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Assessment of Potassium Concentration in Biochar before and after the After-burner of a Biomass Gasifier

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Small scale biomass gasifiers are gaining continuously attention due to the renewability of the fuel, the high feed-in tariffs and the novel systems with high efficiency that are becoming available in the market. Gasification is a thermochemical conversion process which mainly produces a gaseous fuel, i.e. syngas, but also other by-products. The most important ones are the solid phase residues, i.e. char and ash which represent 2-5 % of the initial input by mass. The small scale of operation does not allow the operators to develop centralized efficient strategies for managing char and ash. Thus, onsite strategies have been developed like the after-burner which converts part of the char and the alkali and heavy metals from solid to gas in order to reduce the concentrations of specific substances within the environmental limit. Commercial software are not able to properly model the operation of an after-burner and, therefore, not all the product streams of interest can be calculated. This work introduces a three phase thermodynamic model that aims to assist the operation of commercial software in modelling an after-burner. The key aspect of this three-phase model is that it uses the yield of char as a control variable for modelling the concentration potassium and how it fluctuates among the different phases. Combustion of potassium has the characteristic of creating several intermediate oxides that distribute among the solid and the gaseous phase for a wide range of operating conditions contrary to the majority of heavy and alkali metals which concentrate completely in the solid phase until a tipping point when they completely convert to gaseous products. The model returns results consistent with the onsite measurements and also is able to provide all the additional data, i.e. the molar fractions of gases and the amount of reactive oxygen, which can assist the optimization of the after-burner.

1. Introduction

The aim for reducing the environmental footprint of the energy industry has increased the interest in technologies with higher co-generation efficiencies. Biomass gasification is at the moment one of the most promising technologies for substitution of fossil fuels (Pinto et al., 2015). Technological applications of gasification can mainly be divided in large and small scale. In principle larger scale gasifiers utilize gas turbines and, by means of the Brayton cycle, electricity and heat are produced. Another potential advantage of large scale energy facilities is that the output heat from the gas turbines can be used downstream in a steam turbine, i.e. Rankine cycle, for additional production of electricity. The overall efficiency is increased by applying integrated combine cycles.
Nonetheless, in smaller scale energy plants under 1 MW_e the utilization of turbines comes with an efficiency penalty. In particular the isentropic efficiency is significantly influenced from the size of the turbine and in such low ranges of production the application of turbines is not viable (Vakalis and Baratieri, 2015b). In smaller scale facilities, gas internal combustion engines operate with high conversion efficiencies. Small scale gasification plants have become viable investments by taking advantage novel technological possibilities like improved -and usually patented- reactors, advanced filtering systems and internal combustion engines which operate with high

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compression ratios. Small scale gasifiers operating with biomass are gaining the most attention due to the renewability of the fuel (Vakalis et al., 2014).
A characteristic of small scale gasifiers is that - except the production of electricity and heat - other byproducts are generated that should be managed accordingly. The main by-products are tar compounds, which are heavy hydrocarbons, and the solid residues, i.e. char and ash, which exit together from the gasifier. Char is the carbon-rich solid product of gasification which has relatively high calorific value and its structure is similar to graphite. It usually has a 2 - 5 % product yield in comparison to the input biomass feedstock (Vakalis et al., 2015a). Finally ash consists primarily from the minerals but also from the alkali and heavy metals that remain in the solid phase after the gasification reaction. These alkali and heavy metals are of high interest due to their high environmental impact even in low concentrations. The management of the char and ash fraction is a high environmental priority but in small scale facilities the total mass flow of char and ash is low and does not allow the implementation of centralized efficient strategies. Vakalis et al. (2016) suggested that the most efficient method to process char and ash is by integrating onsite management strategies. The authors introduced a secondary reactor which utilized the char for further gas production. This method can increase significantly the co-generation efficiency of the plants but would require high capital investments for the installation of the suggested secondary reactors.

Figure 1: Basic design of a Joos gasifier (Spanner RE website, 2016)

