Abstract—The interest on biomass utilization has been enhanced in recent years. Especially the production of so called Secondary Generation Fuels (SGF), like Substitute Natural Gas (SNG) has been focus of research and development. With the Biomass-Heatpipe-Reformer (HPR), an innovative pressurized allothermal gasification technology, a hydrogen-rich product gas can be generated, which is well suitable for production of SNG. A robust and flexible mathematical model of the HPR was developed and implemented into commercial simulation software within this work. Based on this model the thermo-chemical conversion process of solid biomass in the HPR was analyzed. The operating parameters reactor temperature and pressure as well as mean residence time were varied and their influence on amount and composition of residue char was determined. Further an efficiency diagram, characterizing the operation state of the HPR, was created.

Keywords—Biomass gasification, Biomass-Heatpipe-Reformer, Mathematical modeling, Sensitivity analysis, Substitute Natural Gas

I. INTRODUCTION

The use of biomass as renewable and sustainable energy carrier is one promising option to increase the contribution of renewable energy production and lower the dependency of primary fossil fuels. Thereby particular attention is paid to the production of so called Secondary Generation Fuels (SGF), like Substitute Natural Gas (SNG), Bio Hydrogen (BioH2) or Fischer-Tropsch fuels. Because of the high conversion efficiency and the already existing gas infrastructure, especially the SNG production pathway seems to be reasonable.

For the thermo-chemical conversion of solid biomass into SNG, a gasification technology generating a product gas with a suitable composition is required. The Biomass-Heatpipe-Reformer (HPR), a patented gasification technology for the generation of a hydrogen-rich product gas from renewable fuels by allothermal pressurized steam gasification, produces a syngas well suitable for the production of SNG [1].

The objective of the present work has been the development of a robust and flexible mathematical model to describe the thermo-chemical conversion of solid biomass in the HPR. Based on this model the gasification process as well as the influence of the most important operation conditions was analyzed. In detail the influence of reactor temperature and pressure as well as residence time of the biomass char in the reformer on fuel conversion rate and composition of residue char and product gas was determined. Further an efficiency diagram, characterizing the operation state of the HPR, was created.

II. THE BIOMASS-HEATPIPE-REFORMER

The Biomass-Heatpipe-Reformer is a patented innovative development for allothermal pressurized steam gasification of solid biomass [2], [3]. Fig. 1 illustrates the three main parts of the HPR.

In the first part, the Reformer, designed as a bubbling fluidized bed gasifier, the endothermic gasification process of
the solid biomass takes place at a pressure up to 5 bar. The fuel is fed into the Reformer from the upper part through a lock hopper system. As gasification agent, as well as for fluidization, superheated steam is used.

The second of the main parts is an integrated sand filter, where dust and char particles are separated from the product gas before leaving the Reformer. The separated particles are fed into the combustion chamber.

The atmospheric stationary fluidized bed combustion chamber is the third part of the HPR. Here a part of the fuel is combusted together with the residue char remaining from gasification in order to supply the demanded heat for the endothermic gasification process.

Heat is transferred from the combustion chamber to the reformer using so called Heatpipes. Heatpipes are enclosed metal pipes containing an alkali metal working fluid (e.g. Na, K). The working fluid evaporates in the area of the exothermic combustion chamber fluidized bed (≈900°C) whereby it consumes energy, which is then released in the area of the endothermic gasification fluidized bed (≈800°C) by condensation. The resulting heat transfer coefficients are orders of magnitudes higher than for forced gas convection.

A 500 kWth pilot plant of the Biomass Heatpipe Reformer has been in operation in Pfaffenhofen (Germany) over the past two years [5]. Further, a commercial sized CHP application with a thermal power input of 1,3 MW is currently under construction in Grassau (Germany).

III. MATHEMATICAL MODELING

A. Classification of mathematical models

Mathematical models can be divided into thermodynamic equilibrium- (EM) and kinetic rate models (KM). KM provide an nth order kinetic approach was implemented in the model. Consider the non-equilibrium heterogeneous fuel conversion, are described using thermodynamic equilibrium equations. To model was developed. The homogeneous gas phase reactions [6].

