

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

3
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21

Abstract

22

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

38

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

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Introduction

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43

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

53

54 The potential for reducing the carbon dioxide (CO₂) emissions during electricity
55 production by biomass gasification is huge: the specific CO₂ emissions of wood gasification
56 followed by internal combustion engine lies in the range of 30–70 g kWh_{el}⁻¹ (Schulzke

56 2012a,b,c). The respective emissions from the German electricity mix (including the steadily
57 increasing share of renewable electricity) dropped in 2017, following first estimations, to
58 489 g kWh_{el}⁻¹ (Icha and Kuhs 2018). For comparison, the emissions from coal fired power
59 stations are much higher. Modern power stations based on hard coal emit approximately
60 755 g kWh_{el}⁻¹ (Gräbner et al. 2010), while power stations fired with lignite emit about
61 855 g kWh_{el}⁻¹ (Andersson and Johansson 2006).

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

70 Due to the high potential for CO₂ emission reduction and the great potential to produce
71 fuels and chemicals from renewable resources in large quantities biomass gasification will gain
72 increasing importance in future. A strong appeal for a general movement towards biomass
73 utilization for energy and chemicals production was enunciated by Adam Brown, a senior
74 energy analyst at International Energy Agency, Paris, at the closing ceremony of the 26th
75 European Biomass Conference in Copenhagen. He stated: “There are many mature
76 technologies available. We need complex technologies, especially in biofuels sector. But we
77 need to start implementing these (mature) technologies now!” (Brown 2018).

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

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Fundamentals of gasification

84

85 The thermochemical conversion of woody biomass into a gaseous energy carrier is a
86 process involving three main steps – drying, pyrolysis and gasification. In some reactor
87 configurations, a fourth step – combustion – is also integrated, but only partially, as full
88 combustion would result in a flue gas without any chemical energy content. Fig. 1 shows how

89 these basic processes take place with increasing temperature, and the main products released
90 during these steps.

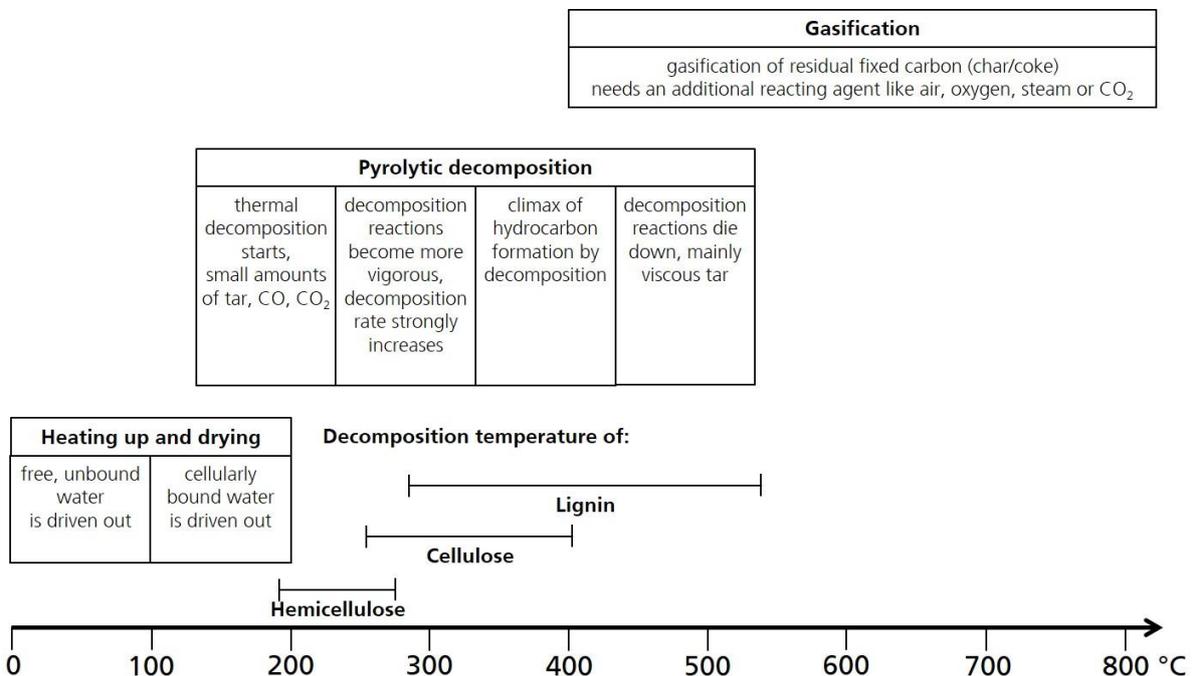
91 At low temperatures between ambient and approximately 200 °C the biomass is dried,
92 firstly releasing the free, unbound water from the interstice between the cells. The water bound
93 inside the cells is liberated to the surrounding gas atmosphere during the upper portion of this
94 temperature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

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

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

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

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107 **Fig. 1.** Processes in thermochemical conversion of lignocellulosic biomass according to

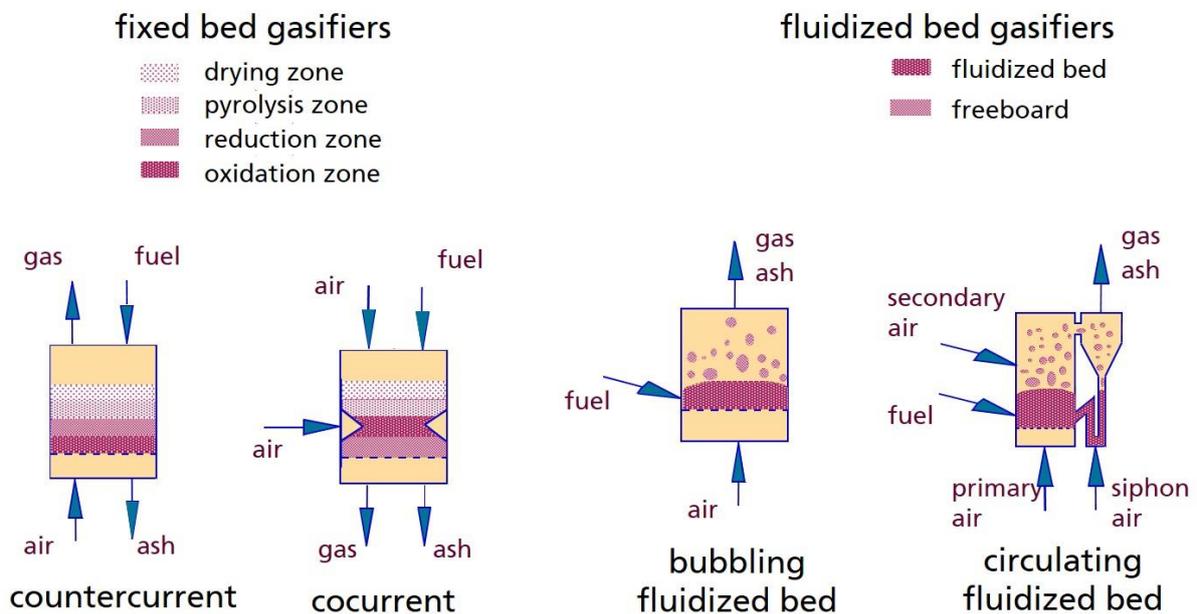
108 Kaltschmitt and Baumbach (2001)

109

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

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

119



120

121 **Fig. 2.** Typical reactor types for biomass gasification

122

123 In ideal fixed bed reactors, that are actually moving beds as the solid fuel moves slowly
 124 from the feed supply at the top to the ash removal at the bottom, well-defined zones exist, in
 125 which the basic conversion steps take place spatially separated. The most simple reactor design
 126 is the so-called downdraft gasifier, where a solid fuel and a gasifying agent (for this type of
 127 reactor nearly always air) move in co-current flow from the top downwards to the bottom, where
 128 ash and the producer gas are withdrawn. In the upmost section the fuel particles are dried
 129 followed by heat induced pyrolysis. In the third zone the mixture of evolved gases and air ignites
 130 and releases heat of combustion by oxidizing part of the combustible gases, because these
 131 homogeneous gas phase reactions are much faster than direct combustion of char. Additionally,
 132 the tar compounds released during pyrolysis are partly combusted by air and partly reformed

133 by steam and CO₂ in this very hot oxidation zone. Subsequently in the reduction zone, the CO₂
134 and steam produced in the oxidation and drying zones are reduced by the residual solid carbon
135 char giving CO and hydrogen. This very simple setup implies some operational difficulties,
136 which led to the well-accepted development of a throated reactor. The throat is installed in the
137 region of the reactor where the oxidation zone is intended to occur. The majority of the
138 oxidizing air is introduced to the reactor in this area of reduced cross section instead of the top
139 of the reactor. But even with this improvement, the burnout of the fuel leaving the reduction
140 zone is incomplete, and the “ash” withdrawn from a co-current fixed bed gasifier usually is
141 made up of unliberated carbon in the range of 50 wt%. In summary, the main characteristics
142 are poor fuel burnout, and at least the potential of very low tar content in the producer gas. The
143 main difficulty in downdraft gasifier operation is to achieve a uniform distribution of the
144 gasifying air over the cross section. Therefore, these types of gasifier require very uniform
145 feedstock particles (very narrow particle size distribution, preferably rectangular shape around
146 30 mm x 30 mm x 50 mm), which leads to the necessity of high feedstock pretreatment
147 (Hofbauer et al. 2009).

