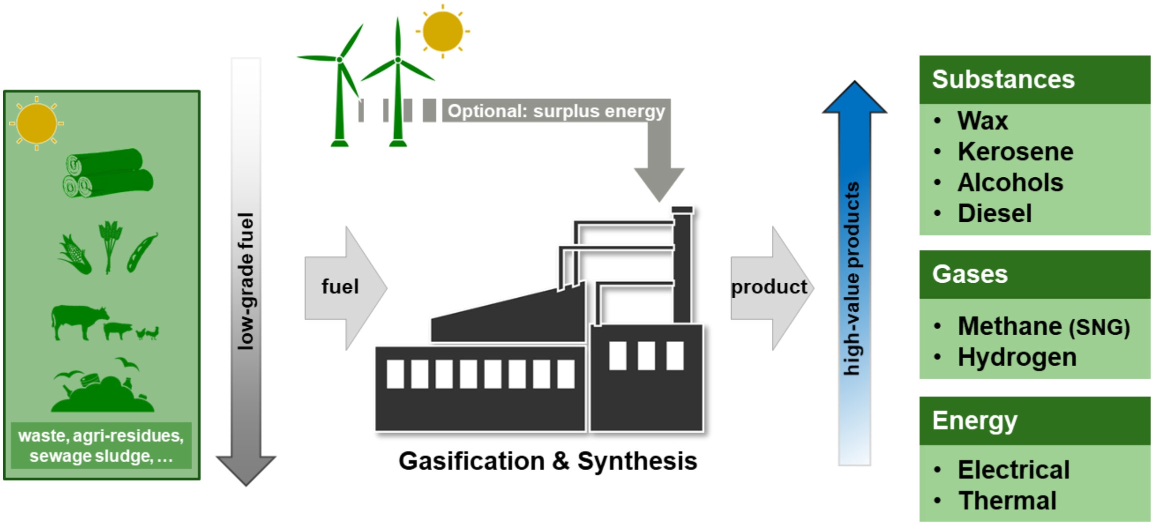

Figure 2-1: Concept of utilising biogenous fuels to produce different products via a thermo-chemical pathway consisting of gasification and various synthesis routes.

2.1 Heat and Power Utilisation

2.1.1 Heat Utilisation

Product gas can be combusted directly to utilise the heat obtained. For direct heat utilisation only minimal gas cleaning is necessary. When using the product gas in industrial processes it is possible to directly use conventional gas burners, optionally with slight adaptions to accommodate the lower heating value compared to natural gas. The use of product gas is especially interesting in pulp and paper as well as in the cement industry. Alternatively the product gas can also be combusted to provide low temperature district heat. [23]

2.1.2 Power Utilisation

Product gas can also be combusted to provide power. The combustion can either occur externally heating up a fluid powering a heat engine, or internally in a gas motor, gas turbine or fuel cell. Internal combustion generally leads to higher efficiencies compared to external combustion. [23]

2.2 Product Gas Cleaning

To be able to further utilise the product gas for syntheses several impurities have to be removed from the gas stream. Several different impurities occur in product gas ranging from nitrogen compounds (e.g. ammonia, hydrocyanic acid), halogens (e.g.: hydrochloric acid) and sulfuric compounds (e.g.: H_2S, COS, mercaptan). Also, the tar formed by condensable hydrocarbons can be problematic. It is therefore of importance to remove these impurities for downstream synthesis applications. [40–43]

For clarity the product gas cleaning processes will be described in the order they will occur in an industrial plant.

2.2.1 Catalytic Hot Gas Cleaning for Tar Reduction

Product gas leaving the gasification reactor is currently loaded with certain amounts of tar. Tar can be removed by using scrubbers (see Subsection 2.2.3) but also by tar reduction at high temperatures (~800 °C) using catalysts. In the last years this field has gained interest in the scientific community and the main results will be described in the following.

At first the use of reformers downstream the gasification reactor has been studied in detail. Ceramic monoliths showed problems during operation due to critical operation conditions like high dust loads and high temperature peaks. Though, metal-based monoliths could be used successfully even in commercial scale. One example of industrial application is the gasification plant in Skive, Denmark which uses metal-based monoliths to reduce the tar content of the product gas downstream the gasification reactor [44]. The tar reformer monolith used in Skive is depicted in Figure 2-2 [45]. It was possible to reach satisfactory results during long-term operation.

One advantage of these monoliths is that they can be used without cooling down the product gas after leaving the gasification reactor leading to temperatures of the monolith of around 800 °C. The surface of the monolith is normally coated with catalytically active coatings and tar reforming occurs by the reaction with steam.

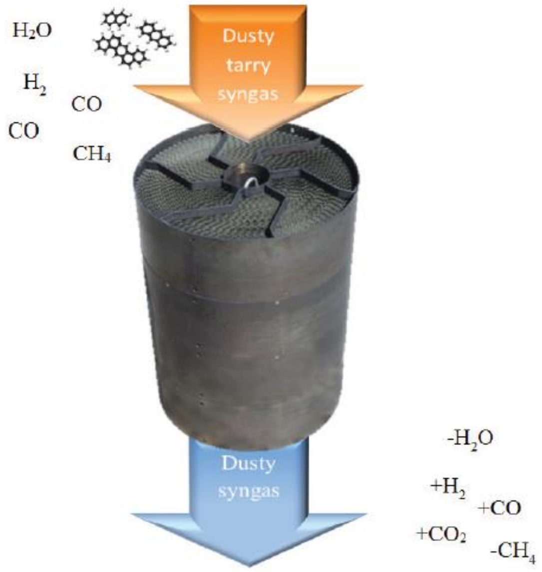

Figure 2-2: Illustration of the tar reformer monolith in Skive, Denmark [45].

Haldor Topsoe and Andritz-Catbona have developed two different reformers to reform both tar and methane. The monolithic, dirty reformer catalyst is positioned before particulate removal and the clean dumped catalyst is placed downstream of particulate removal. Both were tested for extended time frames at pilot scale at Gas Technology Institute. [46]

Catalytic hot gas cleaning can also be performed in active filter candles which are able to reduce both dust and tar in one process step making it a comparably compact unit. The principle itself is similar since tar is also separated at 800 °C. These catalytic filter candles can be positioned directly in the freeboard of a fluidized bed reactor [47]. Most research in the last years focused on the mechanical stability of the candle material since the operation inside the fluidized bed is challenging. The problems that occur are the reducing atmosphere inside the gasification reactor and the high load of dust and particles that are entrained from the fluidised bed.

2.2.2 Dust Filters

Commercial gasification plants typically use conventional bag house filters to remove dust from the product gas stream. Due to the use of bag house filters it is therefore necessary to cool down the product gas stream below 200 °C. Apart from dust also residual char particles are collected in the dust filter. The impurities collected in the dust filter are normally summarised under the term fly char, which is either returned internally (e.g. into the gasification reactor in a DFB system) or discharged as a waste stream.

Electrostatic precipitators (ESP) are an alternative to bag house filters to separate dust from the product gas stream. ESPs are especially suited to remove smaller dust particles. An electrostatic charge is used to remove particles from the product gas stream. They are used in industrial scale with certain fluidised bed air gasification reactors being one example of application. Though, the high carbon content in the product gas stream makes an application of ESPs for downstream cleaning challenging. Apart from ESPs also wet ESPs can be used as an alternative for cooling and condensing to remove aerosols of solids or liquids.

2.2.3 Rapeseed Oil Methyl Ester Tar Scrubber

Product gas from DFB steam gasification has a significant tar load. Tars are undesired and problematic since they can cause problems with downstream units or catalysts. One way to remove tar from the gas stream is a wet scrubber. For this the gas has to be cooled down. An additional advantage is that the steam in the gas stream is condensed as well. Scrubbers using RME have proven useful for the use in commercial DFB steam gasification plant. RME scrubbers were used in the DFB steam gasification plants in Güssing and Oberwart, Austria and Senden/Ulm, Germany [48–50], as well as at the GoBiGas plant in Sweden [51].

RME scrubbers typically contain packings which are wetted by the cooled RME flowing downwards. The product gas passes in counter-current flow ensuring good contact with the RME, cooling down the product gas below the water dew point. It is therefore possible to condense water, which adsorbs part of the ammonia in the product gas. The resulting emulsion of RME and water is separated in the scrubber basin below the scrubber. The density difference between RME and water allows for a single-step separation. Not all of the condensate can be removed from the RME. The heavier condensate collects at the bottom of the basin filling up the lower part halfway with condensate. The emulsion remaining is separated and burnt in the combustion reactor supplying additional heat to the system. It is therefore possible to prevent any waste streams from RME scrubbing. [52]

The current state of the art and latest research regarding RME scrubbers in commercial DFB steam gasification plants was summarised by Bardolf [52]. The experience from the GoBiGas plant with RME scrubbers was described by Thunman et al. [51]. The RME scrubber is typically operated at 50 °C only removing parts of the tar load (tar content decreased from 5 to 1.5 $g \cdot m^{-3}$) and condensing all steam. At the temperatures used for RME scrubbing BTEX components are not, and naphthalene only partially, removed. This removal is typically sufficient for heat and power utilisation but a second RME scrubber at cooler temperatures is necessary for synthesis applications or H_2 production.

2.2.4 Amine Scrubber

Amine scrubbing is a suitable technology to separate CO_2 from gas streams and has been used since 1930 [53]. An aqueous amine solvent reacts with CO_2 from the gas stream to form water-soluble salts. Even low concentrations of CO_2 can be separated [54]. The main challenges during amine scrubbing are the corrosive properties of amines, the formation of non-soluble salts and foaming [55].

