Biomass Gasification – Conversion of Forest Residues into Heat, Electricity and Base Chemicals

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Abstract

Gasification of biomass can play a major role in the future’s energy system as a source of renewable electricity, process heat, fuels, and chemicals. The composition of wood poses some constraints for the operation: below a certain limit of gasification agent, parts of the carbon stays solid and must be considered as an efficiency loss. Thermodynamic calculations allow the determination of this solid carbon boundary and give hints for the process optimization. Several examples for gasifiers, gas cleaning approaches - primarily focusing on tar as the main operating difficulty and dust - and producer gas applications are given and evaluated, including some aspects of scale. Finally, the great potential for the production of transportation fuels and base chemicals from renewable resources is discussed. Possible products are methane, methanol, dimethyl ether, gasoline, Fischer-Tropsch liquids and mixed alcohols. If installations for the gasification of woody biomass with chemicals production are combined with water electrolysis from renewable electricity, the carbon conversion efficiency of the process will be raised to 100% or the combined PBtX-installation (Power and Biomass to X) will offer significant balancing power to the electricity transmission network.

Keywords: Gasification; Gas cleaning; Combined heat and power; Power-to-X

Introduction

Wood gasification is currently only commercially viable in a few countries worldwide, e.g. India, China and some countries in Europe independent of the specific choice of the final producer gas application. Some small-scale applications (predominantly for combined heat and power production) have shown long-term economic viability, sometimes even without subsidies. Larger scale installations with higher capacities are only operated to demonstrate the technical feasibility of the technology and after the phase-out of initial subsidies they are shut down, mothballed or dismantled. Examples of such unpleasant development are the Värnamo gasifier (Bengtsson 2011), the Güssing gasifier (meinbezirk.at 2017) and the GoBiGas-project for the production of substitute natural gas SNG from forestry residues.

The potential for reducing the carbon dioxide (CO₂) emissions during electricity production by biomass gasification is huge: the specific CO₂ emissions of wood gasification followed by internal combustion engine lies in the range of 30–70 g kWh⁻¹ (Schulzke
The respective emissions from the German electricity mix (including the steadily increasing share of renewable electricity) dropped in 2017, following first estimations, to 489 g kWh\textsuperscript{−1} (Icha and Kuhs 2018). For comparison, the emissions from coal fired power stations are much higher. Modern power stations based on hard coal emit approximately 755 g kWh\textsuperscript{−1} (Gräbner et al. 2010), while power stations fired with lignite emit about 855 g kWh\textsuperscript{−1} (Andersson and Johansson 2006).

Even with this high potential for the reduction of greenhouse gas emissions there are generally possible alternatives for the production of electricity with negligible carbon footprint such as wind turbines and solar power; however, they also have their respective drawbacks, e.g. fluctuating production. Though, for the production of chemicals in the future there will be no alternative carbon source coming from renewable resources than biomass. While specialty chemicals might be effectively produced by aerobic or anaerobic fermentation/digestion processes, large scale bulk chemicals can only be provided by gasification followed by synthesis gas chemistry.

Due to the high potential for CO\textsubscript{2} emission reduction and the great potential to produce fuels and chemicals from renewable resources in large quantities biomass gasification will gain increasing importance in future. A strong appeal for a general movement towards biomass utilization for energy and chemicals production was enunciated by Adam Brown, a senior energy analyst at International Energy Agency, Paris, at the closing ceremony of the 26\textsuperscript{th} European Biomass Conference in Copenhagen. He stated: “There are many mature technologies available. We need complex technologies, especially in biofuels sector. But we need to start implementing these (mature) technologies now!” (Brown 2018).

The aim of this review is to recall the general principles and understanding of gasification processes, to illustrate its potential through successful examples, and to avoid the replication of past mistakes.

**Fundamentals of gasification**

The thermochemical conversion of woody biomass into a gaseous energy carrier is a process involving three main steps – drying, pyrolysis and gasification. In some reactor configurations, a fourth step – combustion – is also integrated, but only partially, as full combustion would result in a flue gas without any chemical energy content. Fig. 1 shows how
these basic processes take place with increasing temperature, and the main products released during these steps.

At low temperatures between ambient and approximately 200 °C the biomass is dried, firstly releasing the free, unbound water from the interstice between the cells. The water bound inside the cells is liberated to the surrounding gas atmosphere during the upper portion of this temperature range.

With a further temperature increase the wooden material composed of the natural polymers hemicellulose, cellulose and lignin is thermally decomposed to

- light gases (carbon monoxide (CO), CO₂, methane (CH₄), steam (H₂O), etc.),
- tar (heavy organics like polyaromatic hydrocarbons) and
- char.

These first two steps are induced by heat alone and would take place even in the absence of any externally added reactant. The third basic process called gasification transfers the residual char formed by the pyrolysis step into the gas phase by converting it mainly into CO. This final chemical conversion step requires the presence of an oxidizing agent like air, oxygen, steam or CO₂.

Fig. 1. Processes in thermochemical conversion of lignocellulosic biomass according to Kaltschmitt and Baumbach (2001)
For the conversion of wood (and more generally any carbon containing feedstock like lignocellulosic or plastic material) into a gaseous energy carrier many different reactors were designed, which can be generally divided into three main categories: fixed bed, fluidized bed and entrained flow reactors with increasing engineering complexity. A sophisticated description of the main characteristics of these reactor types is given for instance by Hofbauer et al. (2009). Therefore, the different reactor types are discussed only briefly here.

Fig. 2 depicts two out of the three main reactor setups – fixed bed and fluidized bed – with two typical implementations each. For the sake of simplicity air is denoted as the gasification agent, but others are generally possible for the same reactor design.

**fixed bed gasifiers**
- drying zone
- pyrolysis zone
- reduction zone
- oxidation zone

**fluidized bed gasifiers**
- fluidized bed
- freeboard

![Fig. 2. Typical reactor types for biomass gasification](image)

In ideal fixed bed reactors, that are actually moving beds as the solid fuel moves slowly from the feed supply at the top to the ash removal at the bottom, well-defined zones exist, in which the basic conversion steps take place spatially separated. The most simple reactor design is the so-called downdraft gasifier, where a solid fuel and a gasifying agent (for this type of reactor nearly always air) move in co-current flow from the top downwards to the bottom, where ash and the producer gas are withdrawn. In the upmost section the fuel particles are dried followed by heat induced pyrolysis. In the third zone the mixture of evolved gases and air ignites and releases heat of combustion by oxidizing part of the combustible gases, because these homogeneous gas phase reactions are much faster than direct combustion of char. Additionally, the tar compounds released during pyrolysis are partly combusted by air and partly reformed.
by steam and CO$_2$ in this very hot oxidation zone. Subsequently in the reduction zone, the CO$_2$ and steam produced in the oxidation and drying zones are reduced by the residual solid carbon char giving CO and hydrogen. This very simple setup implies some operational difficulties, which led to the well-accepted development of a throated reactor. The throat is installed in the region of the reactor where the oxidation zone is intended to occur. The majority of the oxidizing air is introduced to the reactor in this area of reduced cross section instead of the top of the reactor. But even with this improvement, the burnout of the fuel leaving the reduction zone is incomplete, and the “ash” withdrawn from a co-current fixed bed gasifier usually is made up of unliberated carbon in the range of 50 wt%. In summary, the main characteristics are poor fuel burnout, and at least the potential of very low tar content in the producer gas. The main difficulty in downdraft gasifier operation is to achieve a uniform distribution of the gasifying air over the cross section. Therefore, these types of gasifier require very uniform feedstock particles (very narrow particle size distribution, preferably rectangular shape around 30 mm x 30 mm x 50 mm), which leads to the necessity of high feedstock pretreatment (Hofbauer et al. 2009).