148 In counter-current gasifiers, also referred to as updraft gasifiers, the two lowest zones
149 are interchanged in comparison to co-current gasifiers. The reason is that in counter-current
150 gasifiers the air enters at the bottom, where the ash is withdrawn from the grate. The air oxidizes
151 the remaining carbon in the fuel, and as no combustible gases are present in the oxidation zone
152 of this reactor type (which would compete for the oxidant and react with faster kinetics), the
153 char can be converted completely. The flue gases rise to the reduction zone and the CO₂
154 contained in these flue gases converts parts of the char produced in pyrolysis to CO. This gas
155 mixes with the primary vapors emerging from the pyrolysis and (further up) with the steam
156 evaporated from the fuel in the drying zone. As the temperature consistently drops from the
157 bottom to the top, the tar compounds released in the pyrolysis zone have no chance to
158 decompose or react until they leave the reactor at the top. Only very heavy compounds condense
159 on the particle surface within the drying zone and are circulated back to pyrolysis. The main
160 characteristics of this reactor type are very good burnout of the fuel and very high tar content
161 of the producer gas. This type of gasifier design is quite tolerant regarding fuel quality. A wide
162 range of particle sizes (typically 20 mm to 200 mm) can be processed in the same reactor and
163 even high moisture content can be accepted (Hofbauer et al. 2009).

164 In fluidized beds the majority of the solid inventory – more than 90 wt% – is made of
165 bed material in contrast to fixed beds, where only the wooden fuel is present as solid. The bed
166 material mainly acts as heat transfer agent, which has much higher heat capacity than the gases.

167 The gasification agent together with the evolving vapors and gases from the basic conversion
168 steps must be flowing upwards fast enough to keep the bed material in suspension. In bubbling
169 fluidized beds the bed is more or less expanded, but the gas velocity is not high enough to
170 transport the particles out of the reactor. Above the fluidized bed there is a distinct freeboard,
171 where only homogeneous gas phase reactions take place. On the contrary, in circulating
172 fluidized beds the gas velocity is so high that the bed particles are blown out of the reactor as
173 in pneumatic transport and they must be separated from the producer gas in a cyclone and
174 recycled to the reactor. To prevent the gases from entering the particle recirculation line a loop
175 seal must be installed, usually in the form of a siphon. In such a reactor there is no distinct
176 freeboard but at the bottom a more dense area and an area with lower particle concentration
177 above with a smooth transition in between.

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

196 The gasifier reactors shown in Fig. 2 are typically used in commercial applications for
197 wood gasification from left (co-current fixed bed) to right (circulating fluidized bed) with
198 increasing plant capacity from a few kW of fuel input to some hundreds of MW. Not shown in
199 this figure is the third reactor type generally applicable to gasification – the entrained flow
200 reactor. This reactor is known from coal or petcoke gasification in very large scale applications

201 (several hundreds of MW) and applies average fuel particle sizes of below 100 μm (Chen et al.
202 2012). Currently there is no commercial biomass gasifier of this type operating. For such large
203 capacity, biomass logistics becomes an open issue, because biomass with comparatively low
204 volumetric energy density must be transported over a long distance. To overcome this problem
205 several approaches are discussed, commonly based on volumetric energy densification in a
206 decentralized first conversion step followed by transportation of densified intermediate to the
207 large scale entrained flow gasifier. Examples of such approaches are the BioTfuel project for
208 woody biomass (Viguié et al. 2013), which applies torrefaction and pelletization as
209 densification step, and the bioliq[®] process for agricultural residues (Dahmen et al. 2012), which
210 uses fast pyrolysis to produce a slurry of pyrolysis oil and char as the transportable intermediate.

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

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

230 The main purpose of the gasifying agent is the conversion of the remaining solid carbon
231 after the release of the volatiles in drying and pyrolysis. CO_2 and steam can be used for that
232 purpose following the well-known Boudouard-Equilibrium (Eq. 1) and the heterogeneous water
233 gas reaction (Eq. 2).



237

238 Both reactions are endothermic in the carbon consuming direction. Therefore gasifiers
239 operated with either CO₂ or steam as the gasifying agent need an external heat supply to cover
240 the heat demand by the basic steps and the char conversion. If the heat is supplied from outside
241 of the gasifier, the process is called allothermal. As the amount of the gasifying agent fed to the
242 reactor and the operating temperature are not directly linked in this type of operation there is an
243 additional degree of freedom in comparison to autothermal gasification. Heat supply to the
244 allothermal gasification system can be very diverse in principal, although in the majority of
245 research installations and in all demonstration and commercial units a heat transfer material
246 circulates between the gasifier and a furnace, where it is heated by combustion of residual char,
247 fresh biomass and other additional (biogenic) fuel or a mixture of those possibilities. But with
248 increasing availability of renewable electricity from wind, photovoltaics or water, electrical
249 resistance heaters become an interesting option and in the past even waste heat from nuclear
250 power stations was discussed as a heat source for gasifiers (Verfondern and Lensa 2010).

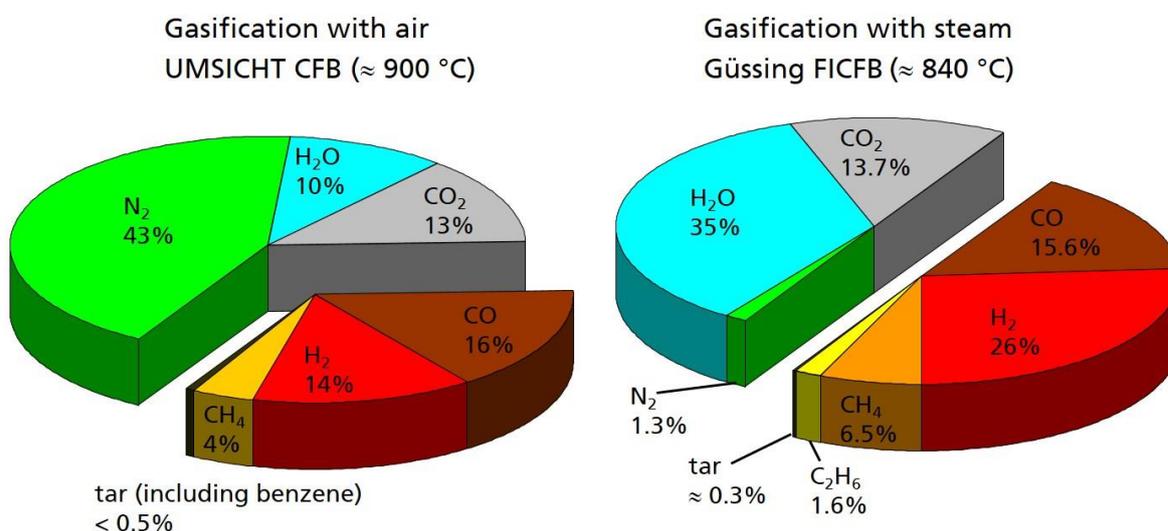
251 The impact of the gasifying agent on the average composition of the producer gas is
252 described in detail elsewhere (Hofbauer 2007, Hofbauer et al. 2009). For the understanding of
253 the following paragraphs a broad summary is sufficient. Fig. 3 gives a comparison of average
254 gas composition for an air blown circulating fluidized bed gasifier (left part, operated at
255 Fraunhofer UMSICHT in Germany; diagram taken from Ising et al. 2004) and a steam blown
256 bubbling fluidized bed gasifier (right part, Gasifier operated at Güssing, Austria; diagram taken
257 from Pfeifer et al. 2007). This figure shows that air gasification results in a very lean gas with
258 up to 50 vol% of nitrogen, which can run a gas engine or gas turbine for combined heat and
259 power production, but it is not suitable for synthesis gas chemistry (nitrogen cannot be separated
260 from CO in an efficient manner). The lower heating value H_i of such gases is in the range of
261 5 MJ m^{-3} at standard temperature and pressure (stp).

262 In comparison, producer gases from steam gasification are virtually free of nitrogen and
263 exhibit a lower heating value of about $H_i \approx 9.2 \text{ MJ m}^{-3}$ (stp) on wet basis. If the water vapor is
264 removed, e.g. simply by condensation, the lower heating value increases to approximately
265 $H_i \approx 12.5 \text{ MJ m}^{-3}$ (stp). Such producer gas can be used in gas engines or turbines for combined
266 heat and power production as producer gases from air gasification, but they are also suitable for
267 utilization in synthesis gas chemistry if first subjected to gas cleaning and conditioning.

268 The use of CO₂ as gasifying agent would also lead to a producer gas virtually free of
 269 nitrogen and exhibiting a similar lower heating value as with steam gasification. But as reaction
 270 rates in CO₂ gasification are much lower than with any other medium discussed here, this gas
 271 presently is not used in any demonstration or commercial gasifier as it would lead to much
 272 larger reactors due to the longer residence times required. But for the future use this is an
 273 interesting option, because unreacted CO₂ from the chemical synthesis could be recycled in the
 274 process and its application does not require heat of evaporation like steam production.