The most commonly used aqueous solutions are monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA). CO_2 has a high affinity for these solvents making it possible to operate the amine scrubber at ambient conditions. The regeneration of the scrubbing solution is very energy intensive due to the high capacity and high selectivity of the amine solution. The needed energy is normally provided as process heat. Some of the aqueous solution is lost to evaporation so it is necessary to add new solution regularly. Apart from CO_2 H_2S is also absorbed but an intentional removal of H_2S would necessitate higher temperatures during regeneration. [56]

The loading capacity of the amine scrubber is mainly depending on the concentration of active components and the possible loading capacity according to the thermodynamic equilibrium. The use of MEA allows for the fastest reaction rate and highest loading capacity compared to DEA and MDE but more heat is necessary for regeneration. [57]

Today, a mixture of MDEA and piperazine is commonly used in amine scrubbers. This mixture is also called activated MDEA (aMDEA). In this mixture piperazine acts as a catalyst to speed up the absorption of CO_2. Many major chemical suppliers (BASF, DOW chemicals, Shell, Taminco) currently sell aMDEA [58–60]. Regarding the CO_2 removal efficiency different solvents can be sorted accordingly: water < MDEA < DEA < MEA. aMDEA has a similar CO_2 removal efficiency to MEA but is considered less corrosive. MDEA also requires less energy for regeneration compared to MEA and DEA [61]. Figure 2-3 shows the principle of an amine scrubbing unit with amine regeneration.

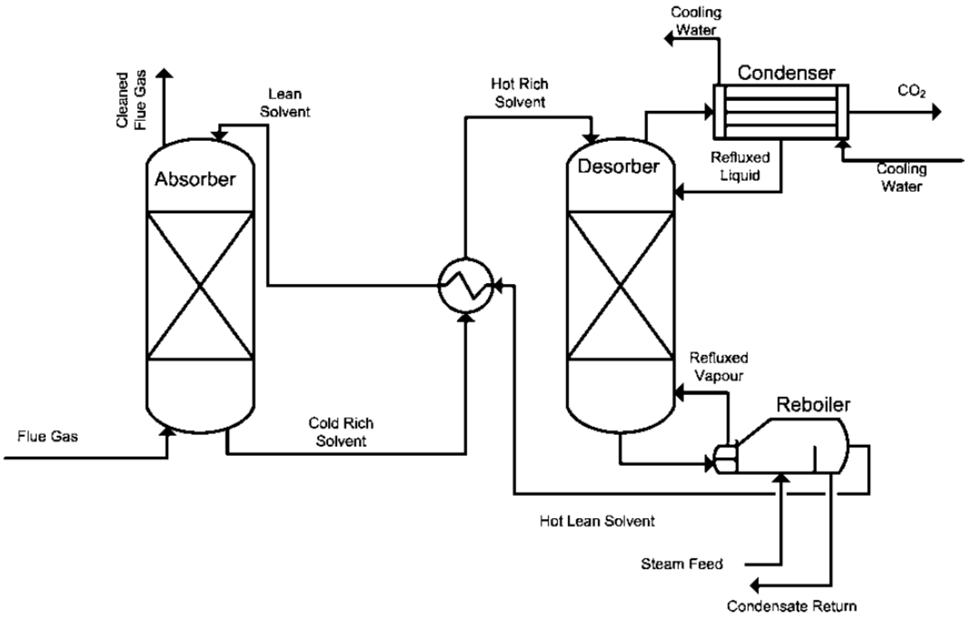

Figure 2-3: Simplified flowchart of an amine scrubbing process [54].

A gas stream rich in CO_2 (1) is fed into the absorber so that CO_2 is removed from the gas stream, resulting in a CO_2-lean gas stream (3). Regenerated amine solution (called lean amine due to its low CO_2 content) is supplied from the top of the absorber (2) and rich amine saturated with CO_2 exits at the bottom (4). The rich amine is preheated and enters at the top of the stripper (5). Inside the stripper the rich amine solution is flowing down to the bottom where it is heated up to desorb CO_2 and generate steam. The generated gas stream flows upwards, counter-current to the rich amine to heat it up. The gas stream leaves the stripper at the top (6). Afterwards, the steam is condensed together with parts of evaporated amine and led back into the stripper (7). The now dry CO_2 gas stream leaves the stripper (9). The regenerated lean amine is removed from the bottom (8) and cooled to be used again in the absorber (2).

Bauer et al. [58] postulate that CO_2 removal efficiencies of up to 99.8 % can be reached for biogas with a CO_2 volumetric fraction of 40% in the gas. Ryckebosch et al. [62] state CO_2 removal efficiencies of up to 99.5%. A more rigorous CO_2 purification would make it possible to improve CO_2 quality to food-grade standard [57].

Typical operating parameters of amine scrubbers are summarized in Table 2-1. The operating conditions depend on both the CO_2 concentration in the gas and the applied amine solvent.

Table 2-1: Typical operating parameters of amine scrubbers.

Parameters	Values	Units	Sources
Stripper temperature	100 to 160	°C	[53,56,58,63,64]

Absorber temperature	40 to 65	°C	[58,63,64]
Electricity demand	300 to 700	kJ kg^{-1} absorbed CO2	[58,65–68]
Heat for regeneration	1 400 to 4 000	kJ kg^{-1} absorbed CO2	[58,65,66,68–70]
Solvent consumption	0.35 to 2	kg t^{-1} absorbed CO2	[57,67,69]

2.2.5 Further Gas Cleaning

Further gas cleaning might be necessary depending on the used fuel. Especially the use of sewage sludge necessitates more gas cleaning compared to many other fuels. The challenges regarding sewage sludge utilisation will be described thoroughly at a later point in Section 0.

2.3 Catalytic Gas Conversion

2.3.1 Water Gas Shift

A WGS unit is a possible way to both increase the H_2 yield and decrease the CO content of the product gas. WGS units are well-established in industry to produce H_2 or set the CO:H_2 ratio of product gas. Equation 19 shows the WGS reaction occurring in WGS units.

$$\mathbf{CO + H_2O \leftrightarrow H_2 + CO_2} \qquad \mathbf{\Delta H = -41.2\ kJ \cdot mol^{-1}}$$

Equation 19

The equilibrium constant for the WGS reaction decreases with temperature. The products are therefore favoured at lower temperatures (see Figure 2-4) [5].

Depending on the application one or more fixed bed reactors are necessary for WGS units. For adjusting the CO:H_2 ratio for synthesis reactions a by-pass high temperature (HT) WGS stage is enough. When producing H_2 2-3 WGS stages, lowering the temperature from stage to stage, are necessary to reach a sufficient CO conversion.

A variety of catalysts are available fort WGS units. Fe-Cr-based catalysts are primarily used HT WGS. The HT stage is operated at gas inlet temperatures of 350 to 550 °C and space velocities ranging from 400 to 1200 h^{-1}. The operating pressure can be selected according to plant requirements [5]. Sulphur poisoning by H_2S is not a problem for Fe-Cr-based catalysts, at least at the concentrations typically observed for biomass steam gasification [71,72]. For low temperature (LT) stages, on the other hand, Co-Mo or Cu-Zn-based catalysts are typically used. LT stages are typically operated at around 200 °C. Co-Mo catalysts are activated by sulphur, therefore preferring higher sulphur amounts in the gas. However, the amount of H_2S in the product gas from DFB steam gasification is typically too low to activate Co-Mo catalysts [71,73]. Though, LT catalysts based on Cu-Zn are very sensitive to sulphur poisoning [5], it is therefore necessary to remove sulphur upstream of the WGS unit. In the following the description of WGS units will focus on Fe-Cr-based catalysts as they are especially suitable for the application in DFB biomass steam gasification plants [74–76].

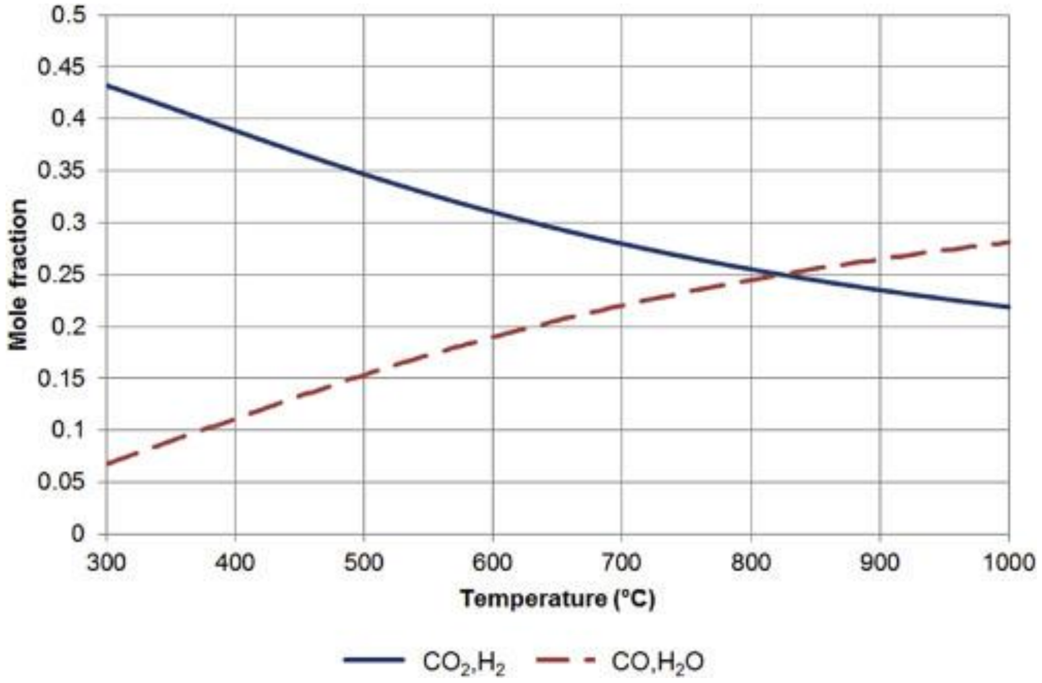

Figure 2-4: Equilibrium concentrations for the WGS reaction dependant on temperature [29].