In counter-current gasifiers, also referred to as updraft gasifiers, the two lowest zones are interchanged in comparison to co-current gasifiers. The reason is that in counter-current gasifiers the air enters at the bottom, where the ash is withdrawn from the grate. The air oxidizes the remaining carbon in the fuel, and as no combustible gases are present in the oxidation zone of this reactor type (which would compete for the oxidant and react with faster kinetics), the char can be converted completely. The flue gases rise to the reduction zone and the CO$_2$ contained in these flue gases converts parts of the char produced in pyrolysis to CO. This gas mixes with the primary vapors emerging from the pyrolysis and (further up) with the steam evaporated from the fuel in the drying zone. As the temperature consistently drops from the bottom to the top, the tar compounds released in the pyrolysis zone have no chance to decompose or react until they leave the reactor at the top. Only very heavy compounds condense on the particle surface within the drying zone and are circulated back to pyrolysis. The main characteristics of this reactor type are very good burnout of the fuel and very high tar content of the producer gas. This type of gasifier design is quite tolerant regarding fuel quality. A wide range of particle sizes (typically 20 mm to 200 mm) can be processed in the same reactor and even high moisture content can be accepted (Hofbauer et al. 2009).

In fluidized beds the majority of the solid inventory – more than 90 wt% – is made of bed material in contrast to fixed beds, where only the wooden fuel is present as solid. The bed material mainly acts as heat transfer agent, which has much higher heat capacity than the gases.
The gasification agent together with the evolving vapors and gases from the basic conversion steps must be flowing upwards fast enough to keep the bed material in suspension. In bubbling fluidized beds the bed is more or less expanded, but the gas velocity is not high enough to transport the particles out of the reactor. Above the fluidized bed there is a distinct freeboard, where only homogeneous gas phase reactions take place. On the contrary, in circulating fluidized beds the gas velocity is so high that the bed particles are blown out of the reactor as in pneumatic transport and they must be separated from the producer gas in a cyclone and recycled to the reactor. To prevent the gases from entering the particle recirculation line a loop seal must be installed, usually in the form of a siphon. In such a reactor there is no distinct freeboard but at the bottom a more dense area and an area with lower particle concentration above with a smooth transition in between.

Due to the high movement of the bed particles, fluidized beds reveal a typical behavior of an ideally stirred tank reactor with virtually no temperature distribution within the fluidized bed. Only in bubbling fluidized beds there is a noticeable temperature drop from the fluidized bed to the freeboard. Due to the stirred tank characteristic of the fluidized bed there are no distinct zones where the basic conversion steps occur spatially separated. They take place in parallel everywhere in the reactor, while at a single fuel particle they still occur consecutively from drying over pyrolysis to gasification. Due to the well-mixed gas phase and the uniformly high temperature, the primary tar compounds produced during pyrolysis can on one side react to synthesis gas constituents like carbon monoxide, methane or ethylene, but on the other side also form secondary and tertiary tar compounds of higher molecular weight and more condensed aromatic rings. This leads to a medium tar level and in comparison to fixed bed reactors different composition of tar compounds. The particle size requirements of fluidized bed reactors is the lowest among the discussed reactor types. The maximum size is determined by the gas flow velocity, as the fuel particles must be fluidized (typically below 70 mm). Fine particles can be present in the fuel as well (Hofbauer et al. 2009), but only if the fuel is introduced into the lower part of the fluidized bed. Otherwise, if introduced from the top, the small fuel particles would be blown out of the reactor without enough residence time to be completely converted.

The gasifier reactors shown in Fig. 2 are typically used in commercial applications for wood gasification from left (co-current fixed bed) to right (circulating fluidized bed) with increasing plant capacity from a few kW of fuel input to some hundreds of MW. Not shown in this figure is the third reactor type generally applicable to gasification – the entrained flow reactor. This reactor is known from coal or petcoke gasification in very large scale applications.
(several hundreds of MW) and applies average fuel particle sizes of below 100 µm (Chen et al. 2012). Currently there is no commercial biomass gasifier of this type operating. For such large capacity, biomass logistics becomes an open issue, because biomass with comparatively low volumetric energy density must be transported over a long distance. To overcome this problem several approaches are discussed, commonly based on volumetric energy densification in a decentralized first conversion step followed by transportation of densified intermediate to the large scale entrained flow gasifier. Examples of such approaches are the BioTfuel project for woody biomass (Viguié et al. 2013), which applies torrefaction and pelletization as densification step, and the bioliq® process for agricultural residues (Dahmen et al. 2012), which uses fast pyrolysis to produce a slurry of pyrolysis oil and char as the transportable intermediate.

Regarding economically necessary scale of entrained flow gasifiers there are some recent investigations and economic estimations performed at Technical University Munich (Tremel et al. 2013, Briesemeister et al. 2017, Kremling et al. 2017). Their results indicate that such gasifiers might become already economically competitive in a fuel capacity range of around several MW, the size of which is presently applied only in research installations.

Apart from reactor type gasification can also be characterized by the gasification agent that is used in the process. As all the process steps – heating up, drying, pyrolysis and gasification – are endothermic reactions, the necessary heat must be somehow supplied to the reactor. This is connected to the gasification agent applied. If oxygen or air (which contains oxygen as the active component) is used, then part of the combustible gaseous products, and potentially part of the residual char, is burnt inside the gasifier releasing heat to drive the basic gasification steps. The more oxygen is fed to the gasifier, the more heat is released inside and consequently the higher the operating temperature becomes, which increases the reaction kinetics. On the other hand as more oxygen is fed to the reactor, more valuable products are burnt, consequently lowering the chemical power contained in the producer gas. More details of these dependencies are described in the following paragraph. By the use of oxygen or oxygen containing gases as the gasifying agent, the heat released by combustion is equal to the heat consumption for gasification processes directly inside the gasifier itself. This kind of operation is called autothermal.

The main purpose of the gasifying agent is the conversion of the remaining solid carbon after the release of the volatiles in drying and pyrolysis. CO₂ and steam can be used for that purpose following the well-known Boudouard-Equilibrium (Eq. 1) and the heterogeneous water gas reaction (Eq. 2).
\[
\begin{align*}
C + CO_2 & \rightleftharpoons 2 CO \\
C + H_2O & \rightleftharpoons CO + H_2
\end{align*}
\]

Both reactions are endothermic in the carbon consuming direction. Therefore gasifiers operated with either CO\(_2\) or steam as the gasifying agent need an external heat supply to cover the heat demand by the basic steps and the char conversion. If the heat is supplied from outside of the gasifier, the process is called allothermal. As the amount of the gasifying agent fed to the reactor and the operating temperature are not directly linked in this type of operation there is an additional degree of freedom in comparison to autothermal gasification. Heat supply to the allothermal gasification system can be very diverse in principal, although in the majority of research installations and in all demonstration and commercial units a heat transfer material circulates between the gasifier and a furnace, where it is heated by combustion of residual char, fresh biomass and other additional (biogenic) fuel or a mixture of those possibilities. But with increasing availability of renewable electricity from wind, photovoltaics or water, electrical resistance heaters become an interesting option and in the past even waste heat from nuclear power stations was discussed as a heat source for gasifiers (Verfondern and Lensa 2010).