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

279



280

281 **Fig. 3.** Comparison of representative gas composition depending on gasification agent (Ising
 282 et al. 2004 (left), Pfeifer et al. 2007 (right))

283

284 **Table 1.** Typical producer gas composition for different gasifying agents

285

	UMSICHT ^a	Güssing ^b	Chrisgas ^c	CUTEC ^{d,*}
Gasifying agent	Air	Steam	Oxygen (+Steam)	Oxygen (+Steam)
Pressure	Atmospheric	Atmospheric	10-15 bar	Atmospheric
H ₂	14	26	11.8	32
CO	16	15.6	11.9	27

CO ₂	13	13.7	27.9	35
CH ₄	4	6.5	8.2	2
C ₂₊	n.a.	1.6	1.6	n.a.
H ₂ O	10	35	37.7	3
N ₂	43	1.3	< 0.9 [#]	< 0.3

286 n.a. not analyzed; *after water quench (H₂O concentration at reactor exit approx.. 30-40%); [#]by difference

287 a Ising et al. 2004

288 b Pfeifer et al. 2007

289 c Kirm et al. 2007; Brandin and Liliedahl 2011

290 d Carlowitz et al. 2003

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292

Thermodynamics of (air-blown) gasification

293

294 The conversion of woody biomass in an air-blown gasifier involves many different
 295 reactions that describe the basic conversion steps of drying, pyrolysis and gasification. The
 296 network of reactions comprises of a primary reaction of “biomass decomposition” followed by
 297 a set of homogeneous gas phase reactions (seven individual reactions) and a set of
 298 heterogeneous gas-solid reactions (five individual reactions), resulting in total in a set of at least
 299 13 consecutive and parallel reactions (Ising 2002). For the calculation of the chemical
 300 equilibrium two different approaches exist: the stoichiometric and the non-stoichiometric
 301 approach. Both approaches start off with the identification of possible components being
 302 present in equilibrium. Within the stoichiometric approach a network of independent reactions
 303 has to be identified and the equilibrium constants as a function of temperature, pressure and
 304 composition for all these reactions must be determined and solved together with the mass and
 305 energy balances. For the non-stoichiometric approach no specific reaction network has to be
 306 identified. If all thermodynamic data for the species identified as being present in equilibrium
 307 are available, the equilibrium composition can be calculated by minimizing the Gibb’s energy
 308 of the system together with the material and energy balances. Done properly, both approaches
 309 give identical results (Prins et al. 2003, Prins 2005) and the method can be chosen based on
 310 convenience. Many studies on thermodynamics of the gasification process are reported in the
 311 literature (e.g. Desrosiers 1981, Huang and Ramaswamy 2009, Ahmed et al. 2014,
 312 Chaiwatanodom 2014, Mondal and Ghosh 2015), applied to the different reactor types and not
 313 restricted to biomass, as Xu et al. (2017) published a study on thermodynamic equilibrium in
 314 municipal solid waste gasification. The most debatable point in the studies is the “correct”
 315 choice of the temperature applied to calculate the equilibrium. For entrained flow and fluidized

316 bed gasifiers the choice of temperature is straight forward, as in entrained flow the temperature
 317 at the entry of the quench determines the equilibrium and in fluidized beds there is more or less
 318 a uniform temperature throughout the reactor. Only in fixed bed gasifiers there are temperature
 319 profiles from room temperature up to potentially 1,200 °C and more, and here the choice of
 320 temperature is not so easy. For the sake of simplicity the following section gives the results for
 321 fluidized beds, but with some degree of abstraction they are – at least in their basic messages –
 322 also applicable for fixed bed reactors.

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

329 Fuel was represented by an average composition of wood comprising of 50 wt% carbon,
 330 6 wt% hydrogen and 44 wt% oxygen on dry and ash-free basis (Perry et al. 1984), resulting in
 331 a representative molecular formula of $\text{CH}_{1.44}\text{O}_{0.66}$. The non-stoichiometric approach for
 332 calculating the equilibrium by minimizing the Gibb's free energy of the system was used. The
 333 following species were considered as being possibly present in the equilibrium: solid carbon
 334 C(s), carbon monoxide CO, carbon dioxide CO₂, hydrogen H₂, steam H₂O, oxygen O₂, nitrogen
 335 N₂, argon Ar, methane CH₄, ethylene C₂H₄, ethane C₂H₆, benzene C₆H₆, phenol C₆H₅OH and
 336 naphthalene C₁₀H₈. The method applied is described in detail in Mevissen et al. (2009) and
 337 Schulzke and Unger (2011). All calculations presented hereafter are based on a fuel feed rate
 338 of 1 t h⁻¹ of dry, ash-free wood.

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

342



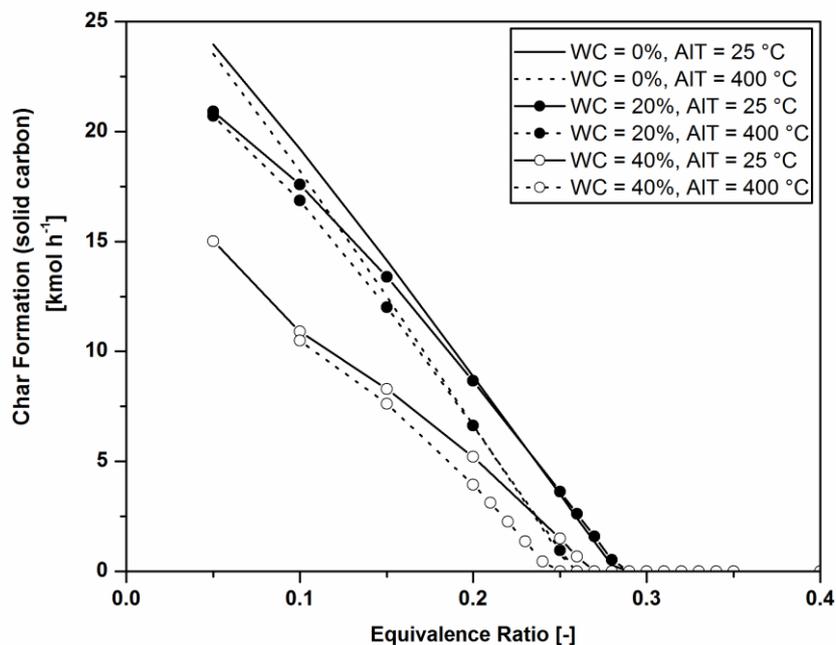
344

345 With an assumed composition of dry air of 21 vol% O₂, 78 vol% of N₂ and 1 vol% Ar
 346 the stoichiometric air demand for complete combustion is determined as 5.914 kg air per kg
 347 dry, ash-free wood. The equivalence ratio is defined as ratio of air actually used for gasification

348 to the stoichiometric air demand. An ER equal to 1 represents stoichiometric combustion and
 349 an ER of 0 implies pyrolysis only. Gasification lies somewhere in between these limits.

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

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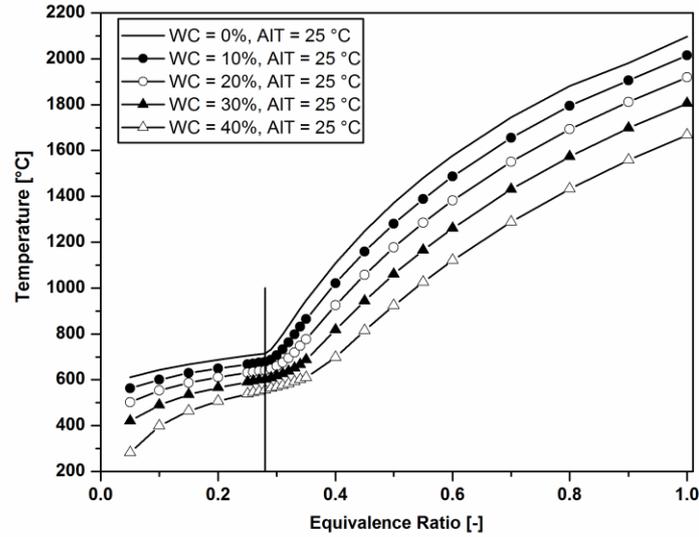
365 **Fig. 4.** Char formation as a function of equivalence ratio (Schulzke and Unger 2011)

366

367 As air was used as gasifying agent in the thermodynamic equilibrium calculations of
 368 autothermal fuel conversion, there is a clear dependency of the operating temperature of the
 369 gasifier – called adiabatic flame temperature AFT – and the air-fuel-ratio expressed as the

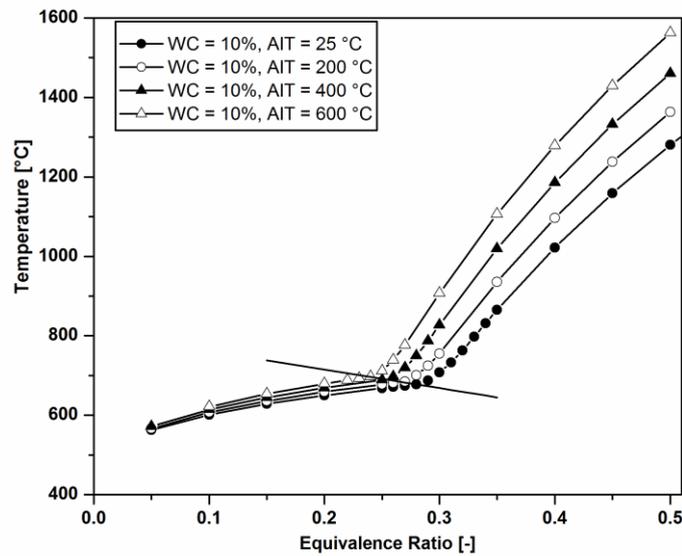
370 equivalence ratio ER . The calculated values for the adiabatic flame temperature around and
371 especially below the solid carbon boundary are far too low to achieve chemical equilibrium in
372 a real reactor. Especially, more methane would be formed than calculated from chemical
373 equilibrium at such low temperature and the amount of tars formed would increase dramatically
374 with decreasing temperature in real applications. Nevertheless, the reasoning that can be
375 deduced from these theoretical results gives valuable hints for proper gasifier operation and
376 therefore it is worth closer consideration. In addition, it should always be kept in mind that
377 higher operating temperature allows better approach to equilibrium and therefore turn these
378 results more practical.