An alternative approach for onsite management of the char and the ash has been the integration of an after-burner; a secondary reaction stage of char and ash with air in order to reduce the final mass of the solid residues. Another advantage of the after-burner is correlated with the concentration of alkali and heavy metals in the final solid phase. Gasification process takes place in lower temperatures than combustion and these reaction conditions allow several alkali and heavy metals to remain almost totally in the final solid phase. Therefore the concentration of these substances increases significantly and surpasses the concentration levels that are acceptable for safe disposal in landfills. The after-burner reduces the concentration of alkali and heavy metals that are of interest and thus convert the solid fraction of gasification into a material that is allowed to be disposed in landfills. Contrary to the solution of integrating a secondary reactor, the after-burner has already commercial applications. Figure 1 shows a commercial Joos gasifier which uses an after-burner.
The operating principle of the after-burner is relatively straight forward but the actual operating conditions that would be optimal is a matter of analysis. Therefore the operation is enhanced by means of thermodynamic modelling, but also elemental analysis of the input and output streams. Modelling primarily focuses on one hand on the yield of char and on the other hand on the optimal distribution of alkali and heavy metals between the gaseous and the solid phase in order to keep their concentration under the environmental limits. It has to be stated that software can be found in the market which specialize on the thermodynamic equilibrium of metals. Nonetheless, these software have the fundamental flaw of treating char as elemental carbon and not as graphite. Therefore it is unable to estimate the final char yield in relation to the reactive oxygen since all the carbon is returned to the gaseous phase in all cases. Thus no optimization can be performed by means of modelling in respect to the char yield. The inability to predict accurately the distribution of carbon between the phases denotes the inability of commercial models to predict correct compositions of gases like carbon dioxide and carbon monoxide that are products of the reactions between air and char. Finally, this model-assisted method is that the after-burner is air-tightly and compactly connected to the heat exchanging part of the gasifier and the direct measurements of input air are inherently problematic.
Table 1 shows that heavy and alkali metals tend to stay in the solid yield or totally disperse in the gaseous phase. Therefore, conventional thermodynamic modelling is not of great assistance since the majority of these

substances do not fluctuate among the gaseous and the solid phase for the temperatures of interest. The exception is potassium which shows an interesting distribution among the phases.

Table 1: Distribution of heavy metals among the different phases from treatment at 650 °C at the after-burner.

	Gas	Liquid	Solid
Al	0.0 %	0.0 %	100.0 %
Ba	0.0 %	0.0 %	100.0 %
Cl	100.0 %	0.0 %	0.0 %
Cr	0.0 %	0.0 %	100.0 %
Cu	0.1 %	0.0 %	99.9 %
K	20.8 %	0.0 %	79.2 %

The present work introduces a three phase thermodynamic model that has the scope to predict accurately the char yield, the reactant and product gases but also the concentration of potassium after the after-burner. This model aims not to replace well established commercial models but to assist their operation for peculiar cases like gasification facilities.

2. Materials and Methods

2.1.1 Development of the Thermodynamic Model

Thermodynamic models are generally preferred due to the less demanding computational power and less required input parameters. The scope of this work was the utilization of an opersource software for maximum adjustment possibilities. Therefore, the thermodynamic equilibrium solver Cantera was used for the development of the model. As mentioned before, the model is a 3-phase model where all the phases interact with each other as shown in Figure 2.

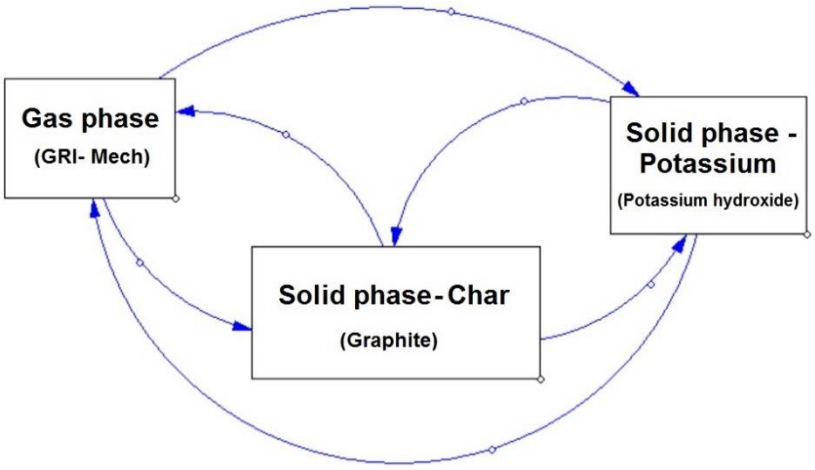

Figure 2: Fundamental operation scheme of the proposed model

The gaseous phase describes the input air and the final gas yield which is a product of the char-gas reactions and is represented by the GRI-Mech mechanism. The graphite mechanism is used for the char fraction. Finally, the potassium hydroxide mechanism includes potassium and potassium ions. The operating principle is the fluctuation/ reaction of char for different amounts of reactive oxygen. Then, for a given amount of oxygen - and for specific temperatures – the concentration of product gases and potassium is calculated. An additional feature of the model is that it can operate in "reverse- mode", which means that if the initial and final yields of char are known, then the oxygen and temperature can be calculated. This is a very useful feature since measuring the mass of the char before and after the after-burner is a rather simple and straightforward task.
For both modes of operation, Cantera can calculate the yields of the products with two different methods. The minimization of the elemental potential by using the RAND algorithm or the minimization of the Gibbs free energy by using the Villars–Cruise–Smith algorithm. It should be denoted that usually the two methods produce similar results.