The impact of the gasifying agent on the average composition of the producer gas is described in detail elsewhere (Hofbauer 2007, Hofbauer et al. 2009). For the understanding of the following paragraphs a broad summary is sufficient. Fig. 3 gives a comparison of average gas composition for an air blown circulating fluidized bed gasifier (left part, operated at Fraunhofer UMSICHT in Germany; diagram taken from Ising et al. 2004) and a steam blown bubbling fluidized bed gasifier (right part, Gasifier operated at Güssing, Austria; diagram taken from Pfeifer et al. 2007). This figure shows that air gasification results in a very lean gas with up to 50 vol% of nitrogen, which can run a gas engine or gas turbine for combined heat and power production, but it is not suitable for synthesis gas chemistry (nitrogen cannot be separated from CO in an efficient manner). The lower heating value \(H_i\) of such gases is in the range of 5 MJ m\(^{-3}\) at standard temperature and pressure (stp).

In comparison, producer gases from steam gasification are virtually free of nitrogen and exhibit a lower heating value of about \(H_i \approx 9.2\) MJ m\(^{-3}\) (stp) on wet basis. If the water vapor is removed, e.g. simply by condensation, the lower heating value increases to approximately \(H_i \approx 12.5\) MJ m\(^{-3}\) (stp). Such producer gas can be used in gas engines or turbines for combined heat and power production as producer gases from air gasification, but they are also suitable for utilization in synthesis gas chemistry if first subjected to gas cleaning and conditioning.
The use of CO$_2$ as gasifying agent would also lead to a producer gas virtually free of nitrogen and exhibiting a similar lower heating value as with steam gasification. But as reaction rates in CO$_2$ gasification are much lower than with any other medium discussed here, this gas presently is not used in any demonstration or commercial gasifier as it would lead to much larger reactors due to the longer residence times required. But for the future use this is an interesting option, because unreacted CO$_2$ from the chemical synthesis could be recycled in the process and its application does not require heat of evaporation like steam production.

If pure oxygen is used in an autothermal process instead of air, the lower heating value is again in a similar range like with steam gasification, but the carbon dioxide content of the producer gas is significantly higher due to solid carbon and CO combustion within the gasifier (see Table 1).

![Fig. 3. Comparison of representative gas composition depending on gasification agent (Ising et al. 2004 (left), Pfeifer et al. 2007 (right))](image)

<table>
<thead>
<tr>
<th>Gasifying agent</th>
<th>UMSICHT$^a$</th>
<th>Güssing$^b$</th>
<th>Chrisgas$^c$</th>
<th>CUTEC$^{d,e}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasifying agent</td>
<td>Air</td>
<td>Steam</td>
<td>Oxygen (+Steam)</td>
<td>Oxygen (+Steam)</td>
</tr>
<tr>
<td>Pressure</td>
<td>Atmospheric</td>
<td>Atmospheric</td>
<td>10-15 bar</td>
<td>Atmospheric</td>
</tr>
<tr>
<td>H$_2$</td>
<td>14</td>
<td>26</td>
<td>11.8</td>
<td>32</td>
</tr>
<tr>
<td>CO</td>
<td>16</td>
<td>15.6</td>
<td>11.9</td>
<td>27</td>
</tr>
</tbody>
</table>
The conversion of woody biomass in an air-blown gasifier involves many different reactions that describe the basic conversion steps of drying, pyrolysis and gasification. The network of reactions comprises of a primary reaction of “biomass decomposition” followed by a set of homogeneous gas phase reactions (seven individual reactions) and a set of heterogeneous gas-solid reactions (five individual reactions), resulting in total in a set of at least 13 consecutive and parallel reactions (Ising 2002). For the calculation of the chemical equilibrium two different approaches exist: the stoichiometric and the non-stoichiometric approach. Both approaches start off with the identification of possible components being present in equilibrium. Within the stoichiometric approach a network of independent reactions has to be identified and the equilibrium constants as a function of temperature, pressure and composition for all these reactions must be determined and solved together with the mass and energy balances. For the non-stoichiometric approach no specific reaction network has to be identified. If all thermodynamic data for the species identified as being present in equilibrium are available, the equilibrium composition can be calculated by minimizing the Gibb’s energy of the system together with the material and energy balances. Done properly, both approaches give identical results (Prins et al. 2003, Prins 2005) and the method can be chosen based on convenience. Many studies on thermodynamics of the gasification process are reported in the literature (e.g. Desrosiers 1981, Huang and Ramaswamy 2009, Ahmed et al. 2014, Chaiwatanodom 2014, Mondal and Ghosh 2015), applied to the different reactor types and not restricted to biomass, as Xu et al. (2017) published a study on thermodynamic equilibrium in municipal solid waste gasification. The most debatable point in the studies is the “correct” choice of the temperature applied to calculate the equilibrium. For entrained flow and fluidized
bed gasifiers the choice of temperature is straightforward, as in entrained flow the temperature
at the entry of the quench determines the equilibrium and in fluidized beds there is more or less
a uniform temperature throughout the reactor. Only in fixed bed gasifiers there are temperature
profiles from room temperature up to potentially 1,200 °C and more, and here the choice of
temperature is not so easy. For the sake of simplicity the following section gives the results for
fluidized beds, but with some degree of abstraction they are – at least in their basic messages –
also applicable for fixed bed reactors.

The following results were calculated for an adiabatic fluidized bed reactor with air as
gasification agent. Adiabatic conditions were chosen to present results which are generally
applicable. Heat losses that obviously occur in real reactors can easily be implemented to the
model, but they are reactor specific as they vary with the reactor geometry (especially the
surface-volume-ratio). The general effects, which were derived from the adiabatic calculations,
would not change with the consideration of reactor-specific heat losses.

Fuel was represented by an average composition of wood comprising of 50 wt% carbon,
6 wt% hydrogen and 44 wt% oxygen on dry and ash-free basis (Perry et al. 1984), resulting in
a representative molecular formula of CH$_{1.44}$O$_{0.66}$. The non-stoichiometric approach for
calculating the equilibrium by minimizing the Gibb’s free energy of the system was used. The
following species were considered as being possibly present in the equilibrium: solid carbon
C(s), carbon monoxide CO, carbon dioxide CO$_2$, hydrogen H$_2$, steam H$_2$O, oxygen O$_2$, nitrogen
N$_2$, argon Ar, methane CH$_4$, ethylene C$_2$H$_4$, ethane C$_2$H$_6$, benzene C$_6$H$_6$, phenol C$_6$H$_5$OH and
naphthalene C$_{10}$H$_8$. The method applied is described in detail in Mevissen et al. (2009) and
Schulzke and Unger (2011). All calculations presented hereafter are based on a fuel feed rate
of 1 t h$^{-1}$ of dry, ash-free wood.

The main parameter varied in the calculations is the equivalence ratio $ER$. This
parameter is based on the stoichiometric oxygen demand for complete combustion, which can
be calculated from Eq. 3.

$$\text{CH}_1.44\text{O}_{0.66} + 1.03 \text{O}_2 \rightleftharpoons \text{CO}_2 + 0.72 \text{H}_2\text{O} \quad (3)$$

With an assumed composition of dry air of 21 vol% O$_2$, 78 vol% of N$_2$ and 1 vol% Ar
the stoichiometric air demand for complete combustion is determined as 5.914 kg air per kg
dry, ash-free wood. The equivalence ratio is defined as ratio of air actually used for gasification
to the stoichiometric air demand. An $ER$ equal to 1 represents stoichiometric combustion and an $ER$ of 0 implies pyrolysis only. Gasification lies somewhere in between these limits.