Review and analysis of biomass gasification models is given in [6]. Pseudo-equilibrium models (Pseudo-EM). A comprehensive relations making them more realistic. Such models are called and optimization. EM are often supported by empirical conditions, what makes them a useful tool for process design thermodynamic limits of performance under different reactor design. EM in contrast are computationally less intensive and independent of reactor design and therefore more convenient for process studies. Moreover, EM predict thermodynamic limits of performance under different conditions, what makes them a useful tool for process design and optimization. EM are often supported by empirical relations making them more realistic. Such models are called Pseudo-equilibrium models (Pseudo-EM). A comprehensive review and analysis of biomass gasification models is given in [6].

In the present work a kinetically modified equilibrium model was developed. The homogeneous gas phase reactions are described using thermodynamic equilibrium equations. To consider the non-equilibrium heterogeneous fuel conversion, an nth order kinetic approach was implemented in the model. This way, the model becomes more predictive for the performance of the gasification process.

B. The Simulation Software IPSEpro

For process modeling the commercial process simulation software IPSEpro [7] was used. IPSEpro is a steady state, equation oriented simulation tool for modeling and analyzing processes in energy- and chemical engineering as well as related areas. With IPSEpro’s Model Development Kit (MDK) new component models can be built up or already existing ones can be modified. Consequently user specified models can be prepared and implemented in an existing model library. For the present work, the IPSEpro Pyrolysis and Gasification Process Library (PGP-Lib) [8] has been used as basic library. The substance classes contained within this library are given in Table I. Except the pure water/steam stream, which consists of pure H2O only, the streams can carry loadings of other substance classes beside the main substance class.

TABLE I

<table>
<thead>
<tr>
<th>Substance class</th>
<th>Species / Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>Ar, C2H2, C2H4, C3H8, CO, CO2, H2, H2O(g), H2S, HCl, HCN, N2, N2O, NH3, NO, O2, SO2</td>
</tr>
<tr>
<td>Organic</td>
<td>C, H, O, N, S, Cl</td>
</tr>
<tr>
<td>Inorganic</td>
<td>K2O, MgO, CaO, SiO2, MgSiO4, Fe2SiO4, MgCO3, CaCO3, CaSiO3, CaOH2</td>
</tr>
<tr>
<td>Pure Water/Steam</td>
<td>H2O(l), H2O(g)</td>
</tr>
</tbody>
</table>

IV. THE HPR-MODEL

The mathematical model of the HPR is subdivided into a model of the combustion chamber and the reformer as shown in Fig. 2.

A. Combustor

The combustor model handles mass and energy balances. The energy balance implemented in each kind of chemical reactor model is formulated using total thermodynamic enthalpies of all streams including their possible loadings. The total thermodynamic enthalpy h(T) additionally includes the enthalpy of formation Δhν298 (1). Thus, heats of reaction are basically considered.

\[ h^\circ(T) = \Delta h^\circ_{298} + \int_{298,15}^{T} c_p(T) \, dT \]  

(1)

Besides mass and energy balances, equations describing the combustion process are implemented in the model. In case of
the excess air coefficient $\lambda > 1$ complete combustion is assumed. In case of incomplete fuel conversion ($\lambda < 1$), the amount and composition of char must be specified. The char leaves the combustion chamber together with the ash as a loading of the flue gas. Inorganic solids (ash, dust) are treated as chemically inert and are balanced separately. A possible heat loss towards the environment is included within the energy balance.

B. Reformer

In analogue to the combustor-model, mass and energy balances are implemented in the reformer model too. As already mentioned above, thermodynamic equilibrium equations are used to describe the homogeneous gas phase reactions and consequently to determine the composition of the syngas leaving the reformer. TABLE II shows a summary of these reactions.