HT WGS catalysts consist of Fe_3O_4 and Cr_2O_3 which is the same composition as the catalysts developed by BASG in 1915. The content of Cr_2O_3 makes the catalyst resistant to sintering. Additionally, the catalyst is robust against sulphur and chlorine compounds and relatively cheap. An extensive review of HT WGS catalysts base on Fe was given by Zhu and Wachs [77].

The steam to dry gas ratio is an important parameter influencing the overall heat integration and the overall performance of the Fe-Cr-based WGS. Data available from laboratory and industrial units show that higher steam to dry gas ratios increase the WGS reaction rate. Higher steam to dry gas ratios therefore lead to higher CO conversion and lower CO concentrations at the exit of the WGS unit. Apart from the WGS reaction the steam to dry gas ratio can also have an effect on the FT reaction producing hydrocarbon (mainly methane). A minimal steam to dry gas ratio of 0.4 reduces unwanted side reactions. A certain amount of steam is also advantageous in reducing coking and carbon deposition on the catalyst surface. Typical steam to dry gas ratios are between 0.6 and 2.2 and the steam to carbon ratio between 2.8 and 4.2 depending on the feed of the WGS reactor [78]. The ternary C-H-O-diagram for 1 bar (Figure 2-5) shows at which compositions coking and carbon deposition are favoured.

Several experiments were performed with a WGS pilot plant with three fixed bed reactors in series using a commercial Fe-Cr-based catalyst (Shiftmax 120 from the company Clariant). It was possible to operate this batch for around 3000 hours [75,76] with product gas from the commercial

DFB steam gasification plant Oberwart, Austria. Of those 3000 hours it was possible to operate the WGS unit with tar-rich product gas taken after the product gas filter [76].

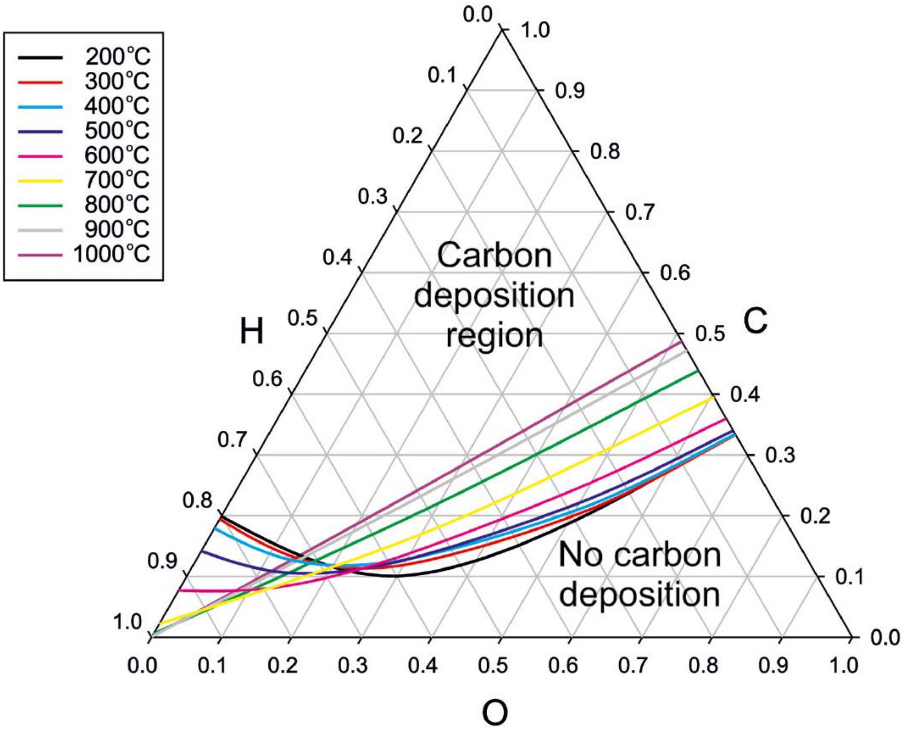

Figure 2-5: Ternary C-H-O-diagram for solid phase of all carbon allotropes at 1 bar [79].

Kraussler et al. [80] compared the effect of the product gas tar content on the WGS pilot plant by using product gas both before and after the RME scrubber and could detect no significant differences. The WGS unit was operated at 350 °C at the reactor inlet and it was possible to achieve a CO conversion of at least 91 % and the CO concentration on the outlet was below 2%. This data shows that it should be possible to operate a WGS unit with product gas directly after filter and an RME scrubber is not necessary.

Apart from the WGS reaction the catalysts for WGS reactions can also hydrogenate other components like HCN and olefins in the product gas. The reaction of COS to H_2S is catalysed as well.

2.3.2 Methanation

Fixed bed methanation reactors are used in industry as gas cleaning units to remove small concentrations of CO in H_2-rich gas streams to avoid catalyst deactivation during ammonia synthesis [72,81]. The reaction heat of this reaction is not of major concern since only small amounts of CO react only slightly heating up the gas stream. Though, if the production of CH_4 is of interest the reaction heat has to be considered. This is realised by a cascade of methanation reactors with intermediate gas cooling and gas recycling of product gas. Several companies distribute fixed bed methanation [82]. One example is the Haldor Topsoe TREMP (Topsøe Recycle Energy-efficient Methanation Process) which was applied at the GoBiGas gasifier to produce SNG from biomass [83,84].

Fluidized bed reactors are often used for large scale operation of heterogeneously catalysed reactions with highly exothermic reactions. One of the major characteristics of fluidized bed reactors are the isothermal conditions which can be maintained even for highly exothermic reactions. This makes it easy to control the operation. Though additional focus has to be given to attrition and entrainment of the catalyst particles. Fluidised bed methanation is currently not commercially available though there were several research projects studying it. At the DFB steam gasification plant in Güssing, Austria, successful operation was demonstrated and is described in literature [85,86].

Not only CO can be used to produce SNG but also CO_2 can react to SNG with H_2 (Equation 13). Though, the reaction with CO is preferred and might even inhibit CO_2 methanation due to the stronger adsorption strength of CO on the catalyst surface [87]. At the moment it is still unclear whether CO is an intermediate of CO_2 methanation. However the kinetics and mechanisms for CO methanation are also not yet clear [88]. Twigg [72] postulated that CO_2 methanation is inhibited until CO concentration below 200 to 300 ppm. Parallel to methanation reactions the WGS reaction (Equation 11) occurs, which can be suppressed by selecting appropriate feed gas mixtures, catalysts, and operating conditions as well as a fitting reactor design [22].

Metals of the groups 8 to 10 of the periodic table are suitable catalysts for methanation reactions. Though, most of the catalysts used in commercial methanation plants are nickel catalysts due to a fitting combination of price, activity and selectivity [22,89].

Fouling caused by carbon deposition has to be considered during CO methanation [90] while no fouling could be observed during CO_2 methanation processes [91]. The C-H-O-ternary-diagram (Figure 2-5) shows that coking and carbon depositions are thermodynamically favoured. According to equilibrium calculation higher steam to carbon or oxygen to carbon ratios are needed to prevent carbon deposition with decreasing temperature. An increased amount of CO_2 can also supress deposition at temperature higher than 1000 °C [79,92].

Carbon deposition and coke formation can be suppressed to comparably low rates under favourable reaction conditions. Though, under unfavourable conditions, carbon deposition and coke formation occur within ours and causes failures of the catalyst and plugging of reactor voids necessitating a shut down. The carbon deposits are formed by the Boudouard reaction (Equation 9) and deposits on the active nickel surface [93]. Carbon depositions are also favoured when olefins like ethylene are present [94,95]. Gas cleaning and conditioning therefore has to occur upstream of the methanation process [90].

2.4 Hydrogen Separation Technologies

Hydrogen removal from a gas stream can be realised with pressure swing adsorption (PSA) or with membrane-based processes. Though for high purity applications (>99%) a PSA has to be used.

2.4.1 Pressure Swing Adsorption

During the PSA process gas molecules physically bind to a solid adsorbent material. Several parameters have an influence on the interactions between gas and adsorbent, namely the gas component, its partial pressure, the type of adsorbent, and the temperature. PSA is used in commercial scale for a variety of applications like air separation, hydrogen production, and biogas upgrading [56,96,97]. A typical flowchart of a PSA process is shown in Figure 2-6.