The most crucial result of thermodynamic equilibrium calculations is that there are certain operating conditions under which not all carbon present in the fuel can be converted into gaseous components and a solid carbon residue leaves the reactor. This residual carbon will remain in the solid phase leaving the reactor, if the equivalence ratio is below a certain value. As can be seen from Fig. 4, the amount of residual char is decreasing with increasing equivalence ratio and it totally disappears at higher values. The lowest equivalence ratio, at which no solid carbon is present in the thermodynamic equilibrium, is called “solid carbon boundary” (Desrosiers 1981). This value slightly depends on other parameters like air inlet temperature $AIT$ (the temperature at which the air enters the gasifier) and the water content $WC$ of the wood fuel. For any application of gasification the knowledge about the location of this solid carbon boundary is important, because the behavior of the gasifier in terms of gas composition and response to changes especially in the air supply is significantly different above and below this characteristic point.

![Fig. 4. Char formation as a function of equivalence ratio (Schulzke and Unger 2011)](image)

As air was used as gasifying agent in the thermodynamic equilibrium calculations of autothermal fuel conversion, there is a clear dependency of the operating temperature of the gasifier – called adiabatic flame temperature $AFT$ – and the air-fuel-ratio expressed as the
equivalence ratio $ER$. The calculated values for the adiabatic flame temperature around and especially below the solid carbon boundary are far too low to achieve chemical equilibrium in a real reactor. Especially, more methane would be formed than calculated from chemical equilibrium at such low temperature and the amount of tars formed would increase dramatically with decreasing temperature in real applications. Nevertheless, the reasoning that can be deduced from these theoretical results gives valuable hints for proper gasifier operation and therefore it is worth closer consideration. In addition, it should always be kept in mind that higher operating temperature allows better approach to equilibrium and therefore turn these results more practical.

The aforementioned $AFT-ER$-dependency is depicted in Fig. 5 with two additional parameters, the fuel water content $WC$ and the air inlet temperature $AIT$. It can be seen clearly that the $AFT$ is rising with increasing air supply and the solid carbon boundary is marked by the distinct bend in each curve. As mentioned above, the behavior of the reactor is different below and above this point. For values of the $ER$ below the solid carbon boundary the majority of additional heat released by combustion reactions due to larger air supply with increasing $ER$ is consumed by endothermic conversion of solid carbon by Boudouard equilibrium (Eq. 1) and heterogeneous water gas reaction (Eq. 2), resulting in a moderate increase of reactor temperature. Above the solid carbon boundary there is no more carbon available for endothermic conversion and hence all the additional heat released by combustion of gaseous combustible components directly leads to rampant temperature increase. The general behavior is the same for all parameters, but with increasing water content $WC$ the overall temperature in the reactor becomes lower due to the necessary heat to evaporate the additional water introduced to the reactor. In addition, the bend in the curve at the solid carbon boundary becomes less pronounced, but the carbon boundary stays at the same $ER$ for all $WC$ (see Fig. 5a). On the contrary, with increasing air inlet temperature for a fixed water content, the solid carbon boundary moves to lower equivalence ratios (see Fig. 5b). Below the solid carbon boundary the $AFT$ is nearly not affected by the additional heat supplied to the gasifier as it is completely compensated by higher conversion of solid carbon to gaseous species following Eq. 1+2. Above the solid carbon boundary the additional heat introduced to the gasifier by the preheated air directly leads to increased $AFT$. 
Another important factor in gasification is the yield in combustible compounds and chemical power in the products. And again, the solid carbon boundary plays a vital role. Fig. 6 shows the amount of chemical power contained in the products of the gasification of wood with a water content of $WC = 10\ \text{wt}\%$ and an air inlet temperature of $AIT = 25\ \text{°C}$, depicting the contribution of the respective combustible components to the chemical power by stacking the individual values to a composite curve. As generally foreseeable the total amount of chemical power contained in the gasification products decreases with the increase of $ER$, because an increasing part of the fuel is combusted. But below the solid carbon boundary a part of the combustible products contributing to the chemical power is solid carbon, which is not accessible.
to the downstream producer gas utilization. The chemical power contained in the gas phase, which is delimited by the bold solid line on top of the hydrogen contribution, is increasing with rising ER until the solid carbon boundary, where it has its maximum value, and decreasing with further increase of ER above that point. From this picture another important conclusion can be drawn immediately: although methane has a by far higher net calorific value at standard temperature and pressure (1,025.13 hPa, 0 °C) of $H_i = 35.883$ MJ m$^{-3}$ compared to carbon monoxide ($H_i = 12.633$ MJ m$^{-3}$) and hydrogen ($H_i = 10.783$ MJ m$^{-3}$), it is not advisable to operate the gasifier in a way that maximizes the methane content of the producer gas. Such an approach to optimization would sacrifice a large amount of chemical power to the solid phase of products, as methane is practically present in the producer gas only below the solid carbon boundary. (Schulzke 2013)

![Diagram showing chemical power content in synthesis gas as a function of equivalence ratio and gas composition (according to Schulzke and Unger 2011)](image)

The cold gas efficiency of a gasifier is defined as the ratio of chemical power of the gaseous products expressed as lower heating value at 25 °C and the chemical power of the fuel feed. As the chemical power of the wooden fuel is the same for all equivalence ratios, the cold
gas efficiency equals the bold solid line of chemical power contained in the product gases presented in Fig. 6 divided by a constant factor, which gives an identical development of cold gas efficiency over \( ER \). The highest thermodynamically possible cold gas efficiency is achieved exactly at the solid carbon boundary, which again emphasizes the importance of this point. For the shown example of a fuel with a water content of \( WC = 10 \text{ wt}\% \) and an air inlet temperature of \( AIT = 25 \degree C \) the maximum cold gas efficiency equals approximately 86%.

As can be seen from Fig. 5, the adiabatic flame temperature \( AFT \) is a continuously rising function of the equivalence ratio \( ER \). Therefore, the abscissa can be explicitly and nonambiguously expressed by the \( AFT \). Fig. 7 shows the cold gas efficiency as a function of \( AFT \), which for fluidized beds is identical with the bed operating temperature. The maximum value of cold gas efficiency for any combination of air inlet temperature \( AIT \) and fuel water content \( WC \) marks the solid carbon boundary. For a certain combination of \( AIT \) and \( WC \) the cold gas efficiency dramatically drops below the temperature representing the solid carbon boundary, while it decreases comparatively smooth above that point. From this result a fairly easy control strategy for optimized operation – at least for fluidized bed systems – can be deduced: the temperature representing the solid carbon boundary should be determined experimentally for the given gasifier and fuel, and subsequently the gasifier should be operated at a temperature slightly above it to retain a certain security for the control system to definitively avoid operation below the solid carbon boundary. A slight increase in air supply or decrease in wood fuel supply – both measures slightly increasing the equivalence ratio \( ER \) – would increase the operating temperature if necessary and vice versa.
In general thermodynamic equilibrium calculations exhibit some shortcomings if compared to experimental measurements at real gasifiers. Even at very low adiabatic flame temperatures, hydrocarbons higher than methane and aromatic compounds with one or more rings are not present in equilibrium in contrast to real producer gases and also the content of methane in real producer gases is much higher than calculated from thermodynamic equilibrium. So, thermodynamic equilibrium is never reached in real gasifiers (Schulzke and Unger 2011), except of entrained flow gasifiers operating at very high temperatures, where the chances to achieve equilibrium are better. Even if the heat losses to the surrounding for a specific reactor are taken into account, the results only become slightly better.