**TABLE II**
**HOMOGENEOUS GASIFICATION REACTIONS**

<table>
<thead>
<tr>
<th>Reaction Equation</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$</td>
<td>Water gas shift reaction (R1)</td>
</tr>
<tr>
<td>$\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2$</td>
<td>Methane steam reforming (R2)</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_6 + 2\text{H}_2\text{O} \leftrightarrow 2\text{CO} + 4\text{H}_2$</td>
<td>Ethylene steam reforming (R3)</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_4 + 2\text{H}_2\text{O} \leftrightarrow 2\text{CO} + 5\text{H}_2$</td>
<td>Ethane steam reforming (R4)</td>
</tr>
<tr>
<td>$\text{C}_3\text{H}_8 + 3\text{H}_2\text{O} \leftrightarrow 3\text{CO} + 7\text{H}_2$</td>
<td>Propane steam reforming (R5)</td>
</tr>
<tr>
<td>$\text{N}_2 + 3\text{H}_2 \leftrightarrow 2\text{NH}_3$</td>
<td>Ammonia synthesis (R6)</td>
</tr>
<tr>
<td>$\text{NH}_3 + \text{CO} \leftrightarrow \text{HCN} + \text{H}_2\text{O}$</td>
<td>Cyanide formation (R7)</td>
</tr>
</tbody>
</table>

It is well known, that even the homogeneous gas phase reactions of the biomass gasification process are not completely governed by thermodynamic equilibrium. Thus, thermodynamic equilibrium should not be stringent defined by the model, it should be possible to define a deviation from the equilibrium state. Therefore, the parameter $p\delta_{eq}$, calculated by the logarithm of the ratio of the actual partial pressure product and the equilibrium constant, is implemented into the reformer model [8]:

$$p\delta_{eq}(p_i, T) = \log_{10} \left[ \prod_i \left( \frac{p_i}{p_i^e} \right)^{\nu_i} \right].$$

(2)

The thermodynamic equilibrium constant $K_p(T)$ is calculated directly from thermodynamic data according to the following equation:

$$K_p(T) = \exp \left( \frac{-\Delta G^o_p(T)}{RT} \right) = \prod_i \left( \frac{p_i^e}{p_i} \right)^{\nu_i}$$

(3)

with the partial pressures of the species at thermodynamic equilibrium $p_i^e$ and the Gibbs free enthalpy of reaction $\Delta G^o_p(T)$ at standard pressure $p_0$ and temperature $T$.

If $p\delta_{eq} < 0$, the actual state of the drain gas is on the product side and thus the reaction can only proceed towards the reactants. In case of $p\delta_{eq} = 0$, thermodynamic equilibrium is fulfilled. By this, it is possible to describe thermodynamic equilibrium of certain reactions on the one hand. Otherwise it can be calculated, to what extend thermodynamic equilibrium is reached with respect to a certain chemical reaction for a given syngas composition.

A determining influence on the energy balance of the HPR as well as on product gas composition can be attributed to the fuel conversion rate. For calculation of the fuel conversion, heterogeneous reactions have to be considered within the model. The thermo-chemical conversion of solid biomass with steam is described by the overall reaction

$$C_nH_{2n+2} + (x - z)\text{H}_2\text{O} \leftrightarrow x \text{CO} + \left( \frac{y}{2} + x - z \right)\text{H}_2,$$

(R8)

According to [9] and [10], the kinetic behavior of the steam gasification process is primarily governed by the heterogeneous water gas reaction (R9). Thus, the gasification of wood char with steam can be described with this reaction.

$$C(x)_z + \text{H}_2\text{O} \leftrightarrow \text{CO} + \text{H}_2$$

(R9)

As known, the heterogeneous water gas reaction is endothermic and connected with a volume increase. Therefore, thermodynamic equilibrium is shifted towards the products CO and H$_2$, with increasing temperature and decreasing pressure.