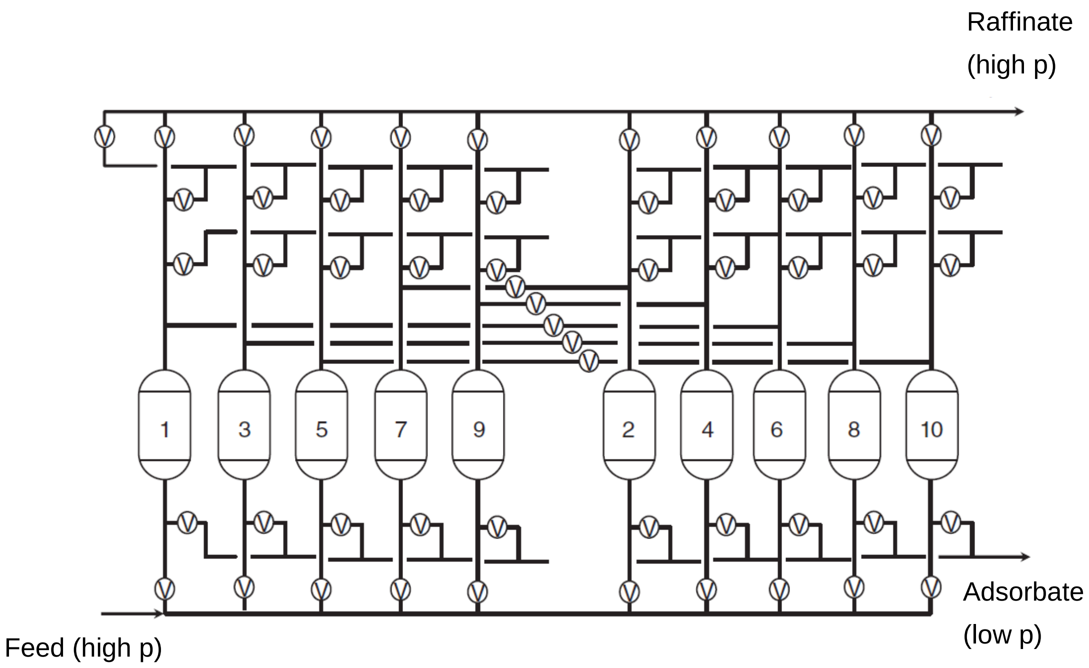

Figure 2-6: Simplified flowchart of a multicolumn PSA unit. Based on [5].

Before entering the PSA unit, the gas is compressed and fed into the different adsorber vessels. The vessels that are not in use at the moment can be regenerated by reducing the pressure and flushing with high-pressure product (raffinate). The obtained low-pressure product (adsorbate) contains the contaminants of the feed. The adsorbate is reused in upstream or downstream processes.

Activated carbon is used in the PSA units. The main gas components have a different adsorption strength on the activated carbon with the following order $CO_2 > CH_4 > CO > H_2$ [5]. CO_2 is therefore adsorbed preferably and therefore most easily removed from the feed gas stream and also H_2 meaning that activated carbon can be used to produce pure H_2.

Several experiments were performed with PSA units processing product gas from DFB biomass steam gasification plants Güssing and Oberwart, both in Austria [12,75]. The goal was to obtain H_2 with a sufficient purity to be used in a fuel cell. During these experiments it was possible to reach H_2 recovery rates of up to 80%.

The H_2 recovery can be increased to 90% by an additional CO_2 separation before the PSA and other optimisation measures. Though if the H_2 recovery is increased the H_2 purity normally decreases. To obtain high grade H_2 (purity above 99.999%) it is necessary to reduce the H_2 recovery significantly. Additionally, it is possible to internally use the adsorbate, for example as additional fuel.

2.4.2 Gas Permeation through Membranes

Similarly to PSA units, gas permeation through membranes is also driven by pressure differences. In contrast to PSA units it is possible to operate membranes continuously and operation is typically more easily controlled. Membranes allow the diffusion of some chemical species through the membrane while other molecules cannot pass the membrane. A typical layout of a membrane unit is shown in Figure 2-7. The membrane is positioned in a housing (pressure vessel) together making up the membrane module. After entering the gas stream is separated into the raffinate and the permeate. The permeate is the fraction that contains molecules that more easily diffuse through the membrane (e.g. H_2) . [5]

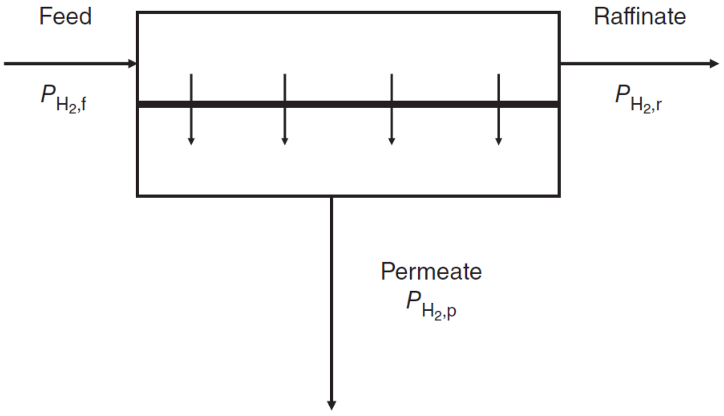

Figure 2-7: Schematic of a hydrogen separation membrane and membrane module [5].

Four different types of membranes are currently used in commercial scale or are currently developed for H_2 separation. The four different types of membranes are polymeric membranes, porous (ceramic, carbon, metal) membranes, dense metal membranes, and ion - conductive membranes, see Table 2-2. At the moment, only polymeric membranes are used in commercial scale.

Table 2-2: Comparison of Membrane Types for Hydrogen Separation [5].

Parameters	**Membrane Type**			
	Polymeric	**Nanoporous**	**Dense Metal**	**Ion Conducting**
Typical composition	Polyimide; cellulose acetate	Silica; alumina; zeolites; carbon	Palladium alloys	Water-swollen, strong-acid, cation exchange membranes; dense ceramics (perovskites)
Diffusion mechanism	Solution-diffusion	Size exclusion	Solution-diffusion	Solution-diffusion
Driving force	Pressure gradient	Pressure gradient	Pressure gradient	Ionic gradient
Operating temperature in °C	≤110	≤1000	≤150-700	≤180 (polymeric); 700-1000(ceramic)
Relative permeability	Moderate-high	Low-moderate	Moderate	Moderate
Typical selectivity	Moderate	Low-Moderate	Very high	Very high

2.5 Possible Pathways to Obtain Green Gases from Gasification

In this section possible pathways to obtain green gases are presented. All processes are based on thermo-chemical conversion routes, utilising wood chips via DFB steam gasification and subsequent product gas handling. However, all these pathways could be realised by utilising different fuels or different unit operations.

Figure 2-8 illustrates a simplified flowchart of a H_2 production pathway from wood chips via DFB steam gasification. This specific process chain is characterised by the simple setup and no gas recycling is applied. The generated product gas is fed in a WGS unit to convert CO in H_2 via the catalysed WGS reaction. In addition, lowering the CO fraction is beneficial in hydrogen separation in the PSA [5]. Applying the WGS unit upstream the RME scrubber provides energetic advantages in terms of temperature level and steam content. The drawback is, that the WGS catalyst is exposed to tar-rich product gas. However, Kraussler et al. [76] showed the basic suitability for this configuration in long-term experiments, processing real product gas derived from DFB steam gasification of wood chips. Beside hydrogen a second gas stream, the low-pressure adsorbate, which is rich in CH4, is generated.

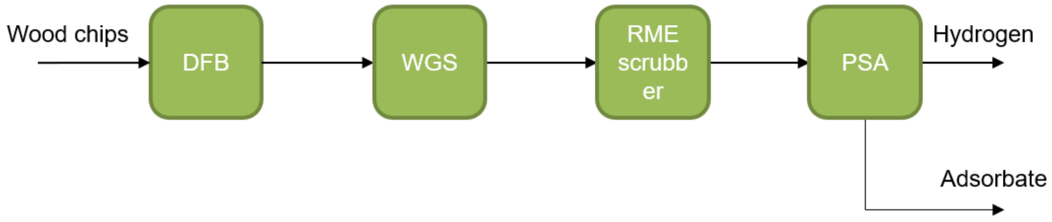

Figure 2-8: Simplified flowchart of a hydrogen plant.

The concept, as illustrated in Figure 2-8 and described above, can also be used to produce a mixture of hydrogen and methane. This mixture is also referred to as hythane or HNG.

In order to maximise the hydrogen yield, the CH_4 rich adsorbate can be utilised. This is carried out via SR of the gas. Figure 2-9 illustrates a hydrogen production route, maximised for the hydrogen production via SR. CH_4 is converted into a mixture of CO and H_2, which is recycled back into the process. This leads on one hand to a significant increase in hydrogen yield, on the other hand, caused by the requirements of the SR catalyst, a higher intensity of gas cleaning becomes obligatory. In addition, a recycle loop would accumulate compounds like CO_2 and N_2. However, issues mentioned can be addressed by applying an amine scrubber into to process chain, which will discharge CO_2 and the majority of the sulphur compounds. In addition, CO_2 can be used instead of N_2 for inertisation reasons (e.g. feeding system, filter cleaning), which will reduce the amount of N_2 in the product gas stream.