A possible work-around was suggested by Kersten et al. (2002) with the concept of quasi-equilibrium approach. In that approach the temperature to calculate the equilibrium was chosen to be (significantly) lower than the measured operating temperature of the gasifier. With this measure the calculated composition of the producer gas was considerably closer to the measured values, especially concerning the methane content. But still, no light hydrocarbons and tar constituents are present in the calculated results.
These missing compounds can also be incorporated in the model calculations as there are distinct correlations of volatile organic compounds (light hydrocarbons) and tar constituents (phenolic and polyaromatic hydrocarbons) with methane and ethylene concentration (Dufour et al. 2011). Both model improvements – temperature approach and correlation of tar and hydrocarbon content with methane concentration – are specific to every combination of gasifier and fuel. They are helpful to describe and predict the behavior of the specific reactor under consideration in more detail and precision, but they don’t model and represent the general interrelations and can therefore be omitted for first principle investigations.

The same method applied to understand the general behavior of gasification is also very helpful to investigate the fate of different fuels under the same conditions, as fuel composition influences the stoichiometric air demand, adiabatic flame temperature and producer gas composition. Mac an Bhaird et al. (2009) made comparative calculations for four different solid fuels for gasification based on elemental analysis. The composition of the four fuels is given in Table 2 in comparison to the values used for the results presented in the preceding paragraphs.

Table 2. Composition of investigated fuels based on dry, ash-free matter

<table>
<thead>
<tr>
<th></th>
<th>C wt%</th>
<th>H wt%</th>
<th>N wt%</th>
<th>O wt%</th>
<th>formula</th>
<th>$h_i$ MJ kg$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference$^a$</td>
<td>50.0</td>
<td>6.0</td>
<td>0.0</td>
<td>44.0</td>
<td>CH$<em>{1.44}$O$</em>{0.66}$</td>
<td>18.72</td>
</tr>
<tr>
<td>Wood (Spruce)</td>
<td>47.9</td>
<td>6.3</td>
<td>0.1</td>
<td>45.7</td>
<td>CH$<em>{1.56}$N$</em>{0.002}$O$_{0.718}$</td>
<td>17.9</td>
</tr>
<tr>
<td>Miscanthus</td>
<td>45.9</td>
<td>6.4</td>
<td>0.5</td>
<td>47.2</td>
<td>CH$<em>{1.66}$N$</em>{0.01}$O$_{0.771}$</td>
<td>17.4</td>
</tr>
<tr>
<td>Willow</td>
<td>44.8</td>
<td>6.5</td>
<td>0.3</td>
<td>48.4</td>
<td>CH$<em>{1.772}$N$</em>{0.006}$O$_{0.81}$</td>
<td>17.8</td>
</tr>
<tr>
<td>Peat</td>
<td>55.8</td>
<td>5.4</td>
<td>1.4</td>
<td>37.3</td>
<td>CH$<em>{1.159}$N$</em>{0.021}$O$_{0.5028}$</td>
<td>20.2</td>
</tr>
</tbody>
</table>

$^a$ as in above calculations, composition taken from Perry et al. (1984)

Fig. 8 depicts the results of the thermodynamic equilibrium calculations for the four different fuel compositions as char formation (a) and adiabatic flame temperature $AFT$ (b) over equivalence ratio $ER$. The general behavior of all fuels is identical to the results presented for the reference composition of wood in more detail above. The location of the solid carbon boundary as well as the absolute value of adiabatic flame temperature depend on the varying composition of each fuel, but for all fuels there is a distinct solid carbon boundary and the behavior below and above this boundary changes in a similar way as described for the reference composition of wood.
Fig. 8. Solid carbon formation (a) and adiabatic flame temperature (b) as a function of equivalence ratio for different fuels (Mac an Bhaird et al. 2009)
Calculations of thermodynamic equilibrium for every new fuel, which is intended to be gasified in an existing reactor, gives insight in which direction the other fuel composition will drive the reactor’s behavior and is therefore to be recommended before applying the first batch of new fuel to the gasifier.

**Producer gas utilization I: heat and power**

Fig. 9 depicts the general options for the utilization of producer gas, where the shown circulating fluidized bed is only illustrative and can be replaced by any other type of reactor. The gases could be used directly to substitute primary fuels in thermal processes or gas fired boilers, alternatively in combined heat and power stations either using gas engines or gas turbines and finally in fuel cells or chemical syntheses producing substitute natural gas (SNG) or liquid biofuels like methanol, higher alcohols or Fischer-Tropsch products (Biomass-to-Liquids, BtL). From top to bottom the degree of necessary gas cleaning and conditioning is steadily increasing.

**Fig. 9.** General options for producer gas utilization

Several examples exist for the direct substitution of fossil fuel in thermal processes from very small scale to very large scale: on one side a pottery in Bavaria uses a fixed bed downdraft
wood gasifier with a thermal capacity of about 200 kW to replace approximately one third of their fuel demand in the tunnel furnace to fire the pottery and on the other hand at the cement factory of Rüdersdorf near Berlin a circulating fluidized bed gasifier with a fuel capacity of 100 MW is used to fire the calciner. The last gasifier was commissioned in 1997 and since 2000 it is operational on full capacity with several waste materials ranging from refuse derived fuel (RDF) to tar paper (Scur 2000, Yates and Lettieri 2016). Both installations only apply a dust/fly ash/char removal by a quite simple filter.

The utilization of producer gas in a gas-fired boiler, e.g. for the production of steam, also requires a comparatively low gas cleaning, but results in low efficiency, if the steam is used to produce electricity. More efficient electricity production options like gas turbines or internal combustion engines need the removal of particulate matter, tar, water and potentially other contaminants. To reduce the complexity of the description clean wood chips are assumed as possible fuel to any type of gasifier. This eliminates all potential contaminants with the exception of dust, tar and water, but still gives several challenges in gas cleaning. For the three remaining contaminants the sequence of removal and especially for tar the method of reducing the concentration needs to be determined.

As tar is the most problematic contaminant on one hand and from thermodynamic point of view it should not even be present in the producer gas on the other hand, the primary approach would be to operate or modify the gasifier in such a way, that the producer gas really becomes free of tar. Entrained flow gasifiers operate at very high temperatures of above 1,200 °C and their product gas therefore is inherently free of tar (but mainly for large capacities). On the other end of the capacity range there are some examples of modified fixed bed reactors like the Viking gasifier (Henriksen et al. 2006), Notar gasifier (Berger et al. 2011) or the SYNCRAFT®-Werk (Dumfort et al. 2015). All these examples are based on a common design principle: spatial separation of drying/pyrolysis from oxidation/reduction in fixed bed reactors (typically downdraft) using two physically separated reactors. Only recently Danish Technological University DTU tried to apply this principle to larger scale fluidized bed systems (Gadsbøl et al. 2018).

In the medium capacity range fluidized beds are typically applied. In such gasifiers the main approach for tar-free operation is the addition of catalytically active bed material – either as single bed material or as additive to non-reactive materials like silica sand – but this turns out to be either quite expensive or incomplete in tar conversion. Examples are dolomite, olivine (Ising et al. 2004, Corella et al. 2004b, Ptasinski et al. 2004) and Ni-doped materials (e.g. olivine (Pfeifer et al. 2004) or glass ceramics (Felix et al. 2009)). The most common partially active
bed material towards tar conversion already inside the gasifier is olivine (Ising et al. 2004, Rauch et al. 2006, Thunman et al. 2018).

However, most gasifiers in the field, especially fluidized bed gasifiers but not limited to, – research installations as well as commercial ones – exhibit at least a certain amount of residual tar in the producer gas together with dust and water. To determine a proper removal sequence generally six options exist with three contaminants to be treated. Table 3 shows the two most common sequences together with the seventh option to remove all three contaminants together in a single piece of equipment and some general advantages and disadvantages of these sequences.