The reaction rates of heterogeneous reactions are orders of magnitude lower, compared to homogeneous gas phase reactions. Hence, thermodynamic equilibrium is not reached for typical gasification conditions (temperature, residence time of the char). Due to the deviation from equilibrium, which is partly rather large, an equilibrium approach is not reasonable for calculation of the fuel conversion rate. Instead, a kinetic approach is implemented in the reformer model. Following [10] and [11], an $n^{th}$ order approach is used to formulate the kinetic approach. Although this approach is characterized by a low effort for implementation and a low calculation time, it provides sufficient good results [9]. As it is widely used, the required kinetic parameters can be found in literature for different wood types. In the present work the kinetic parameters for beech char according to [10] are used (TABLE III).

**TABLE III**
**KINETIC PARAMETERS FOR BEECH CHAR [10]**

<table>
<thead>
<tr>
<th>Activation Energy $E_a$</th>
<th>211 ± 6,1 kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequency factor $k_0$</td>
<td>$1,71 \cdot 10^7 \pm 1 \cdot 10^7$ s$^{-1}$bar$^n$</td>
</tr>
<tr>
<td>Reaction order $n$</td>
<td>0,51 ± 0,05</td>
</tr>
</tbody>
</table>

Because of the large deviation from thermodynamic equilibrium, only the forward reaction of (R9) has to be considered. This leads to the following correlation for the conversion of solid carbon in the reformer:
Recent Researches in Mechanics

where

\[ X_C = m_c k_0 \frac{e^{\frac{-E_g}{R_T}}}{p_{H_2O}^n} \]  \hspace{1cm} (4)

with \( m_c \) the mass of fixed carbon in the reformer and \( p_{H_2O} \) the partial pressure of H\(_2\)O in the gas phase. The mass of fixed carbon in the reformer is calculated from the biomass input \( m_{f,\text{fuel}} \), the amount of carbon in the residue char \( \varphi_{C,\text{res}} \) referring to the fuel input and the mean residence time \( \tau \).

\[ m_c = m_{f,\text{fuel}} \varphi_{C,\text{res}} \tau \]  \hspace{1cm} (5)

The conversion of solid carbon further can be described based on the carbon balance over the reformer:

\[ X_C = m_{f,\text{fuel}} \left( \varphi_{C,\text{pyr}} - \varphi_{C,\text{res}} \right) \]  \hspace{1cm} (6)

Here \( \varphi_{C,\text{pyr}} \) is the amount of carbon in the primary pyrolysis char referring to the fuel input.

Combination of (4) to (6) leads to following equation for \( \varphi_{C,\text{res}} \):

\[ \varphi_{C,\text{res}} = \frac{\varphi_{C,\text{pyr}}}{1 + k_0 e^{\frac{-E_g}{R_T}} p_{H_2O}^n \tau} \]  \hspace{1cm} (7)

With the mass fraction of carbon in the residue char \( \mu_{C,\text{res}} \) as well as in the primary pyrolysis char \( \mu_{C,\text{pyr}} \), and the volatile matter of the biomass \( \varphi_{\text{volatile}} \), the amount of residue char \( \varphi_{\text{res}} \) can finally be calculated according to (8).

\[ \varphi_{\text{res}} = \frac{\mu_{C,\text{pyr}}}{\mu_{C,\text{res}}} \left( 1 - \frac{\varphi_{\text{volatile}}}{\mu_{C,\text{pyr}}} \right) \]  \hspace{1cm} (8)

The composition of the residue char is determined based on the pyrolysis char composition. Both chars are assumed to consist of C, H and O only. During gasification of the fixed char, a decrease of H- and O-content can be expected. In case of complete conversion, the residue char consists of pure carbon only. A linear progress with the fixed char conversion \( X_{\text{char}} \) is assumed within the model.

\[ \mu_{H,\text{res}} = \left( 1 - \frac{X_{\text{char}}}{100} \right) \mu_{H,\text{pyr}} \]  \hspace{1cm} (9)

\[ \mu_{O,\text{res}} = \left( 1 - \frac{X_{\text{char}}}{100} \right) \mu_{O,\text{pyr}} \]  \hspace{1cm} (10)

The fixed char conversion is defined as the mass of fixed carbon converted in the reformer related to the fixed carbon input.