379 The aforementioned $AFT-ER$ -dependency is depicted in Fig. 5 with two additional
380 parameters, the fuel water content WC and the air inlet temperature AIT . It can be seen clearly
381 that the AFT is rising with increasing air supply and the solid carbon boundary is marked by the
382 distinct bend in each curve. As mentioned above, the behavior of the reactor is different below
383 and above this point. For values of the ER below the solid carbon boundary the majority of
384 additional heat released by combustion reactions due to larger air supply with increasing ER is
385 consumed by endothermic conversion of solid carbon by Boudouard equilibrium (Eq. 1) and
386 heterogeneous water gas reaction (Eq. 2), resulting in a moderate increase of reactor
387 temperature. Above the solid carbon boundary there is no more carbon available for
388 endothermic conversion and hence all the additional heat released by combustion of gaseous
389 combustible components directly leads to rampant temperature increase. The general behavior
390 is the same for all parameters, but with increasing water content WC the overall temperature in
391 the reactor becomes lower due to the necessary heat to evaporate the additional water introduced
392 to the reactor. In addition, the bend in the curve at the solid carbon boundary becomes less
393 pronounced, but the carbon boundary stays at the same ER for all WC (see Fig. 5a). On the
394 contrary, with increasing air inlet temperature for a fixed water content, the solid carbon
395 boundary moves to lower equivalence ratios (see Fig. 5b). Below the solid carbon boundary the
396 AFT is nearly not affected by the additional heat supplied to the gasifier as it is completely
397 compensated by higher conversion of solid carbon to gaseous species following Eq. 1+2. Above
398 the solid carbon boundary the additional heat introduced to the gasifier by the preheated air
399 directly leads to increased AFT .



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a)



402

b)

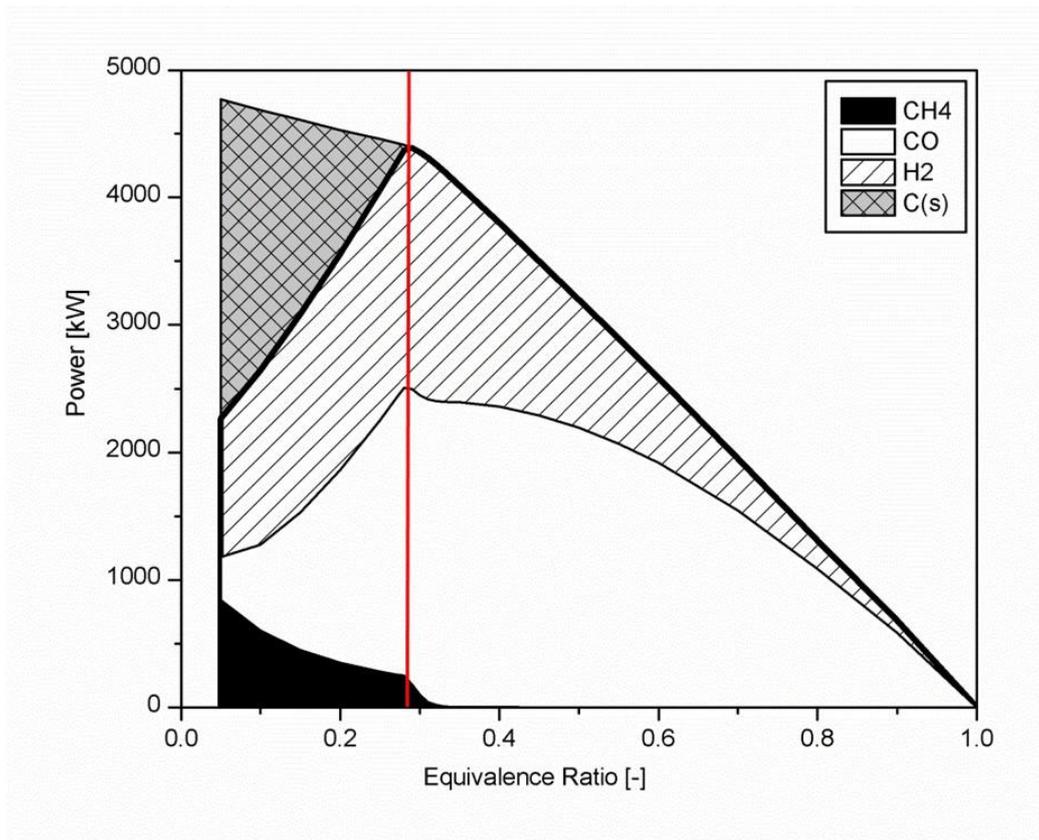
403 **Fig. 5.** Adiabatic flame temperature as a function of equivalence ratio, depending on water
 404 content (a) and air inlet temperature (b) (Mevissen et al. 2009b)

405

406 Another important factor in gasification is the yield in combustible compounds and
 407 chemical power in the products. And again, the solid carbon boundary plays a vital role. Fig. 6
 408 shows the amount of chemical power contained in the products of the gasification of wood with
 409 a water content of $WC = 10$ wt% and an air inlet temperature of $AIT = 25$ °C, depicting the
 410 contribution of the respective combustible components to the chemical power by stacking the
 411 individual values to a composite curve. As generally foreseeable the total amount of chemical
 412 power contained in the gasification products decreases with the increase of ER , because an
 413 increasing part of the fuel is combusted. But below the solid carbon boundary a part of the
 414 combustible products contributing to the chemical power is solid carbon, which is not accessible

415 to the downstream producer gas utilization. The chemical power contained in the gas phase,
 416 which is delimited by the bold solid line on top of the hydrogen contribution, is increasing with
 417 rising ER until the solid carbon boundary, where it has its maximum value, and decreasing with
 418 further increase of ER above that point. From this picture another important conclusion can be
 419 drawn immediately: although methane has a by far higher net calorific value at standard
 420 temperature and pressure (1,025.13 hPa, 0 °C) of $H_i = 35.883 \text{ MJ m}^{-3}$ compared to carbon
 421 monoxide ($H_i = 12.633 \text{ MJ m}^{-3}$) and hydrogen ($H_i = 10.783 \text{ MJ m}^{-3}$), it is not advisable to
 422 operate the gasifier in a way that maximizes the methane content of the producer gas. Such an
 423 approach to optimization would sacrifice a large amount of chemical power to the solid phase
 424 of products, as methane is practically present in the producer gas only below the solid carbon
 425 boundary. (Schulzke 2013)

426



427

428 **Fig. 6.** Chemical power content in synthesis gas as a function of equivalence ratio and gas
 429 composition (according to Schulzke and Unger 2011)

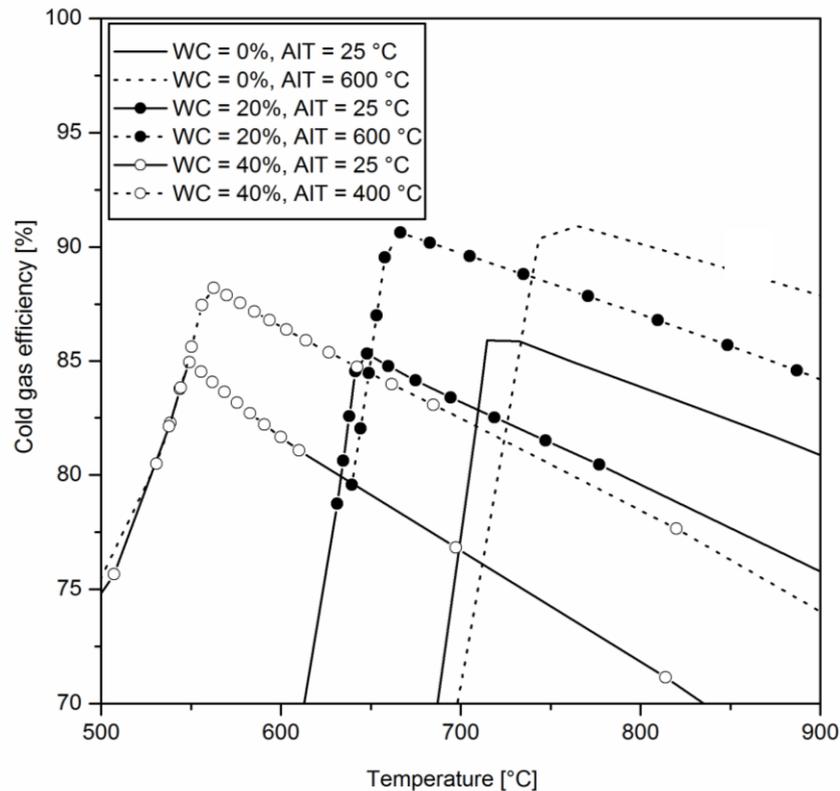
430

431 The cold gas efficiency of a gasifier is defined as the ratio of chemical power of the
 432 gaseous products expressed as lower heating value at 25 °C and the chemical power of the fuel
 433 feed. As the chemical power of the wooden fuel is the same for all equivalence ratios, the cold

434 gas efficiency equals the bold solid line of chemical power contained in the product gases
435 presented in Fig. 6 divided by a constant factor, which gives an identical development of cold
436 gas efficiency over ER . The highest thermodynamically possible cold gas efficiency is achieved
437 exactly at the solid carbon boundary, which again emphasizes the importance of this point. For
438 the shown example of a fuel with a water content of $WC = 10$ wt% and an air inlet temperature
439 of $AIT = 25$ °C the maximum cold gas efficiency equals approximately 86%.