2.1 Measurements and validation

Onsite measurements have been used for the assessment of the model's reliability. As mentioned in the section "Introduction" the after-burner is integrated in commercial Joos gasifier systems. A Joos HK-30 was used for extrapolating actual operating measurements. The gasifier is located in the Technical School of Zittau/ Görlitz and is operated in the framework of the project "Zittau power plant laboratory". The monitoring strategy of the plant is described by Salomo (2015).

3. Results and discussion

The monitoring results returned a 70 % recovered char yield and 80 % of potassium recovered yield for operation at 650 °C. As mentioned in the section "Introduction", commercial software diverts all the carbon in the gaseous phase since all of it is considered to react. This result is far from true, since a significant amount of the initial char is still present after the treatment in the after- burner. Figure 3 shows the reduction of the char yield in correlation with the reactive air at a temperature of 650 °C. For low equivalent ratio of 0.1 – 0.2 a final char yield of higher than 80 % is returned. Even for equivalent ratios of 0.4 the expected char yields are almost 60 % of the initial mass.

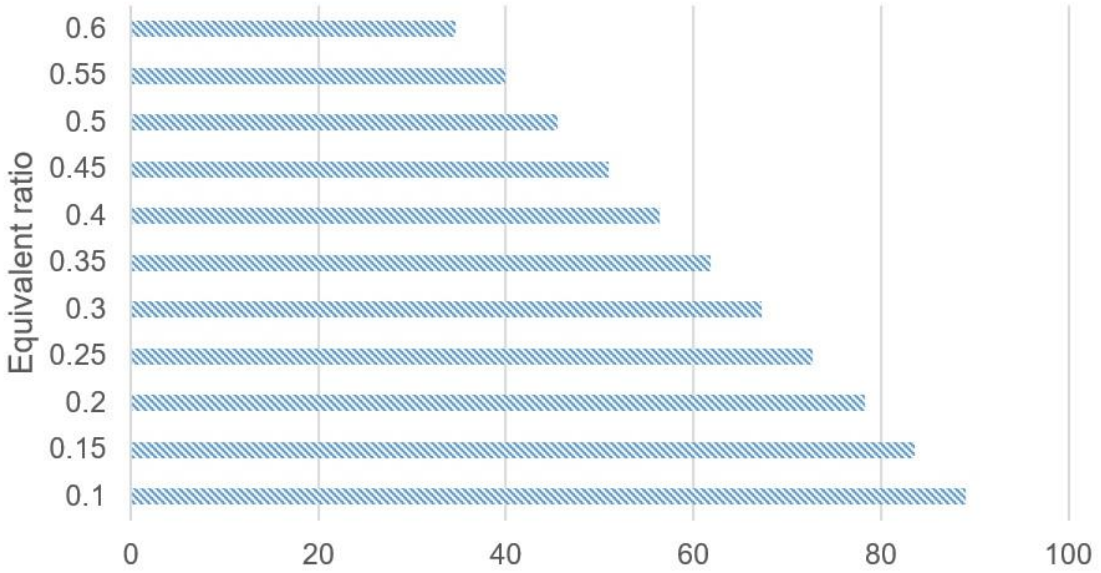

Figure 3: Final char yields for different amounts of reactive oxygen and a temperature of 650 °C.

By using this calculation we can find the reactive oxygen, which is 0.25 if calculated as equivalent ratio of the input char. As equivalent ratio we define the moles ratio of air and fuel in a thermal process with 0 representing an oxygen deprived thermolysis and 1 representing stoichiometric combustion. The value of 0.25 is by correlating the modelling results with the char yields that we monitored on the actual gasifier. Although it is expected that the calculated value of oxygen from the model is close to the actual number, thermodynamic models assume equilibrium which is not necessarily the case. Therefore, the amount of input oxygen could be slightly underestimated. Contrary to the yield of carbon, modelling has shown that the thermodynamic equilibrium of potassium is not sensitive to oxygen but to temperature. The reason is because potassium ions, like potassium nitrate, have melting points above 600 K. Above 1,010 K potassium oxide reaches its boiling point and the concentration of potassium in the gaseous phase increasing rapidly. Figure 4 shows the solid yields of potassium after (modelled) treatment in the afterburner in respect to temperature (in Kelvin). For 850 K, the solid yield of potassium is over 80 %, gradually decreases with increasing temperature and reaches as low as 53 % for a temperature of 1,050 K.