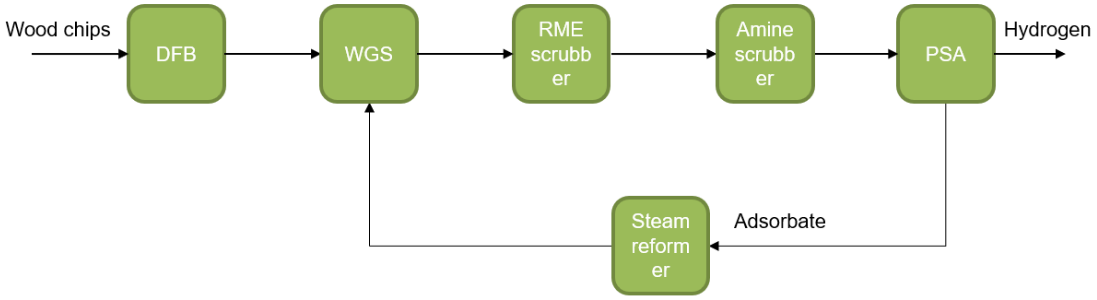

Figure 2-9: Simplified flowchart of a hydrogen plant, including gas recycling in order to maximise hydrogen production.

Several plants producing hydrogen via gasification of residues are currently in operation. In 2015 The Japanese chemical enterprise Showa Denko started a hydrogen production at their site in Kawasaki to revalorise waste plastics and produce high valuable hydrogen. This hydrogen is planned to be tested in fixed fuel cells, fuel cell vehicles and delivered over a pipeline to an ammonia producer [98–100]. The company Bio Energy Netherlands (BEN) is focussing on gasification of biomass in special woody residues. A modular plant aiming to produce heat, power and hydrogen has been developed. In November 2017 they announced a plant in Amsterdam with a size of 15 MWh of combined heat, power and hydrogen production. The start of the first project phase was planned in 2019. [101]

Apart from hydrogen, it is also possible to produce methane. Figure 2-10 illustrates a possible concept. The generated product gas is first subjected to a WGS unit, in order to set the H_2:CO-ratio. Followed by an RME scrubber and gas cleaning. The cleaned and conditioned gas is then subsequently fed into the methanation synthesis. Finally, remaining CO_2 is removed and the produced CH_4 is cleaned, according the requirements.

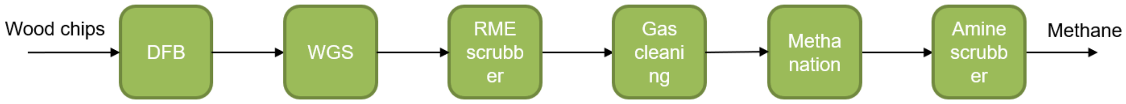

Figure 2-10: Simplified flowchart of a SNG plant.

3 Sewage sludge gasification

3.1 Why Sewage Sludge Utilization

Sewage sludge is a waste stream with a wide relevance in today's society. The production of sewage sludge will not cease in the years to come. A variety of harmful substances like heavy metals, pathogenic organisms and hazardous organic substances are concentrated in sewage sludge during wastewater treatment. Still, sewage sludge is also rich in nutrients like nitrogen and phosphorus and contains organic matter. By further utilising sewage sludge it is possible to extract these valuable nutrients adding value to an otherwise discarded waste stream. Further using sewage sludge is not part towards a circular economy. In 2020 the European Commission initiated a new Circular Economy Action Plan showing the importance of circular economy for the European Union and our future [102].

In 2016 almost 8 Mt dry basis (db.) of sewage sludge were produced in the EU 28 [103]. Around half of the sewage sludge was used in agriculture and around 1 Mt were incinerated. In Austria around 53% of the accruing sewage sludge were incinerated in 2016 (127 248 t db. of 237 938 t db.) [104]. At the moment more and more countries ban the use on fields due to the content of various hazardous materials like heavy metals and pathogens. This also removes valuable nutrients like phosphorus and nitrogen from the fields. Therefore, Austria aims to recover phosphorus from 65-85% of the sewage sludge produced [105]. At the moment mostly mono-incineration and subsequent phosphorus recovery from the ashes is considered as technology to achieve this goal. By combusting the sewage sludge pathogens are destroyed and the nutrients are concentrated in the ash. Though, also other technologies are able to achieve these goals. During gasification of sewage sludge phosphorus is also concentrated in the ash while pathogens are destroyed. With gasification it is even possible to produce higher value products like chemicals and fuels, while during sewage sludge incineration only heat and power production is possible.

3.2 Sewage Sludge Fuel Properties

Sewage sludge has a high water content (normally between 93-99.5% [106]) making it necessary to dry it before combustion or gasification. It is first dewatered mechanically and further dried thermally, if necessary. During drying sewage sludge also changes its mechanical properties. At higher water contents (above 85%) sewage sludge is pumpable and free-flowing. Between 70 and 80% sewage sludge is rather firm and becomes crumbly at around 60% water content. Below 15% water content sewage sludge is powdery [106].

Mechanical dewatering of sewage sludge from high to low water contents is challenging. At a water content around 40-55% the shear strength increases making mechanical drying impossible [106]. A possible approach is to increase the dry matter content above this phase by adding dried sewage sludge, making it granulated. Above 90% dry matter sewage sludge becomes stable and possible to store [106].

Table 3-1 compares fuel properties for softwood, which is mostly used for gasification applications, and pelletised sewage sludge. It can be seen that sewage sludge has a considerably higher ash content as well as higher contents in nitrogen and sulphur. The heating value is around half compared to softwood. During pelletising of sewage sludge, the water content was reduced below 9 %.

Table 3-1: Fuel properties of softwood and sewage sludge pellets.

	Unit	Softwood pellets [107]	Sewage sludge pellets [108]
Water content	wt%	7.2	8.7
Ash content	wt% db.	0.2	52.3
Carbon	wt% db.	50.7	25.48
Hydrogen	wt% db.	5.9	3.02
Nitrogen	wt% db.	0.2	3.46
Sulphur	wt% db.	n.d.[a]	1.18
Chlorine	wt% db.	n.d.[a]	0.106
Oxygen	wt% db.	43,00	14.45
Volatile matter	wt% db.	85.4	44.55
Lower heating value, dry	MJ kg^{-1} db.	18.9	10.02

[a] not detectable

Table 3-2 shows the ash composition of both softwood pellets and sewage sludge pellets. It can be seen that sewage sludge ash is considerably richer in Si, Al, P and Fe, while softwood ash contains relevant amounts of Ca, K, Mg and Mn. It has to be considered that the low ash content of softwood ash means that even the elements that are contained much less in sewage sludge on a percentage basis, are more abundant in sewage sludge on a pure mass basis.

Table 3-2: Fuel ash composition of softwood and sewage sludge pellets.

Content wt% ash	**Softwood pellets [107]**	**Sewage sludge pellets [108]**
ZrO_2	0.02	0.06
SrO	0.47	0.11
PbO	0.02	0.01
As_2O_3	n.d.[a]	0.01
ZnO	0.59	0.29
CuO	0.11	0.11
NiO	0.02	0.02
Co_3O_4	0.01	n.d.
Fe_2O_3	0.91	8.50
MnO	5.44	0.07
Cr_2O_3	0.02	0.04
TiO_2	0.12	0.83
CaO	55.16	13.18
K_2O	13.40	1.29
Cl	1.20	0.14
SO_3	2.95	4.80
P_2O_5	3.07	14.85
SiO_2	6.62	33.23
Al_2O_3	1.63	17.59
MgO	8.35	3.52
Na_2O	1.07	1.37

n.d. not determined

3.3 Sewage Sludge Gasification Performance

Table 3-3 gives the product gas composition as well as other relevant gasification performance data for gasification with softwood pellets and sewage sludge pellets. Comparable heating values and product gas yields could be obtained, though the product gas yield is based on ash free fuel, so around double the amount of sewage sludge including ash is necessary to obtain the same product gas yield. Even though the H_2 content is lower during sewage sludge gasification, a higher H_2:CO ratio (2.6 compared to 1.9 for softwood gasification) could be obtained.

Table 3-3: Product gas composition determined for softwood and sewage sludge pellets gasification.

	Unit	Softwood pellets [34]	Sewage sludge pellets [108]
Water content	vol%	37	62
H_2	vol% db.	43.9	32.6
CO	vol% db.	22.6	12.6
CO_2	vol% db.	21.1	33.5
CH_4	vol% db.	9.7	10.8
C_2H_4	vol% db.	0.85	2.3
C_2H_6	vol% db.	0.05	0.11
N_2	vol% db.	1.27	2.1-2.2
Product gas yield	Nm^3_{db}. kg^{-1}_{daf} [a]	1.46	1.46
Product gas heating value	MJ Nm^3_{db}	11.6	10.53

[a] dry basis ash free

3.4 Additional Gas Cleaning

To upgrade the gas cleaning unit to be able to handle the increased impurity content of sewage sludge (compare Table 3-4) several approaches exist. Fly char and dust can be removed by filtration as described in chapter 2.2.2. Tars can be removed by biodiesel scrubbing as described in chapter 2.2.3. For further necessary fine gas cleaning also adsorption-based approaches seem to be promising. Beside tar also sulphuric impurities can be removed by this approach [51,109,110]. Ammonia, which is also present in high amounts cannot be removed in the biodiesel scrubber as it works with wood as fuel, but needs an own acidic scrubber to allow a proper removal.

Table 3-4: Comparison of product gas impurities determined for softwood and sewage sludge gasification.