440 As can be seen from Fig. 5, the adiabatic flame temperature AFT is a continuously rising
441 function of the equivalence ratio ER . Therefore, the abscissa can be explicitly and
442 nonambiguously expressed by the AFT . Fig. 7 shows the cold gas efficiency as a function of
443 AFT , which for fluidized beds is identical with the bed operating temperature. The maximum
444 value of cold gas efficiency for any combination of air inlet temperature AIT and fuel water
445 content WC marks the solid carbon boundary. For a certain combination of AIT and WC the
446 cold gas efficiency dramatically drops below the temperature representing the solid carbon
447 boundary, while it decreases comparatively smooth above that point. From this result a fairly
448 easy control strategy for optimized operation – at least for fluidized bed systems – can be
449 deduced: the temperature representing the solid carbon boundary should be determined
450 experimentally for the given gasifier and fuel, and subsequently the gasifier should be operated
451 at a temperature slightly above it to retain a certain security for the control system to definitively
452 avoid operation below the solid carbon boundary. A slight increase in air supply or decrease in
453 wood fuel supply – both measures slightly increasing the equivalence ratio ER – would increase
454 the operating temperature if necessary and vice versa.

455



456

457 **Fig. 7.** Cold gas efficiency as a function of fluidized bed operating temperature, depending on
 458 fuel water content and air inlet temperature (Schulzke and Unger 2011)

459

460 In general thermodynamic equilibrium calculations exhibit some shortcomings if
 461 compared to experimental measurements at real gasifiers. Even at very low adiabatic flame
 462 temperatures, hydrocarbons higher than methane and aromatic compounds with one or more
 463 rings are not present in equilibrium in contrast to real producer gases and also the content of
 464 methane in real producer gases is much higher than calculated from thermodynamic
 465 equilibrium. So, thermodynamic equilibrium is never reached in real gasifiers (Schulzke and
 466 Unger 2011), except of entrained flow gasifiers operating at very high temperatures, where the
 467 chances to achieve equilibrium are better. Even if the heat losses to the surrounding for a
 468 specific reactor are taken into account, the results only become slightly better.

469

A possible work-around was suggested by Kersten et al. (2002) with the concept of
 470 quasi-equilibrium approach. In that approach the temperature to calculate the equilibrium was
 471 chosen to be (significantly) lower than the measured operating temperature of the gasifier. With
 472 this measure the calculated composition of the producer gas was considerably closer to the
 473 measured values, especially concerning the methane content. But still, no light hydrocarbons
 474 and tar constituents are present in the calculated results.

475 These missing compounds can also be incorporated in the model calculations as there
 476 are distinct correlations of volatile organic compounds (light hydrocarbons) and tar constituents
 477 (phenolic and polyaromatic hydrocarbons) with methane and ethylene concentration (Dufour
 478 et al. 2011). Both model improvements – temperature approach and correlation of tar and
 479 hydrocarbon content with methane concentration – are specific to every combination of gasifier
 480 and fuel. They are helpful to describe and predict the behavior of the specific reactor under
 481 consideration in more detail and precision, but they don't model and represent the general
 482 interrelations and can therefore be omitted for first principle investigations.

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

489

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

491

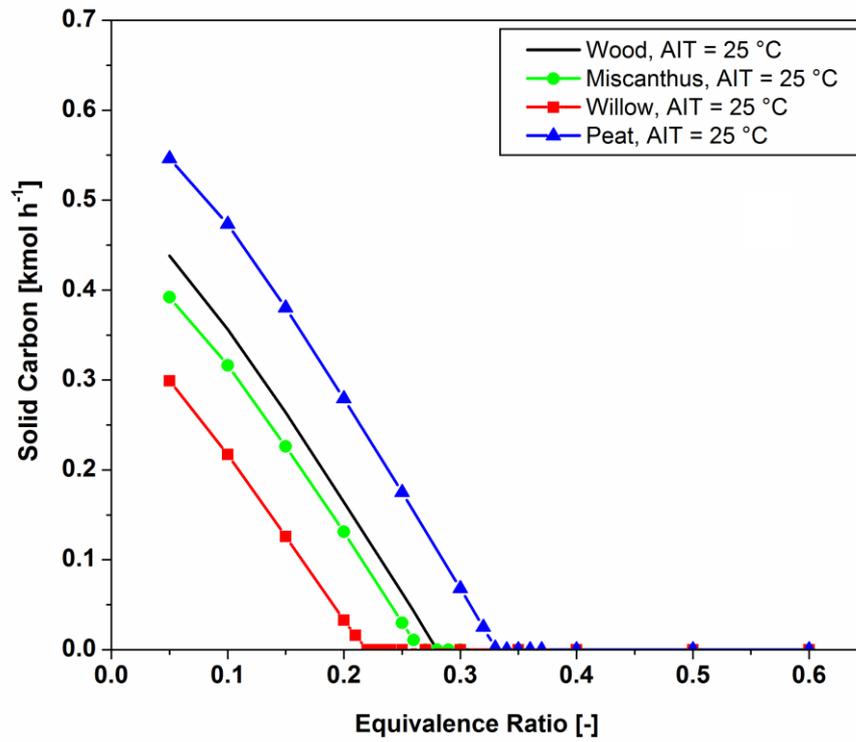
	C	H	N	O	formula	h_i
	wt%	wt%	wt%	wt%		MJ kg ⁻¹
Reference ^a	50.0	6.0	0.0	44.0	CH _{1.44} O _{0.66}	18.72
Wood (Spruce)	47.9	6.3	0.1	45.7	CH _{1.56} N _{0.002} O _{0.718}	17.9
Miscanthus	45.9	6.4	0.5	47.2	CH _{1.66} N _{0.01} O _{0.771}	17.4
Willow	44.8	6.5	0.3	48.4	CH _{1.772} N _{0.006} O _{0.81}	17.8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

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

493

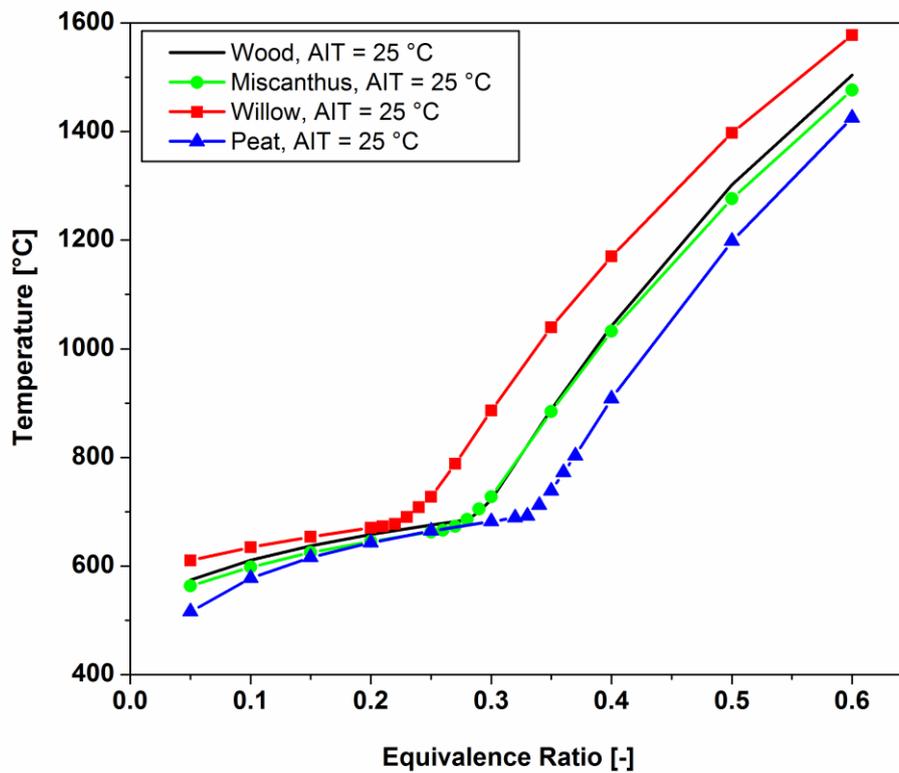
494 Fig. 8 depicts the results of the thermodynamic equilibrium calculations for the four
 495 different fuel compositions as char formation (a) and adiabatic flame temperature *AFT* (b) over
 496 equivalence ratio *ER*. The general behavior of all fuels is identical to the results presented for
 497 the reference composition of wood in more detail above. The location of the solid carbon
 498 boundary as well as the absolute value of adiabatic flame temperature depend on the varying
 499 composition of each fuel, but for all fuels there is a distinct solid carbon boundary and the
 500 behavior below and above this boundary changes in a similar way as described for the reference
 501 composition of wood.