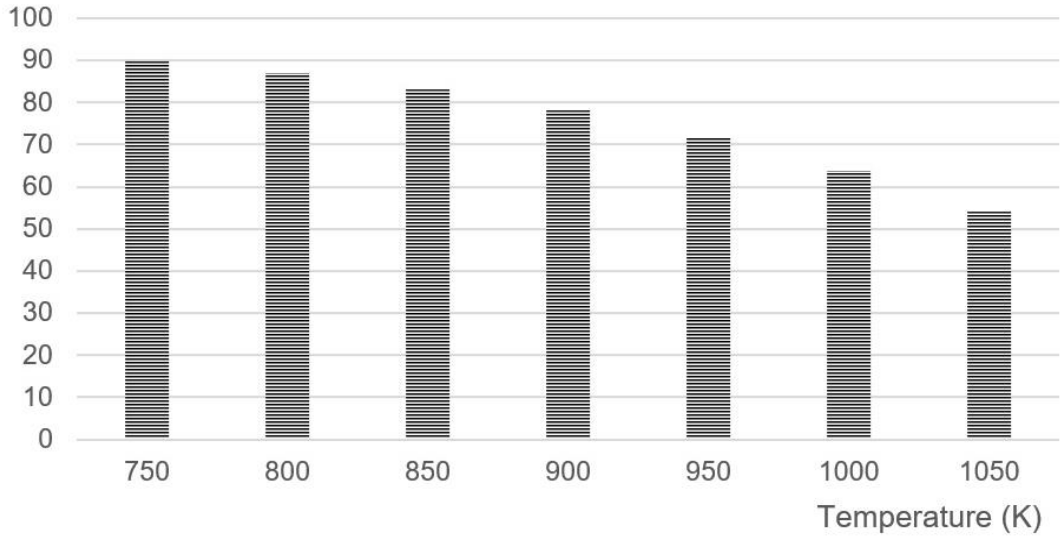

Figure 4: Remaining potassium solid yields after-treatment in the after-burner for different temperatures

Finally, a very interesting result that can be returned by applying this model is the accurate calculation of the main molar fractions of the gaseous phase. This result is not possible to be calculated by means of commercial software because they do not take into consideration the char gas-reactions, e.g. like the Boudouard reaction, which are responsible for the propagation of the gasification/ reduction reactions.
Figure 5 shows the model - calculated gaseous products from equilibration of char with atmospheric air with an air-fuel equivalence ratio of 0.25 and atmospheric pressure. As we observe in Figure 5, at a temperature of approximately 630 – 640 °C, carbon monoxide becomes the dominant species. This is a very useful result, since it shows the tipping point above which the gas becomes flammable.

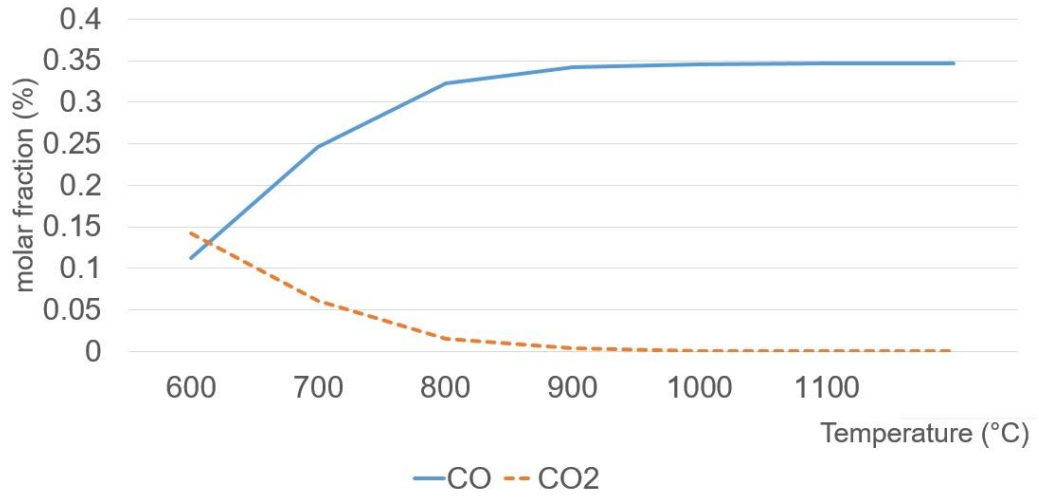

Figure 5: Molar fractions of main gaseous products for different operational temperatures in the after-burner

4. Conclusions

This work presented the development of a three phase model, which is developed in the thermodynamic equilibrium solver Cantera, with the scope to assess the concentration of potassium in the biochar before and after the after burner of a small scale biomass gasifier. The reason behind this study is the inability of commercial software to calculate correctly the char yield, the reactive oxygen and the molar fractions of the product gases. The proposed model was able to estimate the final char yield in relation to the reactive oxygen and the potassium yield in relation to the operating temperature. Finally, by combining both the previous parameters is able to

calculate the molar fractions of the main species of the gaseous phase. These results have also the additional benefit that the calculation of the potassium oxides and the potassium ions become possible.

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