	Unit	Softwood [107]	Sewage sludge pellets [108]
Fly char	g Nm^{-3} db.	1.2	1.1
Dust	g Nm^{-3} db.	0.4	8.1
GCMS tar (without BTEX)	g Nm^{-3} db.	4.5	16.3
Gravimetric tar	g Nm^{-3} db.	1.5	4.75
H_2S	g Nm^{-3}	0.3	21.3
NH_3	g Nm^{-3} db.	1.1	35.0

3.4.1 Experience from Sewage Sludge Incineration

At the moment, no long-term knowledge with sewage sludge gasification or fuels with comparably high amounts of ash and other impurities is available in literature. Though, some specific challenges are known from sewage incineration and will be further elaborated.

Table 3-5 depicts limit values as well as average operating values after gas cleaning for a sludge dewatering and combustion plant in Germany. Gas cleaning in sewage sludge incineration plants can be performed in several ways. Fly ash removal is mainly realised with either bag house filters or ESPs similar to ash removal during gasification (see Section 2.2.2). Cyclones can only remove fly ash insufficiently. Acid crude gas pollutants (e.g. HF, HCl, SO_2) can be removed by conditioned dry sorption with $Ca(OH)_2$, dry sorption with $NaHCO_3$ or acid and basic scrubbers. For the removal of Hg, it is necessary to first convert Hg^0 to Hg^{2+}. This is often achieved by S-doped activated carbon or other adsorbent agents. NO_x reduction and NH_3 separation are either achieved by SNCR or SCR. [111]

Table 3-5: Limits of emission parameters (2017, Germany) as well as average operating parameters of the sludge dewatering and combustion plant Sindlingen after gas cleaning [112].

	Unit	**Limit value**	**Average operating value**
SO_2	mg m^{-3}	50	3.8
NO_x	mg m^{-3}	200	161
CO	mg m^{-3}	50	6.6
Total carbon	mg m^{-3}	10	0.6
Dust	mg m^{-3}	10	0.7
HCl	mg m^{-3}	10	0.78
NH_3	mg m^{-3}	10	0.13
Hg	mg m^{-3}	0.03	0.0019
Dioxins/furans	ng TE[a] m^{-3}	0.1	0.0022

[a] toxicity equivalents

4 Case Study: Full process chain from sewage sludge to H_2

In this chapter a process chain to produce hydrogen from sewage sludge, based on DFB steam gasification, is presented. Mechanically dewatered sewage sludge is used as fuel and the produced hydrogen is delivered at 10 bar and a purity of 99.97% (based on molar fraction).

The scale of the process chain from sewage sludge to hydrogen is assumed to be 20 MW sewage sludge input with a water content from a weight fraction of 65%. The scale is considered in respect to the approximate sewage sludge production of the waste water treatment plant EBS Wien, in Vienna, Austria and the water content is a conservative value after mechanical dewatering. [113]

The proposed hydrogen production route is illustrated in Figure 4-1 and consists of six main unit operations, namely:

- sewage sludge dryer
- DFB steam gasification unit
- gas cleaning
- WGS unit
- PSA
- gas boiler

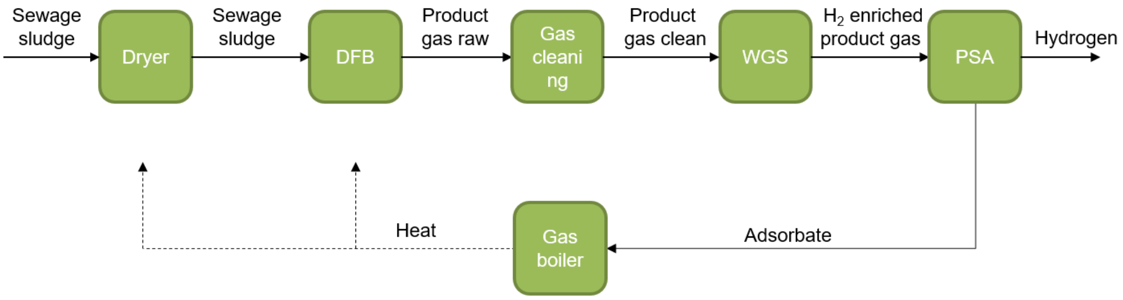

Figure 4-1: Simplified flowchart of the sewage sludge to hydrogen process, based on DFB steam gasification.

First, the mechanically dewatered sewage sludge is fed into a dryer to reduce the water content from a weight fraction of 65%, down to 20%, which is an optimum for fuels used in DFB steam gasification processes. Caused by the challenges of sewage sludge drying (see Section 3.2), this high amount of water has to be removed by thermal drying. The amount of heat needed for the thermal sewage sludge drying is significant: roughly 70 % of the LHV based energy content of the mechanically dewatered sewage sludge is needed. The dried sewage sludge is subsequently used as fuel in the DFB steam gasifier. In the DFB process (see Section 1.4) the sewage sludge is fed into the gasification reactor and turned into product gas. After gasification the generated raw product gas is loaded with undesired components like particles (char, ash, and bed material), higher organic substances (tar), and catalyst poisons (e.g. sulphur components). This issue of impurities was addressed in Section 2.2. Undesired components are discharged from the product gas stream. Especially the amount of ash and the sulphur content (compare Table 3-1) are significantly higher, compared to woody fuel and this increased load of impurities has to be addressed by gas cleaning.

Fundamental understanding of gas cleaning was generated over the last decades by the operation of commercial DFB gasification CHP plants. In these facilities, woody biomass was utilised in order to power gas engines, which requires less gas cleaning compared to catalytic syntheses steps. In this case study, additional gas cleaning, resulting on one hand from using sewage sludge as fuel and on the other hand required by the downstream synthesis units, is not considered. This issue has to be investigated first in small scale test, processing sewage sludge under real-world conditions, using a suitable DFB gasification unit to determine the amount of impurities to be expected.

The product gas predominantly consists of its four main components: H_2, CO, CH_4, and CO_2. In addition, depending on the process step in the overall process chain, there is a significant amount of steam present in the product gas. Downstream the gas cleaning section, the cleaned product gas is then subjected to a WGS unit, where the catalysed WGS reaction takes place: CO is converted into H_2 (see Subsection 2.3.1). This increases the hydrogen yield on one hand, and on the other hand the carbon monoxide content is significantly reduced, which allows a simplified downstream process in terms of hydrogen separation. Downstream the WGS unit the cleaned and H_2-enriched (and lean in CO respectively) product gas is further compressed and fed into a PSA, in order to separate the hydrogen from the remaining gas. The PSA unit separates a gas stream into two (or more) streams. On one hand the high-pressure stream, in this case the hydrogen in high purity, which does not adsorb on the adsorbent (e.g. activated carbon). This fact is a significant advantage, because the gas stream needs to be compressed only once, downstream the PSA unit. The pressure level is usually chosen according to the demands on the raffinate stream. One the other hand, the low-pressure adsorbate, in this case the CO_2- and CH_4-rich fraction. This fraction adsorbs on the adsorbent and is released during the regeneration cycle under lower pressure (see Subsection 2.4.1).

Depending on the primary objective and the framework condition of the overall process, the adsorbate can be utilised in different ways. If maximum H_2 production is of importance, the adsorbate can be recycled in order to maximise the hydrogen yield. In this case the gas stream has to be subjected to a steam reformer to convert the methane, and other minor substances, into additional carbon monoxide and hydrogen, which is than reintroduced downstream the WGS unit to the product gas. In the case of a gas recycling configuration, two main issues have to be addressed: first, carbon dioxide, as main unutilised component, has to be removed from the recycling loop. This can be realised by applying an amine scrubber downstream the PSA. Second, minor components in the product gas stream, are becoming more challenging, as they accumulate with gas recycling. So, this effect of accumulation has to be halted by avoidance of these substances, or by more efficient gas cleaning selective to these substances. Another option to utilise the adsorbate is to generate power via a gas engine, or to utilize it thermally if needed. This relation and the related concepts of gas utilization are discussed and illustrated in subsection 2.5.

In the present case, the adsorbate is utilized thermally to provide heat, which is needed in the overall process. This is caused by the high energy demand for sewage sludge drying in combination with the assumption of a self-sustaining characteristic. Compared to typical woody biomass, the energy demand for drying wood chips is much lower, so even under self-sustaining conditions, the adsorbate can be utilised via gas recycling. The needed thermal energy for the sewage sludge dryer is low-temperature heat. If external low-temperature heat, or steam, is available and can be introduced to the system, this will result in higher feasible gas recycling rates, which will result in an increased hydrogen yield.

To summarise, the DFB gasification technology in general is characterised by its self-sustaining nature since no additional fuel or heat is needed to power the process. This means, product gas, with its chemical energy content, which can be utilised in different ways, and heat can be generated. Thermal energy which is needed to enable the overall DFB gasification process is utilized internally. Heat is recovered from the generated product gas stream and from the flue gas stream. This recovered heat can be utilized to dry the fuel, to preheat air, and to generate the steam needed. For this particular process chain, converting sewage sludge with a water content of a weight fraction of 60%, is characterised as well by its self-sustaining nature. However, processing a fuel, containing as high amounts of water requires a significant amount of thermal energy. This heat is recovered from the two DFB steam gasification gas streams (product gas and flue gas stream). In addition, adsorbate is thermally utilized via a gas boiler, in order to provide enough heat. Figure 4-2 illustrates the energy distribution of the investigated sewage sludge to hydrogen process. It can be seen that 20 MW wet sewage sludge and 1.6 MW electricity are fed into the system to produce 8.4 MW of hydrogen. 13.2 MW are not utilized low temperature heat and losses in the process. This process chain can be described by a LHV based fuel to hydrogen efficiency of 42,1%, and an over-all efficiency of 38,9% respectively (taking the fuel and electricity consumption into account).