502



503

a)



504

b)

505 **Fig. 8.** Solid carbon formation (a) and adiabatic flame temperature (b) as a function of
 506 equivalence ratio for different fuels (Mac an Bhaird et al. 2009)

507

508 Calculations of thermodynamic equilibrium for every new fuel, which is intended to be
 509 gasified in an existing reactor, gives insight in which direction the other fuel composition will
 510 drive the reactor's behavior and is therefore to be recommended before applying the first batch
 511 of new fuel to the gasifier.

512

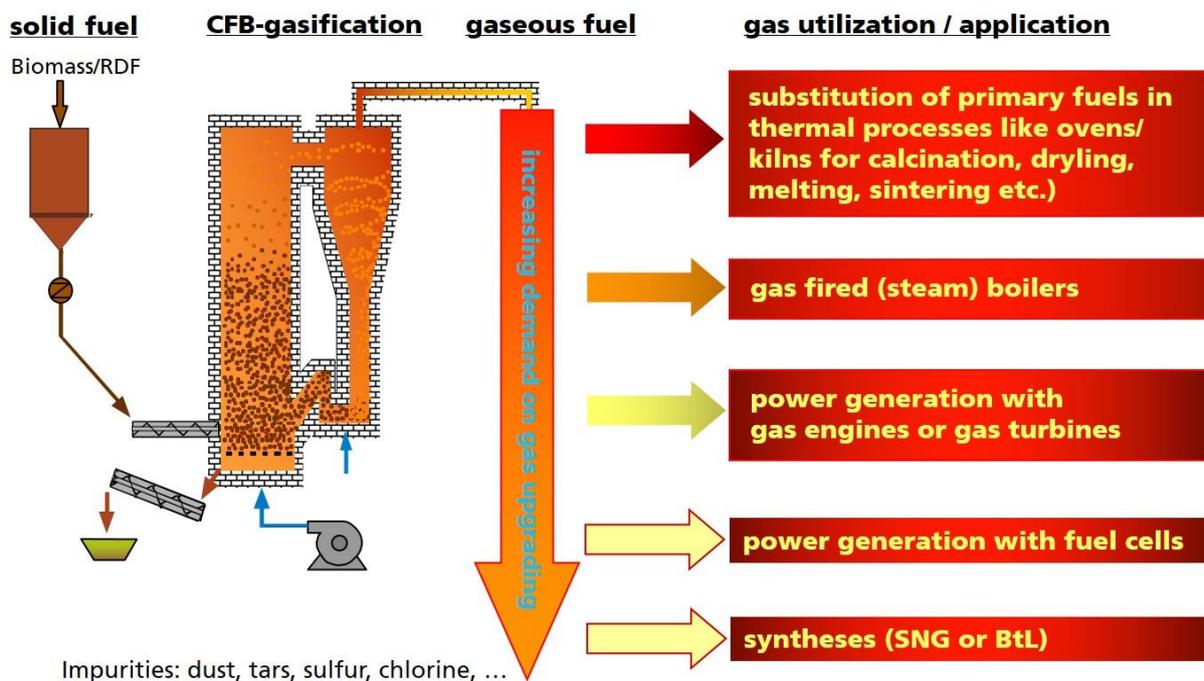
513

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

514

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

523



524

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

526

527 Several examples exist for the direct substitution of fossil fuel in thermal processes from
 528 very small scale to very large scale: on one side a pottery in Bavaria uses a fixed bed downdraft

529 wood gasifier with a thermal capacity of about 200 kW to replace approximately one third of
530 their fuel demand in the tunnel furnace to fire the pottery and on the other hand at the cement
531 factory of Rüdersdorf near Berlin a circulating fluidized bed gasifier with a fuel capacity of
532 100 MW is used to fire the calciner. The last gasifier was commissioned in 1997 and since 2000
533 it is operational on full capacity with several waste materials ranging from refuse derived fuel
534 (RDF) to tar paper (Scur 2000, Yates and Lettieri 2016). Both installations only apply a dust/fly
535 ash/char removal by a quite simple filter.

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

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

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

563 bed material towards tar conversion already inside the gasifier is olivine (Ising et al. 2004,
564 Rauch et al. 2006, Thunman et al. 2018).

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

572

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

574

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

575

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

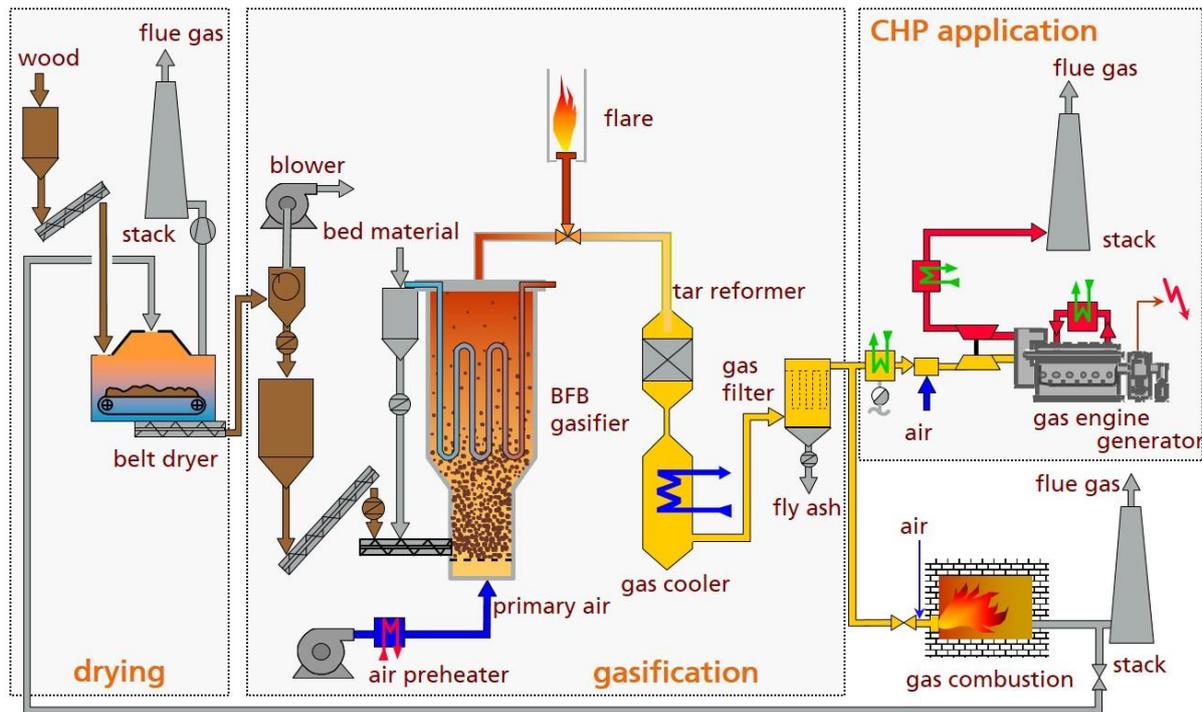
586 For the removal of tar from the producer gas the methods condensation, absorption and
587 adsorption are used or combinations thereof. Commercial applications of tar removal by
588 absorption using bio-diesel in a scrubber, e.g. developed by TU Vienna, were demonstrated at

589 the Güssing gasifier (Pröll et al. 2005) and at the GoBiGas-facility in Gothenburg (Iskov and
590 Rasmussen 2013). ECN in The Netherlands developed a combination of condensation and
591 absorption called OLGA (Rabou et al. 2009, Zwart et al. 2009), in which the producer gas is
592 cooled down in a first heat exchanger to condense the heavy tar components and subsequently
593 scrubbed with a solvent to absorb the remaining light tars. As adsorbent char from gasification
594 or pyrolysis gained new attention in research quite recently (Ahmad et al. 2016, Neubauer and
595 Elhami 2016).

596 Although tar compounds cause major difficulties in producer gas utilization as they
597 condense in the cold parts of the plant provoking fouling and pipe blockage, they also provide
598 a significant contribution to the heating value of the producer gas. While the concentration of
599 tar compounds in total only is around 0.5 vol%, it can make up to 10% of the lower heating
600 value. So, the removal of tar from the producer gas would in consequence lead to a significant
601 loss in energy content and hence process efficiency. Therefore, it is promising to keep the
602 energy content in the gas by converting the tar compounds into typical synthesis gas
603 constituents like methane, carbon monoxide and hydrogen. This can be achieved by thermal
604 cracking on one side or catalytic conversion by steam or dry reforming with CO₂ on the other
605 side. Thermal cracking requires the producer gas to be heated up to temperatures above
606 1,200 °C to achieve temperature induced conversion of the tar compounds. This approach was
607 successfully demonstrated by Nexterra in Vancouver, Canada (Claus 2012). Catalytic tar
608 conversion was investigated for long by many groups (Ising 2002, Corella et al. 2004a, Ising et
609 al. 2004, Pfeifer et al. 2007, Schulzke 2011, Shen and Yoshikawa 2013, Hamel et al. 2014,
610 Simell et al. 2014, Varga 2015, Kaisalo 2017) and commercially demonstrated at the power
611 station in Skive, Denmark (Andersson et al. 2017). Many catalysts are suggested for the
612 conversion of tar compounds, but the vast majority comprise of Ni-based steam reforming
613 catalysts or platinum group metals, also often used for steam reforming (Bock et al. 2015)

614 Finally, a fully developed example for combined heat and power production based on
615 biomass gasification in a scalable configuration is reported in this section. Fig. 10 shows the
616 general plant layout, which was developed and evaluated by Fraunhofer UMSICHT (Schulzke
617 2012a).