Table 3. Most common options for selection of gas cleaning sequence

<table>
<thead>
<tr>
<th>Dust – Tar – Water</th>
<th>Tar – Dust – Water</th>
<th>Simultaneous Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>high temperature filtration required</td>
<td>tar concentration reduction in high dust environment</td>
<td>usually water quench systems applied</td>
</tr>
<tr>
<td>otherwise condensation/adsorption of tar on dust/char particles</td>
<td>classical, low temperature filtration possible</td>
<td></td>
</tr>
<tr>
<td>water condensate virtually free of contaminants</td>
<td>water condensate virtually free of contaminants</td>
<td>results in heavily contaminated water, difficult and expensive to dispose off</td>
</tr>
</tbody>
</table>

Besides the sequence of removal also the method of removal or concentration reduction needs to be determined. For particulates and water this is relatively straight forward: particles are removed by filters and water by condensation, which in turn is the reason why water generally is removed as last “contaminant”. For the filter used to remove particles (dust, fly ash, char and attrited bed material) the operating temperature and hence the position in the sequence is decisive: at low temperatures low cost baghouse filters can be applied while at higher temperatures sinter metal candle filters or ceramic filters at highest temperatures must be applied. For the reduction of tar concentration in the producer gas two general options exist: removal of the tar or conversion of tar constituents into compounds with lower molecular weight.

For the removal of tar from the producer gas the methods condensation, absorption and adsorption are used or combinations thereof. Commercial applications of tar removal by absorption using bio-diesel in a scrubber, e.g. developed by TU Vienna, were demonstrated at
the Güssing gasifier (Pröll et al. 2005) and at the GoBiGas-facility in Gothenburg (Iskov and Rasmussen 2013). ECN in The Netherlands developed a combination of condensation and absorption called OLGA (Rabou et al. 2009, Zwart et al. 2009), in which the producer gas is cooled down in a first heat exchanger to condense the heavy tar components and subsequently scrubbed with a solvent to absorb the remaining light tars. As adsorbent char from gasification or pyrolysis gained new attention in research quite recently (Ahmad et al. 2016, Neubauer and Elhami 2016).

Although tar compounds cause major difficulties in producer gas utilization as they condense in the cold parts of the plant provoking fouling and pipe blockage, they also provide a significant contribution to the heating value of the producer gas. While the concentration of tar compounds in total only is around 0.5 vol%, it can make up to 10% of the lower heating value. So, the removal of tar from the producer gas would in consequence lead to a significant loss in energy content and hence process efficiency. Therefore, it is promising to keep the energy content in the gas by converting the tar compounds into typical synthesis gas constituents like methane, carbon monoxide and hydrogen. This can be achieved by thermal cracking on one side or catalytic conversion by steam or dry reforming with CO₂ on the other side. Thermal cracking requires the producer gas to be heated up to temperatures above 1,200 °C to achieve temperature induced conversion of the tar compounds. This approach was successfully demonstrated by Nexterra in Vancouver, Canada (Claus 2012). Catalytic tar conversion was investigated for long by many groups (Ising 2002, Corella et al. 2004a, Ising et al. 2004, Pfeifer et al. 2007, Schulzke 2011, Shen and Yoshikawa 2013, Hamel et al. 2014, Simell et al. 2014, Varga 2015, Kaisalo 2017) and commercially demonstrated at the power station in Skive, Denmark (Andersson et al. 2017). Many catalysts are suggested for the conversion of tar compounds, but the vast majority comprise of Ni-based steam reforming catalysts or platinum group metals, also often used for steam reforming (Bock et al. 2015).

Finally, a fully developed example for combined heat and power production based on biomass gasification in a scalable configuration is reported in this section. Fig. 10 shows the general plant layout, which was developed and evaluated by Fraunhofer UMSICHT (Schulzke 2012a).
The power plant process starts with a biomass drying section. As displayed in Fig. 10, this dryer can be fired with a dedicated combustion chamber or – more economical – with residual process heat from producer gas cooling. The biomass is gasified in an air-blown atmospheric bubbling fluidized bed at around 915 °C with olivine as bed material, which is partially active for tar conversion. A tar reforming reactor operating in high dust gas is directly connected to the gas outlet of the gasifier. The catalyst within this reactor has a honeycomb structure to cope with the comparatively high particle concentration of about 10 g m$^{-3}$ (stp). After the tar reformer the producer gas can easily be cooled down to temperatures around 120 °C, at which classical baghouse filters can be applied to fully remove the particles from the gas. Finally, the gas can be cooled down to 40 °C to knock out the steam content and to match the gas engine entrance requirements with regard to water vapor. An internal combustion engine based on spark ignition is used to produce electricity and heat, which both are exported to external networks. The process concept is described in detail in Schulzke (2012a).

The potential of such systems was assessed by economic and environmental investigations. The investment cost for total power stations and production cost for electricity were calculated for four different capacities ranging from 100 kW fuel supply to 10 MW (Schulzke 2011a,b, Schulzke 2012a). The estimated investment cost lie well within the range
of published investment cost for similar installations – both for gasification and direct combustion (Schulzke 2011b). The main results of assessment were the large potential for greenhouse gas savings on one hand and high electricity production costs on the other hand. The greenhouse gas emissions range from up to 70 g CO$_2$-equivalent per kWh$_{el}$ in the smallest setup to 32 g CO$_2$-equivalent per kWh$_{el}$ in the largest scale (Schulzke 2012b, Schulzke 2012c) compared to the average of 597 g CO$_2$-equivalent per kWh$_{el}$ in Germany’s electricity mix for the year 2010, where the transmission losses in the grid are included (Thrän et al. 2010). Even for the worst plant configuration still a CO$_2$ emissions reduction of more than 500 g per kWh$_{el}$ could be achieved. The production cost for electricity also vary greatly with plant capacity: at 100 kW fuel input the production cost add up to 930 € per MWh$_{el}$ and drop to 150 € per MWh$_{el}$ for the largest configuration with 10 MW fuel input (Schulzke 2012a,b,c). In 2010 the average production cost of electricity in the German grid was 70 € per MWh$_{el}$ (Thrän et al. 2010). Without the high feed-in tariff, which was in effect in Germany from 2004 to 2012, biomass-based gasification-driven heat and power stations were not economical. And the same holds true for the majority of the developed countries: generally no commercial operation is feasible for gasification power stations in capacities from 1 MW to approximately 50 MW without any form of subsidy.

Besides direct greenhouse gas emissions reduction by substitution of fossil fuels with biomass, gasification-based power stations can compensate fluctuating sources of other renewable electricity by supplying balancing power. Gas engines have a turndown ratio of 1:2 and bubbling fluidized bed reactors can realize a turndown ratio of 1:4. Installing two gas engines that together match the full capacity of the gasifier allows a flexible operation of the power station from 25% to full rated capacity without any technical challenge. Such systems would greatly simplify the integration of fluctuating renewable electricity from wind power and photovoltaics into national grid operation, but presently there is no fair compensation to make up the financial loss due to overall beneficial plant turndown (Schulzke and Unger 2015a).