With equations (8) to (10) the amount and composition of residue char leaving the reformer can be calculated. Besides the kinetic parameters for the \( n^\text{th} \) order approach only the composition of primary pyrolysis char and the volatile matter of the biomass have to be specified within the model. Data regarding the composition of primary pyrolysis char can be found in literature. An ultimate analysis of different wood chars is given in [9]. By adaption of the model parameter “volatile matter”, the calculated results can be fit to measured values.

Since the backward reaction of (R9) is not taken into account within the described \( n^\text{th} \) order kinetic approach, it would be possible, that the predicted conversion rate exceeds the conversion rate at thermodynamic equilibrium for very long residence times. In particular, this has to be regarded at elevated pressures, since a pressure increase results in a decrease of the thermodynamic upper limit for the conversion rate. Therefore, the thermodynamic equilibrium of (R9) is determined according to (2) and (3) and plausibility of the predicted results is checked.

V. RESULTS AND DISCUSSION

A. Basic operation conditions

A fuel analysis of biomass (wood chips) used for simulation is given in TABLE IV. The volatile matter are assumed to be 80 w.% of dry biomass.

<table>
<thead>
<tr>
<th>TABLE IV</th>
<th>FUEL DATA</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>50,41 w.% (waf)</td>
</tr>
<tr>
<td>H</td>
<td>6,74 w.% (waf)</td>
</tr>
<tr>
<td>O</td>
<td>42,69 w.% (waf)</td>
</tr>
<tr>
<td>N</td>
<td>0,15 w.% (waf)</td>
</tr>
<tr>
<td>S</td>
<td>0,01 w.% (waf)</td>
</tr>
<tr>
<td>Water content</td>
<td>19,55 w.%</td>
</tr>
<tr>
<td>Ash content</td>
<td>1,33 w.%</td>
</tr>
<tr>
<td>Lower heating value LHV</td>
<td>14780 kJ/kg</td>
</tr>
</tbody>
</table>

An important operating parameter for the HPR is the steam excess ratio \( \sigma \), which is defined as the quotient of feed steam to stoichiometric steam demand.

At design case, the reformer operates with a steam excess ratio of 2, a gasification temperature of 800°C and a pressure of 5 bar. Further, the superheated fluidization steam is at 460°C and air is supplied to the combustion chamber at a temperature of 600°C. The temperature of the biomass is supposed to be 25°C.

B. Fuel conversion and composition of residue char

In Fig. 3 the predicted fixed char conversion is illustrated as a function of gasification temperature and mean residence time. It shows that an increase in gasification temperature or mean residence time, leads to a higher conversion rate, as expected. In order to reach considerable conversion rates, favorable gasification conditions (high temperature and/or high residence time) are indispensable.

It should be stated, that the predicted results may be overestimated, primarily in the area of high conversion rates, since the backward reaction of (R9) is disregarded. Further, hydrogen inhibits the steam gasification reaction [10], which is also not considered within the \( n^\text{th} \) order kinetic approach.
Fig. 3: Fixed char conversion as a function of gasification temperature and mean residence time

Fig. 4 shows the composition of the residue char as a function of gasification temperature and residence time. A decrease of the H- and O-content is determined by the model with rising conversion. In case of zero conversion of fixed char, the residue char composition matches with that of the primary pyrolysis char. In case of complete conversion, the residue char consists of pure carbon only.

A pressure increase leads to a higher partial pressure of H$_2$O in the gas phase and thus to an increase of solid carbon conversion in the reformer according to (4). Concurrent the thermodynamic equilibrium shifts towards the reactants C($\text{s}$) and H$_2$O and therefore lowers the thermodynamic upper limit for the conversion rate as already explained above. The pressure dependency of the fixed char conversion is illustrated in Fig. 5 for several residence times.