618



619

620 **Fig. 10.** Power plant concept based on bubbling fluidized-bed gasification and dry gas
 621 cleaning (Schulzke 2011b)

622

623

624 The power plant process starts with a biomass drying section. As displayed in Fig. 10
 625 this dryer can be fired with a dedicated combustion chamber or – more economical – with
 626 residual process heat from producer gas cooling. The biomass is gasified in an air-blown
 627 atmospheric bubbling fluidized bed at around 915 °C with olivine as bed material, which is
 628 partially active for tar conversion. A tar reforming reactor operating in high dust gas is directly
 629 connected to the gas outlet of the gasifier. The catalyst within this reactor has a honeycomb
 630 structure to cope with the comparatively high particle concentration of about 10 g m^{-3} (stp).
 631 After the tar reformer the producer gas can easily be cooled down to temperatures around
 632 120 °C, at which classical baghouse filters can be applied to fully remove the particles from the
 633 gas. Finally, the gas can be cooled down to 40 °C to knock out the steam content and to match
 634 the gas engine entrance requirements with regard to water vapor. An internal combustion engine
 635 based on spark ignition is used to produce electricity and heat, which both are exported to
 636 external networks. The process concept is described in detail in Schulzke (2012a).

636

637 The potential of such systems was assessed by economic and environmental
 638 investigations. The investment cost for total power stations and production cost for electricity
 639 were calculated for four different capacities ranging from 100 kW fuel supply to 10 MW
 640 (Schulzke 2011a,b, Schulzke 2012a). The estimated investment cost lie well within the range

640 of published investment cost for similar installations – both for gasification and direct
641 combustion (Schulzke 2011b). The main results of assessment were the large potential for
642 greenhouse gas savings on one hand and high electricity production costs on the other hand.
643 The greenhouse gas emissions range from up to 70 g CO₂-equivalent per kWh_{el} in the smallest
644 setup to 32 g CO₂-equivalent per kWh_{el} in the largest scale (Schulzke 2012b, Schulzke 2012c)
645 compared to the average of 597 g CO₂-equivalent per kWh_{el} in Germany's electricity mix for
646 the year 2010, where the transmission losses in the grid are included (Thrän et al. 2010). Even
647 for the worst plant configuration still a CO₂ emissions reduction of more than 500 g per kWh_{el}
648 could be achieved. The production cost for electricity also vary greatly with plant capacity: at
649 100 kW fuel input the production cost add up to 930 € per MWh_{el} and drop to 150 € per MWh_{el}
650 for the largest configuration with 10 MW fuel input (Schulzke 2012a,b,c). In 2010 the average
651 production cost of electricity in the German grid was 70 € per MWh_{el} (Thrän et al. 2010).
652 Without the high feed-in tariff, which was in effect in Germany from 2004 to 2012, biomass-
653 based gasification-driven heat and power stations were not economical. And the same holds
654 true for the majority of the developed countries: generally no commercial operation is feasible
655 for gasification power stations in capacities from 1 MW to approximately 50 MW without any
656 form of subsidy.

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

666

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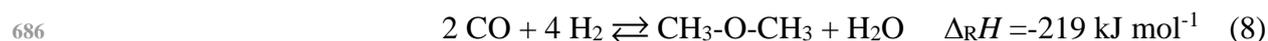
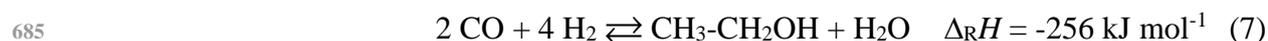
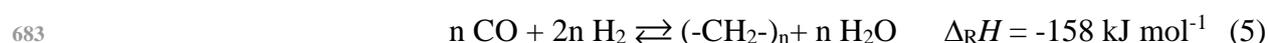
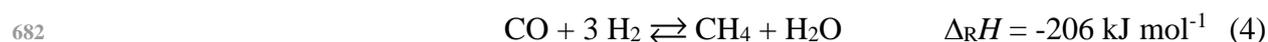
Producer gas utilization II: fuels and base chemicals

668

669 The producer gas generated by biomass gasification could be used for heat and power
670 production as discussed in the previous section. In addition, it will also be suitable for the
671 synthesis of chemicals and fuels, provided the nitrogen content of the producer gas is low
672 enough (virtually zero). In general, the producer gas from allothermal gasification with steam
673 and from autothermal gasification with pure oxygen as gasifying agent could both be applied.

674 The same approach for gas cleaning is applicable for chemical utilization than for power
 675 generation, but a much higher level of contaminants removal/conversion is required. In
 676 addition, especially sulfur needs to be removed, as this is a poison to most of the catalysts used
 677 in chemical synthesis from producer gas. The most common products from synthesis gas in
 678 chemical industry towards base chemicals and (transportation) fuels are methane (Eq. 4),
 679 Fischer-Tropsch-hydrocarbons FT (Eq. 5), methanol (Eq. 6), ethanol (Eq. 7) and dimethyl ether
 680 DME (Eq. 8).

681



687

688 where $\Delta_{\text{R}}H$ is the standard enthalpy of reaction. The synthesis of methane requires a
 689 hydrogen/carbon monoxide-ratio of 3:1 while all other products show a stoichiometric demand
 690 of 2:1. Typically, the producer gas resulting from allothermal steam gasification has a H_2/CO -
 691 ratio around 2:1 and autothermal oxygen gasifiers deliver a producer gas with a H_2/CO -ratio at
 692 about 1:1 (Mevisse et al. 2009a). This would lead to the general conclusion that steam
 693 gasification processes might be more suitable for synthesis reactions.

694

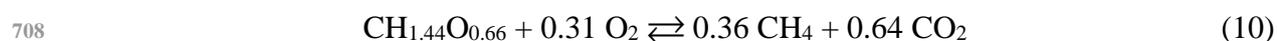


696

697 Either within the chemical reactor or in a separate reactor upstream the chemical
 698 conversion, a homogeneous water gas shift reaction (Eq. 9) can be conducted. When this gas
 699 conditioning reaction is added to any of the above reaction equations with the exception of
 700 methanol (Eq. 6), an overall reaction scheme comes up with an equimolar CO and H_2 demand
 701 on the left hand side and carbon dioxide as coproduct instead of water on the right hand side of
 702 each equation. With this modification, also producer gas from oxygen-blown gasifiers proves
 703 to be as suitable as steam-blown gasification. A last drawback of oxygen-blown gasification for
 704 fuels and chemicals production is at first sight the lower carbon conversion from biomass to the

705 desired products, as Eq. 10 und 11 exemplarily show for methane (Schulzke 2016) on pure
706 stoichiometry neglecting all conversion deficiencies.

707



710

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

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

732 A comprehensive, general review on synthesis gas utilization for the production of fuels
733 and chemicals is given by Rauch et al. (2013). The potential products suggested in Eq. 4-8 are
734 produced in larger amounts from natural gas reforming (except methane) and coal gasification.
735 Methane production options are thoroughly reviewed by Kopyscinski et al. (2010), methanol
736 by Olah et al. (2009), dimethyl ether by Mevissen et al. (2009a), Schulzke et al. (2010) and
737 Landälv et al. (2014) and gasoline production by methanol-to-gasoline process (MtG) by Haro

738 et al. (2013), Dahmen et al. (2012, 2017) and Stöcker (2010). Fischer-Tropsch synthesis also is
739 an old process invented in the early 30's of last century in Germany and intensively developed
740 by Sasol in South Africa. Such plants converting mainly coal to gasoline, kerosene and diesel
741 are operated in very large scales (Dry 2002). Relatively recently mixed alcohols with the major
742 compound ethanol are investigated in research (Rauch et al. 2013, Schulzke et al. 2011), while
743 the other products are produced in world-scale plants, but typically from fossil resources and
744 not from biomass. Synthesis gas from steam reforming of natural gas has a H₂/CO-ratio of 3:1
745 and synthesis gas resulting from coal gasification usually shows H₂/CO-ratios of about 0.5:1.
746 As mentioned above, the respective ratios of synthesis gas derived from biomass lies
747 somewhere in between 1:1 and 2:1. Therefore, the process concept for converting synthesis gas
748 into fuels or chemicals needs some adaptations when transferred from coal gasification or
749 natural gas steam reforming.