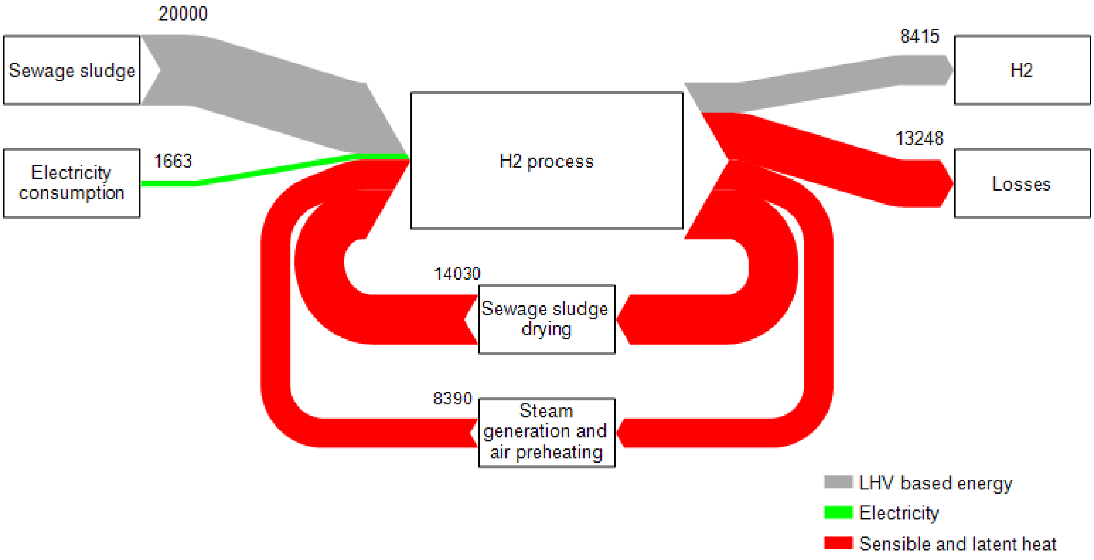

Figure 4-2: Energy distribution of the investigated sewage sludge to hydrogen process. All streams are given in kW.

Efficiencies and the hydrogen yield could be increased, if the sewage sludge fed to the system does not require thermal drying, or if external heat is provided to the hydrogen process. A comparison of this specific values for sewage sludge to bench mark values from wood chips is shown in Table 4-1. The bench mark process, a hydrogen process chain utilising wood chips, is characterised by the following differences: Wood chips are used as fuel, therefore less heat for drying is required. Adsorbate is utilised via gas recycling, this requires additional unit operations (steam reformer and amine scrubber). In addition, heat is provided from external sources to the process. All these distinctive factors result in different key figures, which can be seen as bench mark values. The cold gas efficiency describes the LHV based energy content in the product gas relative to the LHV based energy content in the fuel. It can be seen that gasification of sewage sludge is characterised by a lower cold gas efficiency as gasification of wood chips. This is mainly caused by two reasons: first the high ash content of the sewage sludge, which has to undergo the whole process of drying, gasification, and has to be removed from the product gas stream. Second, there is an increased amount of steam required in the DFB gasification process in order to ensure full conversion of this challenging fuel.

In general, caused by the configuration as single pass through (no gas recycling applied) the lower efficiencies, as indicated in Table 4-1, are expected and do not indicate low efficiencies in the single unit operations. LHV based fuel to hydrogen efficiency and over-all efficiency deviate less from each other in the case study, compared to the bench mark process. This is caused by the fact of the self-sustaining overall process in the case study and the additional heat introduced from external sources in the bench mark process.

Table 4-1: Comparison of key figures from case study to bench mark process.

Parameters	Bench mark – wood chip based process [114]	This case study - sewage sludge-based process
Cold gas efficiency	77.0%	69.6%
LHV based fuel to hydrogen efficiency	68.9%	42.1%
Over-all efficiency	60,0%	38.9%

The presented process chain from sewage sludge to hydrogen represents an innovative, first-of-its-kind approach, which has not been realised in this concept, so far. Therefore, the process and its units will be evaluated by the Technology readiness level (TRL). Incineration of sewage sludge in fluidised bed reactors is state of the art in thermal sewage sludge disposal. Utilizing sewage sludge as fuel for gasification and subsequent hydrogen production is a new approach. The single unit operations were assessed and are summarised in Table 4-2.

Sewage sludge drying and biomass drying are available on a commercial scale by several suppliers and are therefore TRL 9.

The DFB steam gasification of woody biomass can be assigned a TRL of 9 since it has reached commercialisation. DFB steam gasification systems were built several times, from different suppliers in MW-class scale and were operated for several 100,000 hours (e.g. 8 MW_{th} Güssing, Austria, or 14 MW_{th} Senden, Germany). DFB steam gasification of sewage sludge is currently at TRL 4. Processing sewage sludge in a DFB steam gasification system was so far only conducted in small scale (kW-class). At TU Wien a 100 kW_{th} DFB steam gasification unit successfully processed sewage sludge. However, testing was only performed in short-term operation. Sewage sludge incineration in fluidised beds is state of the art in sewage sludge disposal, which adds a certain security to the development of processing sewage sludge in a DFB steam gasification system. To progress in development, technology validation in industrially relevant environment needs to be conducted.

Gas cleaning for DFB steam gasification of woody biomass was already proven in commercial scale and is assigned a TRL of 9. The DFB steam gasification plant GoBiGas in Gothenburg, Sweden operated a full chain from wood and bark gasification to methanation including gas cleaning sufficient for synthesis applications [51]. Though, at the moment only insufficient data is available for the impurities to be expected from long-term sewage sludge DFB steam gasification. It is only to a certain degree possible to transfer the experience from sewage sludge incineration to sewage sludge gasification. Different impurity compositions and concentrations are to be expected due to the reducing atmosphere during gasification. As this equipment remains unspecified, no TRL can be assigned at this point. However, it is assumed, that a gas cleaning section can be developed to meet all downstream requirements based on future findings regarding impurities under real-world conditions of sewage sludge testing in a DFB steam gasification system. Under this assumption, the cleaned product gas can then be subjected to downstream synthesis unit operations without any limitations.

All unit operations downstream of gas cleaning (WGS, PSA, gas boiler) are commercially available and are TRL 9. Since the gas cleaning is dimensioned in a way to reduce the impurities to a sufficiently low level, it is possible to use commercially available downstream equipment used for other hydrogen production processes (e.g. coal gasification).

The full process chain from wood or sewage sludge will be evaluated regarding the TRL as well. This assessment takes the integrated system into account. So far H_2 production from biomass DFB steam gasification was only shown in long-term tests using real product gas in lab-scale equipment [76], therefore assigning a TRL of 5. For sewage sludge DFB steam gasification, the full process chain has so far not been realised in any scale. Only initial concepts (like the case study presented here) are available giving the full process chain a TRL of 2.

It is however necessary to consider further development of single unit operations, as well as the complete process chain. The development of process chains, based on sewage sludge gasification via DFB steam gasification technology, is an on-going research approach and new research results are expected in the near future. Chapter 5 gives an overview on planned an on-going research activity in this field of interest. Furthermore, it will be able to more quickly proceed towards higher TRLs compared to completely new technologies, since sufficient knowledge is available from related technologies like sewage sludge incineration, as well as biomass and coal gasification.

Table 4-2: TRL for the single unit operations needed as well as the full process chain for sewage sludge DFB steam gasification and woody biomass gasification as benchmark.

	Biomass DFB steam gasification	**Sewage sludge DFB steam gasification**
Dryer	TRL 9	TRL 9
DFB steam gasification	TRL 9	TRL 3
Standard gas cleaning	TRL 9	?
WGS unit	TRL 9	
PSA unit	TRL 9	
Gas boiler	TRL 9	
Full process chain	TRL 5	TRL 2

5 Planned Demonstration Plant for Sewage Sludge Gasification

A 1 MW demonstration scale DFB gasifier is currently erected at a site of Wien Energie. The purpose of this demonstration plant is long-term gasification of residuals. This demonstration plant is a major flagship project and has already been nominated in the SET-Plan (SET Plan Implementation Plan Action 8: Bioenergy and Renewable Fuels for Sustainable Transport, Project Güssing Gasifier LIQUID ADVANCED BIOFUELS – THERMOCHEMICAL: gasification and chemicals, 2018-2023) by the Austrian government. A rendering of the planned 1 MW demonstration plant is depicted in Figure 5-1.

Figure 5-1: Simulation of the 1 MW DFB steam gasifier at Simmeringer Haide. Simulation created by SMS Group.

State-of-the-art in commercial DFB gasification plants is the utilization of wood chips as main fuel. The main aim of this demonstration plant is shifting the possible fuel range from woody biomass to more difficult fuels (biogenic residues, wastes from different sources as well as mixtures of those). Details of the gasifier construction (e.g. feeding system) as well as new process steps (e.g. for gas cleaning) were considered during the engineering phase. The considered details were based on the broad knowledge base of TU Wien. Comprehensive investigations of TU Wien in a scale of 100 kWth have created a solid base for the engineering of this demonstration plant.