Further, a significant influence on the conversion rate can be assigned to the steam excess ratio. A raise in $\sigma$ leads to a higher partial pressure of H$_2$O in the gas phase too. Simultaneously the equilibrium of (R9) is shifted towards the products, whereby the thermodynamic upper limit of the conversion rate is heightened.

C. Product gas composition

Thermodynamic equilibrium of the gas phase is assumed for all reactions stated in TABLE II, except for methane steam reforming (R2). Devolatilization of biomass leads to high contents of methane, which do not react completely to equilibrium. Measurements given in open literature [12], show methane contents in the range between 8 and 12 vol% of dry product gas. During operation in the pilot plant in Pfaffenhofen it was observed, that methane content remains relatively constant at about 10 vol% of dry product gas for different operation conditions. Thus, the methane content is set constant to 10 vol% of dry product gas.

Fig. 6 illustrates the influence of fixed char conversion on product gas composition and lower heating value (LHV) for design operation case.

With increasing conversion, more steam is used for the gasification process. The decreasing H$_2$O content in the
product gas shifts the equilibrium of the homogeneous water gas reaction (R1) towards the educts, whereby CO content increases. At the same time H₂ and CO₂ decrease. Due to the higher C/H-ratio the lower heating value rises.

D. Operation state of the HPR

Based on the amount of residue char leaving the reformer, three operation states of the HPR can be distinguished:
- lack of char,
- char limit and
- char excess.

Lack of char means, that the amount of residue char, which is fed into the combustion chamber, does not offer enough energy required for the endothermic gasification. In this case a part of the biomass feedstock has to be fed into the combustion chamber additionally. This corresponds to the standard operation of the HPR.

The char limit is reached, if only residue char is fed into the combustion chamber and no additionally biomass is required.

If more than necessary residue char leaves the reformer, the HPR operates in the area of excess char. The excess char is discharged from the process and its further use is not part of the present study.

According to [13], the described operation states can be represented within an efficiency diagram of the HPR (Fig. 7). The abscissa shows the fixed char conversion and the ordinate the combustion chamber efficiency. To quantify the performance of the various operation states, lines of constant cold gas efficiency are indicated within the diagram.

![Efficiency Diagram of the HPR](image)

Fig. 7: Efficiency diagram of the HPR

The combustion chamber efficiency \( \eta_{\text{comb}} \) is defined as the heat transferred into the reformer via the Heatpipes related to the thermal power input of the combustion chamber (residue char and biomass feedstock).

\[
\eta_{\text{comb}} = \frac{Q_{\text{Heatpipe}}}{m_{\text{res}} LHV_{\text{res}} + m_{\text{fuel,comb}} LHV_{\text{fuel}}} \tag{11}
\]

The cold gas efficiency \( \eta_{\text{chem}} \) is defined as the quotient of thermal power of the product gas to thermal power of the biomass fuel.

\[
\eta_{\text{chem}} = \frac{m_{\text{PG}} LHV_{\text{PG}}}{m_{\text{fuel}} LHV_{\text{fuel}}} \tag{12}
\]

Generally, higher char conversion leads to a more efficient process performance as the cold gas efficiency rises. If the HPR operates with a lack of char, an increase in the combustion chamber efficiency results in higher cold gas efficiency, because more heat is transferred to the reformer for a certain fuel input. In case of char excess, the combustion chamber efficiency shows no influence on the performance of the HPR. This is because the excess char is discharged from the process and not further considered within the energy balance.

VI. CONCLUSION

A kinetically modified equilibrium model of the Biomass-Heatpipe-Reformer was developed and the thermo-chemical conversion process of solid biomass was analyzed. Since the model considers the non-equilibrium heterogeneous fuel conversion, the obtained results show an effective better approximation of the process compared to a conventional equilibrium model. An interesting extension of the model for future work could be the implementation of the hydrogen inhibition effect.

REFERENCES