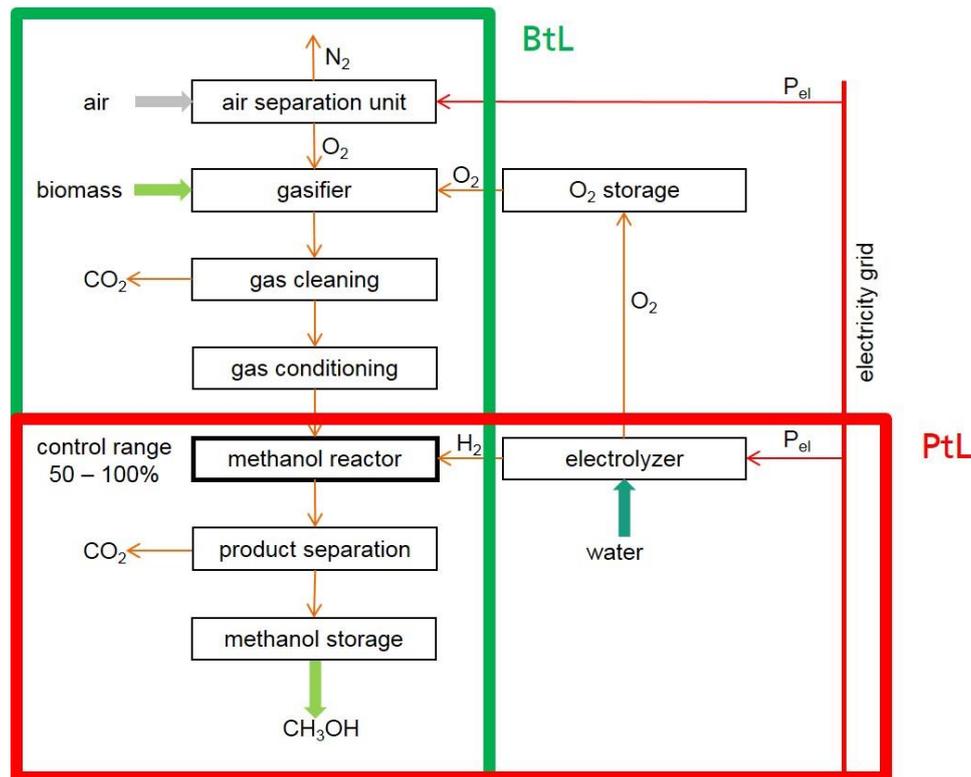
750 Besides synthesis gas composition especially plant capacity is an issue. The production
751 of substitute natural gas (SNG) – or more precisely methane – is demonstrated on the basis of
752 lignite gasification in the Great Plains Synfuels Plant in North Dakota, USA, since 1984 with
753 a capacity of 18,000 t d⁻¹ of lignite as input and – after some plant modifications in 1992 –
754 4.81 Mio. m³ d⁻¹ (Kopyscinski et al. 2010), equivalent to 2.0 GW of chemical energy content
755 of the produced methane. Demonstration systems for the production of SNG based on biomass
756 gasification were operated for instance at the Güssing gasifier with capacities of 10 kW and
757 1 MW (Kopyscinski et al. 2010). The largest demonstration on near-industrial scale was built
758 in Gothenburg, Sweden, with a capacity of 20 MW chemical energy content of SNG product
759 (Karlbrink 2015). The same difference in scale also holds true for the other possible products
760 like FT-liquids or methanol. The largest methanol plants (MegaMethanol) produce 5,000 t d⁻¹
761 from natural gas (Plass 2005), while the largest plant producing methanol from biomass –
762 Värmlands Metanol in Hagfors – is designed for a capacity of 296 t d⁻¹ (Grahn and Hansson
763 2014). And this plant has not yet been built – exemplifying the economic hurdles for biofuels
764 and biochemicals production from biomass. All these production processes strongly benefit
765 from economy of scale, but biomass distribution with low volume-specific energy density over
766 larger areas limit the maximum capacity of a single plant due to logistics reason. A promising
767 trend to overcome the economic difficulties is the development of new reactor concepts like
768 microchannel reactor systems instead of large scale tube bundle or slurry reactors, as
769 demonstrated for Fischer-Tropsch synthesis for instance at the Güssing gasifier in Austria
770 (Rauch et al. 2013, LeViness et al. 2011).

771 As already apparent from Eq. 10+11, the conversion of carbon into any of the desired
772 products is not complete, even for steam-blown allothermal gasifiers, as biomass is deficient in
773 hydrogen (Schulzke and Unger 2015b) and a noticeable amount of carbon dioxide is produced
774 as inevitable coproduct. The addition of renewable hydrogen, produced by water electrolysis
775 with electricity from wind power or photovoltaics, to the chemical reactor can improve the
776 carbon efficiency of all these reactions. This option constitutes a combination of biomass-to-
777 liquid (BtL) or biomass-to-gas (BtG) and power-to-liquid (PtL) or power-to-gas (PtG)
778 approaches. The producer gas coming from the gasifier is used as the CO₂ source for the PtX
779 system. And in such concepts oxygen-blown gasification processes have a clear advantage
780 compared to steam-blown gasifiers: the CO₂ is an integral part of the producer gas and the
781 degree of removal can be reduced, thus simplifying the process scheme. Alternatively, in steam-
782 blown gasification systems only a small amount of the CO₂ coproduct is contained in the
783 producer gas while the majority leaves the reactor system with the flue gas from the combustion
784 reactor applied to supply the process heat. Here, CO₂ recovery must be added to the flue gas
785 system, thus increasing the complexity and hence cost.

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

792 These concepts all assume classical plant operation strategy: ramp up of the plant to
793 nominal capacity followed by continuous operation in the optimal design point for as long as
794 possible. This becomes feasible only with very high shares of renewable electricity in the grid.
795 Fluctuating operation of the electrolyzer following the changing supply of wind and solar power
796 might already get some of these systems into reality as this operation approach could balance
797 supply and demand in the electricity grid without turning down for instance windmills or biogas
798 plants. This concept works in general with all products (FT with the most difficulties among
799 the suggested synthesis products), but it was exemplarily evaluated for methanol by Schulzke
800 and Unger (2015b, 2016) and Schulzke (2016). Fig. 11 shows a block flow diagram of the
801 combined BtL- and PtL-plant for the case of methanol synthesis.

802



803

804 **Fig. 11.** PBtL-concept, combination of methanol production from biomass and renewable
 805 electricity (Schulzke 2016)

806

807 If no surplus renewable electricity is available from the grid, the plant operates as
 808 “classical” BtL-plant with an oxygen-blown biomass gasifier operating at rated capacity
 809 followed by producer gas cleaning and gas conditioning including carbon dioxide removal and
 810 a methanol reactor operating at 50% rated capacity, which is an easy to achieve turndown ratio.
 811 Whenever surplus renewable electricity becomes available from the grid the electrolyzer starts
 812 operation producing hydrogen and oxygen. Oxygen is stored in a tank and hydrogen is
 813 introduced to the methanol reactor while the biomass gasifier continuously operates at rated
 814 power and the CO₂ removal in the gas conditioning system is (partly) bypassed. As possibility
 815 on the other end of the electricity balancing, the air separation unit can be turned down (thus
 816 reducing the electricity taken from the grid) and the stored oxygen can be used in the gasifier
 817 instead. By this means the complete PBtL-system with flexible operation can offer negative
 818 balancing power, increased carbon efficiency and – to a smaller amount – positive balancing
 819 power.

820

821 Some numbers based on the intended methanol plant in Hagfors emphasize the potential
 822 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

823 723 t d⁻¹ of CO₂ to the atmosphere. To double the output of the methanol reactor renewable
824 hydrogen must be added from an electrolyzer with a capacity of 120 MW_{el}. During full load
825 operation of the electrolyzer 56.4% of the CO₂ emissions resulting from the biomass are
826 converted to the desired product. (Schulzke 2016)

827

828

Conclusions

829

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

840 Many configurations of gasifier, producer gas cleaning and gas engine for the
841 production of electricity exist. Many installations have proven the technical feasibility of this
842 approach in very different scales. Presently they are only economically feasible in small scales,
843 mainly with subsidies. Due to the high potential for greenhouse gas emissions reduction of more
844 than 400 g kWh_{el}⁻¹ CO₂-equivalence even for countries like Germany which already have a high
845 share of renewable electricity in their grid, this missing profitability is a great pity and major
846 drawback.

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

854 With the increasing availability of renewable electricity in the grid in the future there is
855 again a great potential for biomass gasification. The deficiency in hydrogen, inherently present
856 in biomass, can be balanced by renewable hydrogen coming from water electrolysis, thus

857 increasing the carbon conversion efficiency eventually up to 100%. Combined installations
 858 with biomass gasification and Power-to-X components will very effectively balance the supply
 859 and demand in electricity grid not only on the level of the distribution network but also on the
 860 level of transmission network, as they can absorb power in the range of hundreds of MW.

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862

863

Symbols

864

865	<i>AFT</i>	adiabatic flame temperature	°C
866	<i>AIT</i>	air inlet temperature	°C
867	<i>ER</i>	equivalence ratio	kg kg ⁻¹
868	<i>H_i</i>	lower heating value (gas)	MJ m ⁻³
869	<i>h_i</i>	lower heating value (solid)	MJ kg ⁻¹
870	Δ_{RH}	standard enthalpy of reaction	kJ mol ⁻¹
871	<i>WC</i>	water content	wt%

872

873

874

Conflict of interest

875

876 There is no conflict of interest.

877

878

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