**Producer gas utilization II: fuels and base chemicals**

The producer gas generated by biomass gasification could be used for heat and power production as discussed in the previous section. In addition, it will also be suitable for the synthesis of chemicals and fuels, provided the nitrogen content of the producer gas is low enough (virtually zero). In general, the producer gas from allothermal gasification with steam and from autothermal gasification with pure oxygen as gasifying agent could both be applied.
The same approach for gas cleaning is applicable for chemical utilization than for power generation, but a much higher level of contaminants removal/conversion is required. In addition, especially sulfur needs to be removed, as this is a poison to most of the catalysts used in chemical synthesis from producer gas. The most common products from synthesis gas in chemical industry towards base chemicals and (transportation) fuels are methane (Eq. 4), Fischer-Tropsch-hydrocarbons FT (Eq. 5), methanol (Eq. 6), ethanol (Eq. 7) and dimethyl ether DME (Eq. 8).

\[
\text{CO + 3 H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O} \quad \Delta_{R}H = -206 \text{ kJ mol}^{-1} \quad (4)
\]

\[
n \text{CO} + 2n \text{H}_2 \rightleftharpoons (-\text{CH}_2-)_n + n \text{H}_2\text{O} \quad \Delta_{R}H = -158 \text{ kJ mol}^{-1} \quad (5)
\]

\[
\text{CO} + 2 \text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} \quad \Delta_{R}H = -98.7 \text{ kJ mol}^{-1} \quad (6)
\]

\[
2 \text{CO} + 4 \text{H}_2 \rightleftharpoons \text{CH}_3\text{-CH}_2\text{OH} + \text{H}_2\text{O} \quad \Delta_{R}H = -256 \text{ kJ mol}^{-1} \quad (7)
\]

\[
2 \text{CO} + 4 \text{H}_2 \rightleftharpoons \text{CH}_3\text{-O-CH}_3 + \text{H}_2\text{O} \quad \Delta_{R}H = -219 \text{ kJ mol}^{-1} \quad (8)
\]

where \(\Delta_{R}H\) is the standard enthalpy of reaction. The synthesis of methane requires a hydrogen/carbon monoxide-ratio of 3:1 while all other products show a stoichiometric demand of 2:1. Typically, the producer gas resulting from allothermal steam gasification has a \(\text{H}_2/\text{CO}\)-ratio around 2:1 and autothermal oxygen gasifiers deliver a producer gas with a \(\text{H}_2/\text{CO}\)-ratio at about 1:1 (Mevissen et al. 2009a). This would lead to the general conclusion that steam gasification processes might be more suitable for synthesis reactions.

\[
\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 \quad \Delta_{R}H = -41 \text{ kJ mol}^{-1} \quad (9)
\]

Either within the chemical reactor or in a separate reactor upstream the chemical conversion, a homogeneous water gas shift reaction (Eq. 9) can be conducted. When this gas conditioning reaction is added to any of the above reaction equations with the exception of methanol (Eq. 6), an overall reaction scheme comes up with an equimolar CO and \(\text{H}_2\) demand on the left hand side and carbon dioxide as coproduct instead of water on the right hand side of each equation. With this modification, also producer gas from oxygen-blown gasifiers proves to be as suitable as steam-blown gasification. A last drawback of oxygen-blown gasification for fuels and chemicals production is at first sight the lower carbon conversion from biomass to the
desired products, as Eq. 10 und 11 exemplarily show for methane (Schulzke 2016) on pure stoichiometry neglecting all conversion deficiencies.

\[
\text{CH}_{1.44}\text{O}_{0.66} + 0.31 \text{ O}_2 \rightleftharpoons 0.36 \text{ CH}_4 + 0.64 \text{ CO}_2 \quad (10)
\]

\[
\text{CH}_{1.44}\text{O}_{0.66} + 0.31 \text{ H}_2\text{O} \rightleftharpoons 0.515 \text{ CH}_4 + 0.485 \text{ CO}_2 \quad (11)
\]

However, in steam-blown gasification the biomass conversion into gaseous compounds is less effective compared to oxygen-blown gasification due to generally lower operating temperature and restricted residence time, which means that a larger amount of residual solid char comes out of the steam-blown gasifier. In addition, the necessary heat supply for executing the endothermic processes in the steam-blown gasifier usually is provided by combustion of the residual char and sometimes some additional biomass or bio-diesel (from tar removal). In an overall balance this results in the same figures for carbon conversion efficiency from biomass to intended chemical building block or transportation fuel. Based on these considerations there is no clear preference for one of the two general gasification concepts. The choice of gasifier for an actual project can be based on secondary reasons rather than fundamental thermodynamic or stoichiometric assessment.

Interestingly, all reactions have very similar characteristics, starting with the fact that they are equilibrium reactions. All reactions (Eq. 4-8) exhibit a considerable reduction in the amount of substance. Therefore, increasing operating pressure of the reactor favors the products. Also, all reactions are highly exothermic, even more pronounced when carbon dioxide is the coproduct. Therefore, lower operating temperature of the reactor favors the products, leading to slow reaction rates and hence larger reactor volumes. A typical engineering trade-off between preferable equilibrium and reaction kinetics has to be established. Based on these common characteristics all these reactions typically are conducted at elevated pressures between 30 and 100 bar and mild temperatures between 200 and 350 °C (Schulzke et al. 2011), often conducted in tube bundle reactors with boiling water at the shell side for cooling.

A comprehensive, general review on synthesis gas utilization for the production of fuels and chemicals is given by Rauch et al. (2013). The potential products suggested in Eq. 4-8 are produced in larger amounts from natural gas reforming (except methane) and coal gasification. Methane production options are thoroughly reviewed by Kopyscinski et al. (2010), methanol by Olah et al. (2009), dimethyl ether by Mevissen et al. (2009a), Schulzke et al. (2010) and Landälv et al. (2014) and gasoline production by methanol-to-gasoline process (MtG) by Haro.
et al. (2013), Dahmen et al. (2012, 2017) and Stöcker (2010). Fischer-Tropsch synthesis also is an old process invented in the early 30’s of last century in Germany and intensively developed by Sasol in South Africa. Such plants converting mainly coal to gasoline, kerosene and diesel are operated in very large scales (Dry 2002). Relatively recently mixed alcohols with the major compound ethanol are investigated in research (Rauch et al. 2013, Schulzke et al. 2011), while the other products are produced in world-scale plants, but typically from fossil resources and not from biomass. Synthesis gas from steam reforming of natural gas has a H₂/CO-ratio of 3:1 and synthesis gas resulting from coal gasification usually shows H₂/CO-ratios of about 0.5:1. As mentioned above, the respective ratios of synthesis gas derived from biomass lies somewhere in between 1:1 and 2:1. Therefore, the process concept for converting synthesis gas into fuels or chemicals needs some adaptations when transferred from coal gasification or natural gas steam reforming.