The demonstration gasifier represents an important, probably the most important, step on the way to an industrial scale plant for the utilization of difficult fuels (e.g. sewage sludge) for gasification and downstream utilization of the cleaned product gas for applications like Fischer-Tropsch synthesis to obtain high quality products for chemical production as well as advanced biofuels for transport and aviation. A further aim is the demonstration of the whole process chain in pilot scale from difficult fuels to product gas via product gas clean-up and finally the production of bio-based FT high quality products via FTS. The demonstration gasifier will furthermore be the basis for other product routes like methanation and H_2 separation.

Based on the experience of more than 10 years of operation the DFB gasification technology will be adapted for more fuel flexibility and to enable the utilization of more difficult and cheaper fuels to significantly improve the economics of the DFB process. The demonstration plant will be developed and engineered by SMS Group. The broad knowledge base of SMS group gives the opportunity to develop a pilot unit including the newest information in the field of difficult fuel handling (e.g. fuel feeding) and to obtain an upscaling of the forth DFB gasifier generation from the TU Wien for aiming on long-term experiments for a number of days (up to 1000 h) to study e.g. the ash accumulation behaviour.

After successful commissioning and start-up phase the first long-term experiments will be conducted. The first long-term experiments will be performed with woody biomass to establish a functioning operation. Then biogenic residues will be selected and investigated in detail. The long-term investigations are aiming on the study of the gasification behaviour of biogenic residues and wastes compared to wood chips. Parameters such as temperatures, pressures, volumetric or mass flows, gas compositions etc. are measured on-line during the test runs. Samples from gases as well as fuel and ashes are taken for further analyses in the laboratory. Obtained measurements give a comprehensive overview of the gasification process using difficult fuels. Important for the downstream utilization of the cleaned product gas are impurities like N- S- and Cl. Extensive analyses will prove the reliability of the used gas cleaning section even with the use of e.g. sewage sludge. Finally, the complete process chain from waste to value, coming from difficult fuels to various gaseous and liquid products, is demonstrated.

Based on results obtained a difficult fuel is chosen for long-term operation over several days up to one week. During this operation, valuable findings in relation to accumulation behaviour, ash related difficulties as well as the opportunity of phosphorous recycling are planned to be investigated. Furthermore, the complete process chain, from waste to value, is envisaged to be demonstrated via the usage of the FT pilot unit (Barrel per day plant) or other downstream synthetic processes (e.g. methanation). The demonstration will show the capability of the pilot gas cleaning section to handle the increased share of impurities and possible catalyst poisons (e.g. sulphur) and to enable long-term operation of a FT unit using product gas based from difficult fuel gasification. The FT produces high quality fuel for the transport sector (e.g. kerosene for aviation) as well as chemicals for industry. Other possible routes for synthesis of marketable products are methanation, hydrogen production or production of mixed alcohols.

Obtained experimental data are used in a simulation program to calculate further information for the judgement of the operation performance. From the simulation additional data (which could not be measured), energetic efficiencies of single steps and the overall plant, separation efficiencies for cleaning steps, etc. are obtained. This simulation program will be sharpened, improved, supplemented, and finally calibrated by the experimental data. In the final stage of the project the simulation tool shall be used for scale up purposes for thermal residue gasification.

5.1 Fischer Tropsch Synthesis

Renewable H_2 is suitable to provide energy in a wide variety of applications. Though, in the transport sector (especially regarding aviation and maritime) the use of liquid fuels is indispensable at least in the near future. By using biofuels, it is possible to also decarbonise this sector. An especially promising advanced biofuel[1] can be obtained via FTS which produces a liquid that can be used in engines without modification. It therefore has a high potential to help fulfilling the EU directives, which have the aim to replace fossil fuels with advanced biofuels. It is a highly exothermic (chain propagation) reaction (-170 kJ/mol CO converted) that converts H_2 and CO into hydrocarbons with a chain length from methane (C1) to molecules with over 100 carbon atoms with methylene ($-CH_2-$) groups acting as the monomer. The product range consists mainly of n-paraffins and a low proportion of linear alpha olefins when using Co-based catalyst. The proportion of linear alpha olefins increases significantly using Fe-based catalysts. The process conditions that significantly affect hydrocarbon formation are temperature, pressure, reactant partial pressure and residence time. The CO-conversion to hydrocarbons is increased by high pressure.

In general, the FTS can be distinguished into HTFT and LTFT (HT and LT FTS). Depending on the catalyst and desired products, the temperature of the HTFT synthesis is between 300 and 375°C and for LTFT between 200 and 250°C. The LTFT is suitable for the production of long-chain linear hydrocarbons (diesel and wax). This can be attributed to the processes on the catalyst surface at which adsorption and desorption take place. In slurry bubble column reactors (SBCR) the catalyst particles are suspended in liquid waxes. The basic principle of this technology is shown in Figure 5-2.

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[1] Advanced biofuels are produced from residues and therefore do not compete with food production.

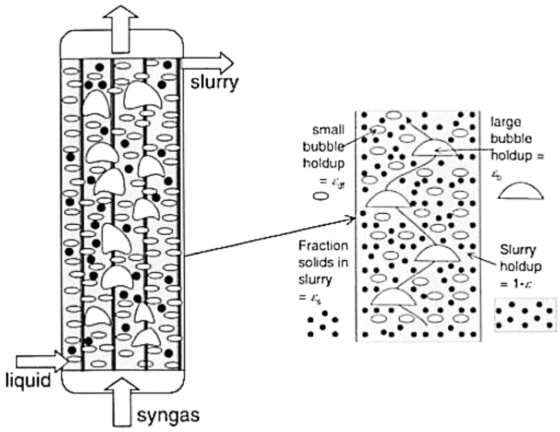

Figure 5-2: Concept design of the FTS technology

Product gas is injected into the reactor at the bottom by using a gas distributor and gas bubbles rise up and react on the catalyst surface. At the top of the reactor the gaseous product can be withdrawn, while the liquid products remain in the reactor. Liquid hydrocarbons are withdrawn at the side of the reactor. SBCR has various advantages over other reactor designs (i.e. fixed bed reactors/multi-tubular reactors and fluidized bed reactors) for FTS. SBCR lead to higher conversions per pass due to excellent heat dissipation, consist of a simple reactor design that allows it to replace catalyst without reactor shutdown and it is possible to convert the process heat into process steam or extra heat produced [115]. The catalyst is also exposed to less abrasion compared to fluidized bed reactors and the use of smaller catalyst particles excludes the intraparticle mass transfer limitations [115].

6 Conclusion

DFB steam gasification of sewage sludge is a suitable approach to produce H_2 from a waste stream. Compared to most other commercial processes to H_2, sewage sludge gasification is not based on fossil fuels, therefore being a carbon-neutral alternative for H_2 production. Compared to electrolysis from renewable electricity (photovoltaic, wind power) sewage sludge gasification can be operated continuously and is not dependent on outer influences ensuring the supply of H_2.

The case study for sewage sludge gasification presented in this report showed over-all efficiencies of nearly 39%. This value can be seen as basis that can be easily improved by various measures like gas recycling and external heat supply. Due to the yet unknown concentration of impurities a single pass through was chosen to give further securities regarding the operability of the full process chain. Most of the unit operations chosen for sewage sludge gasification (especially all product gas upgrading and hydrogen separation units) are already commercially available speeding up market readiness of the full process chain by minimising the uncertainties.

Gas cleaning is the most uncertain aspect of DFB steam gasification of sewage sludge which can at this moment not be predicted correctly. As soon as sufficient long-term data of sewage sludge gasification is available it will be possible to draw from the experience from sewage sludge incineration and conventional gasification (coal and biomass gasification) to select an appropriate gas cleaning set-up. While several unit operations can be assigned a TRL of 9 (dryer, WGS, PSA, gas boiler) sewage sludge gasification has so far only been performed in lab-scale (TRL 3) and the full process chain is at TRL 2. Due to vast existing knowledge regarding all unit operations it will be possible to quickly transition to higher TRLs.

With the currently erected 1 MW plant at Wien Energie it will be possible to obtain the data needed to raise sewage sludge gasification (and after the selection of necessary gas cleaning also the full process chain) directly to TRL 6. While previous DFB steam gasification demonstration and commercial plants (e.g. Güssing, Austria) proved the technology for easy fuels (wood, bark) and low-level utilisation (heat, power) the newly erected 1 MW plant will be able to prove possible operation with drastically more challenging fuels like sewage sludge while also obtaining more valuable products (e.g. H_2, FT diesel).

7 References

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8 Annex

8.1 Abbreviations

aMDEA	activated MDEA
ATR	autothermal reforming
BTEX	benzene, toluene, ethylbenzene, xylene
CPO	catalytic partial oxidation
daf	dry basis ash free
db.	dry basis
DEA	diethanolamine
DFB	dual fluidised bed
ESP	electrostatic precipitators
FT	Fischer Tropsch
FTS	Fischer Tropsch synthesis
HT	high temperature
HTFT	high temperature Fischer Tropsch
LT	low temperature
LTFT	low temperature Fischer Tropsch
MDEA	methyldiethanolamine
MEA	monoethanolamine
nd	not detected
PCDD	polychlorinated dibenzodioxins
PCDF	polychlorinated dibenzofurans
PEM	proton exchange membrane
POX	Non-catalytic partial oxidation
PSA	pressure swing adsorption
RME	rapeseed oil methyl ester
SBCR	slurry bubble column reactor
SER	sorption enhanced reforming
SNG	synthetic natural gas
SR	steam reforming
TE	toxicity equivalent
TRL	technology readiness level
WEP	Wet ESP
WGS	water gas shift

8.2 List of figures

8.3 List of tables