Besides synthesis gas composition especially plant capacity is an issue. The production of substitute natural gas (SNG) – or more precisely methane – is demonstrated on the basis of lignite gasification in the Great Planes Synfuels Plant in North Dakota, USA, since 1984 with a capacity of 18,000 t d⁻¹ of lignite as input and – after some plant modifications in 1992 – 4.81 Mio. m³ d⁻¹ (Kopyscinski et al. 2010), equivalent to 2.0 GW of chemical energy content of the produced methane. Demonstration systems for the production of SNG based on biomass gasification were operated for instance at the Güssing gasifier with capacities of 10 kW and 1 MW (Kopyscinski et al. 2010). The largest demonstration on near-industrial scale was built in Gothenburg, Sweden, with a capacity of 20 MW chemical energy content of SNG product (Karlbrink 2015). The same difference in scale also holds true for the other possible products like FT-liquids or methanol. The largest methanol plants (MegaMethanol) produce 5,000 t d⁻¹ from natural gas (Plass 2005), while the largest plant producing methanol from biomass – Värmlands Metanol in Hagfors – is designed for a capacity of 296 t d⁻¹ (Grahn and Hansson 2014). And this plant has not yet been built – exemplifying the economic hurdles for biofuels and biochemicals production from biomass. All these production processes strongly benefit from economy of scale, but biomass distribution with low volume-specific energy density over larger areas limit the maximum capacity of a single plant due to logistics reason. A promising trend to overcome the economic difficulties is the development of new reactor concepts like microchannel reactor systems instead of large scale tube bundle or slurry reactors, as demonstrated for Fischer-Tropsch synthesis for instance at the Güssing gasifier in Austria (Rauch et al. 2013, LeViness et al. 2011).
As already apparent from Eq. 10+11, the conversion of carbon into any of the desired products is not complete, even for steam-blown allothermal gasifiers, as biomass is deficient in hydrogen (Schulzke and Unger 2015b) and a noticeable amount of carbon dioxide is produced as inevitable coproduct. The addition of renewable hydrogen, produced by water electrolysis with electricity from wind power or photovoltaics, to the chemical reactor can improve the carbon efficiency of all these reactions. This option constitutes a combination of biomass-to-liquid (BtL) or biomass-to-gas (BtG) and power-to-liquid (PtL) or power-to-gas (PtG) approaches. The producer gas coming from the gasifier is used as the CO₂ source for the PtX system. And in such concepts oxygen-blown gasification processes have a clear advantage compared to steam-blown gasifiers: the CO₂ is an integral part of the producer gas and the degree of removal can be reduced, thus simplifying the process scheme. Alternatively, in steam-blown gasification systems only a small amount of the CO₂ coproduct is contained in the producer gas while the majority leaves the reactor system with the flue gas from the combustion reactor applied to supply the process heat. Here, CO₂ recovery must be added to the flue gas system, thus increasing the complexity and hence cost.

Such concepts are discussed for instance for SNG (Ahlström 2018, Iskov and Rasmussen 2013), Fischer-Tropsch (Albrecht et al. 2016) and methanol (Hannula 2015a,b). They all come to the conclusion that for the later future with high share of renewable electricity in the grid network (with potential surplus electrical power) there is potential for economic operation of such plants. Especially for the oxygen-blown system the use of the oxygen coproduct from the water electrolysis turn the air separation unit superfluous.

These concepts all assume classical plant operation strategy: ramp up of the plant to nominal capacity followed by continuous operation in the optimal design point for as long as possible. This becomes feasible only with very high shares of renewable electricity in the grid. Fluctuating operation of the electrolyzer following the changing supply of wind and solar power might already get some of these systems into reality as this operation approach could balance supply and demand in the electricity grid without turning down for instance windmills or biogas plants. This concept works in general with all products (FT with the most difficulties among the suggested synthesis products), but it was exemplarily evaluated for methanol by Schulzke and Unger (2015b, 2016) and Schulzke (2016). Fig. 11 shows a block flow diagram of the combined BtL- and PtL-plant for the case of methanol synthesis.
If no surplus renewable electricity is available from the grid, the plant operates as “classical” BtL-plant with an oxygen-blown biomass gasifier operating at rated capacity followed by producer gas cleaning and gas conditioning including carbon dioxide removal and a methanol reactor operating at 50% rated capacity, which is an easy to achieve turndown ratio. Whenever surplus renewable electricity becomes available from the grid the electrolyzer starts operation producing hydrogen and oxygen. Oxygen is stored in a tank and hydrogen is introduced to the methanol reactor while the biomass gasifier continuously operates at rated power and the CO₂ removal in the gas conditioning system is (partly) bypassed. As possibility on the other end of the electricity balancing, the air separation unit can be turned down (thus reducing the electricity taken from the grid) and the stored oxygen can be used in the gasifier instead. By this means the complete PBtL-system with flexible operation can offer negative balancing power, increased carbon efficiency and – to a smaller amount – positive balancing power.

Some numbers based on the intended methanol plant in Hagfors emphasize the potential of such approach: the rated capacity of the methanol plant in the pure BtL-mode is 296 t d⁻¹ of methanol produced from 1,100 t d⁻¹ woody feedstock (111 MW gasifier capacity), releasing

---

**Fig. 11.** PBtL-concept, combination of methanol production from biomass and renewable electricity (Schulzke 2016)
723 t d\(^{-1}\) of CO\(_2\) to the atmosphere. To double the output of the methanol reactor renewable hydrogen must be added from an electrolyzer with a capacity of 120 MW\(_{el}\). During full load operation of the electrolyzer 56.4\% of the CO\(_2\) emissions resulting from the biomass are converted to the desired product. (Schulzke 2016)

**Conclusions**

The previous sections pointed out that biomass gasification and subsequent producer gas cleaning and utilization for heat, power and chemical reactions is complex and difficult. On the other hand, relatively simple thermodynamic equilibrium and stoichiometric calculations give deep insight into the whole area. They do not completely represent all effects occurring in practical applications, but they describe the limits and allow implications on how to optimize the process effectively. As basic principle the existence of the so-called solid carbon boundary and its effect on gasifier behavior is key for the understanding of the whole process. For every project with new feedstock, the identification of the process conditions at the solid carbon boundary should be the starting point for every consideration towards process design and optimization.

Many configurations of gasifier, producer gas cleaning and gas engine for the production of electricity exist. Many installations have proven the technical feasibility of this approach in very different scales. Presently they are only economically feasible in small scales, mainly with subsidies. Due to the high potential for greenhouse gas emissions reduction of more than 400 g kWh\(_{el}\)^{-1} CO\(_2\)-equivalence even for countries like Germany which already have a high share of renewable electricity in their grid, this missing profitableness is a great pity and major drawback.

Methane, methanol, dimethyl ether, gasoline, Fischer-Tropsch liquids and mixed alcohols can all be produced from producer gas under quite similar reaction conditions. For all these products demonstration plants exist, but no commercial installation is in operation. These technologies suffer from the low energy density of the biomass feedstock and subsequent logistic restraints on the plant site. The competing production sites operating on fossil resources like natural gas or coal have a capacity, which is larger by a factor of 10 to 100, resulting in much lower specific production cost.

With the increasing availability of renewable electricity in the grid in the future there is again a great potential for biomass gasification. The deficiency in hydrogen, inherently present in biomass, can be balanced by renewable hydrogen coming from water electrolysis, thus
increasing the carbon conversion efficiency eventually up to 100%. Combined installations with biomass gasification and Power-to-X components will very effectively balance the supply and demand in electricity grid not only on the level of the distribution network but also on the level of transmission network, as they can absorb power in the range of hundreds of MW.

**Symbols**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFT</td>
<td>adiabatic flame temperature</td>
<td>°C</td>
</tr>
<tr>
<td>AIT</td>
<td>air inlet temperature</td>
<td>°C</td>
</tr>
<tr>
<td>ER</td>
<td>equivalence ratio</td>
<td>kg kg⁻¹</td>
</tr>
<tr>
<td>$H_i$</td>
<td>lower heating value (gas)</td>
<td>MJ m⁻³</td>
</tr>
<tr>
<td>$h_i$</td>
<td>lower heating value (solid)</td>
<td>MJ kg⁻¹</td>
</tr>
<tr>
<td>$\Delta RH$</td>
<td>standard enthalpy of reaction</td>
<td>kJ mol⁻¹</td>
</tr>
<tr>
<td>WC</td>
<td>water content</td>
<td>wt%</td>
</tr>
</tbody>
</table>

**Conflict of interest**

There is no conflict of interest.

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