

Reactivity of biochar gasification in atmospheres of steam, carbon dioxide and their mixtures

T. Kreitzberg, S. Pielsticker, O. Hatzfeld, R. Kneer

kreitzberg@wsa.rwth-aachen.de

Institute of Heat and Mass Transfer (WSA), RWTH Aachen University
Augustinerbach 6, D-52056 Aachen, Germany

Abstract

In this work conversion rates of biogenic char particles stemming from beech wood are measured with a lab-scale fluidized bed reactor in combination with FTIR-exhaust gas analysis at different gas atmospheres containing CO₂, H₂O and mixtures of both gases. The observed reaction rates are compared for all three gas atmospheres in a temperature range from 800 °C to 1000 °C to investigate the governing mechanism behind the gasification reactions in mixtures of CO₂ and H₂O.

Introduction

Heterogeneous reaction kinetics of carbon with carbon dioxide (Boudouard reaction) and carbon with steam (heterogeneous water gas reaction) are studied by a variety of research groups around the globe. Since these reactions are understood to be the slowest in gasification processes limiting the overall efficiency, precise knowledge on the related reaction rates is mandatory for the design and dimensioning of technical apparatuses. In this context, experimentally verified kinetic models of gasification reactions are required for implementation in pertinent CFD simulations.

A big share of experimental investigations focusing on the two above mentioned gasification reactions are conducted in gas atmospheres consisting either of one pure reacting gas (CO₂ or H₂O) or dilutions of them in an inert balance gas (e.g. in N₂ or Ar). Studies where particles are exposed to mixtures of both CO₂ and H₂O at the same time are scarce and reveal inconsistent outcomes regarding the governing mechanism of gasification: Some studies propose an additive mechanism between the two separate reactions of CO₂ and H₂O gasification, resulting in higher overall observed reaction rates. Other studies suggest an inhibitive or competitive mechanism, where observed reactivities lie below the sum of the two single reactions. A review of *Roberts and Harris* [1] gives a summary about the findings from different research groups concerning this issue and underlines the discrepancy of the reported mechanisms.

In this paper, a kinetic study of wood char particles is undertaken regarding gasification reactions in atmospheres containing CO₂, H₂O and mixtures of both gases in a small-scale fluidized bed reactor. The concentrations of the released product gases are continuously measured by FTIR-spectrometry and serve as a

basis for the calculation of particle conversion rates. By fitting model predictions to these conversion profiles, kinetic parameters are derived and compared for the different reacting atmospheres.

Experimental

A small-scale fluidized bed reactor (FBR) has been designed to implement the concept of a well stirred reactor approximating uniform distributions of thermodynamic state variables as well as of reacting species. Small batches of pulverized solid fuel are supplied to a fluidized bed consisting of alumina particles while simultaneously analyzing the exhaust gas. The experimental set-up is completed by a gas feeding system, including thermal mass flow controllers and a Fourier transform infrared spectrometer (FTIR) for product gas analysis.

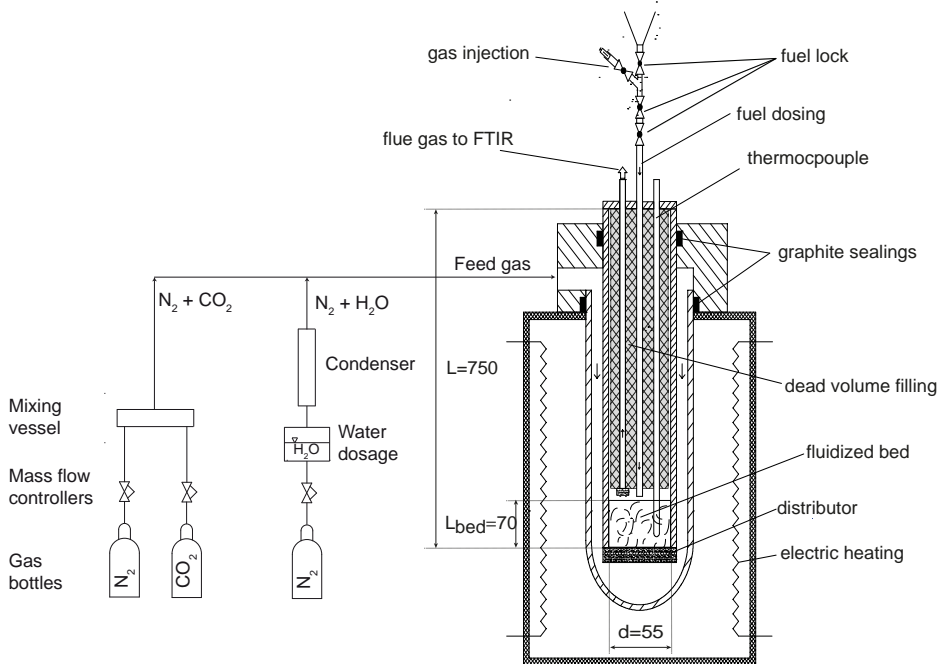


Figure 1. Scheme of the fluidized bed reactor (dimensions in mm)

The employed feed gas system is adapted depending on the type of experiment conducted:

For CO₂ gasification experiments, nitrogen and CO₂ are fed from separate gas bottles into the reactor. The flow of each component is regulated by thermal mass flow controllers. The resulting CO₂ concentration is adjusted by the ratio of the entering nitrogen and carbon dioxide streams.

For gasification experiments containing H₂O and mixtures of H₂O and CO₂ a controlled nitrogen stream is bubbled through a heated water trap; thus, the N₂ gas flow gets enriched with water vapor. This water dosage unit is followed by a

condenser to cool down the N_2/H_2O mixture. In this way, the gas is cooled to the dew point temperature corresponding to the target steam concentration. Excess water is condensed and fed back to the water dosage unit. By these means, a saturated N_2/H_2O gas mixture is obtained which serves as the feed gas for H_2O gasification experiments. CO_2 is added to this stream to achieve a desired gas mixture consisting of equal amounts of CO_2 and H_2O .

The gas enters the inner reactor pipe through a porous distributor plate made from sintered silica glass and fluidizes the bed particles. All ceramic parts of the reactor are located in an electrically heated furnace which can be heated up to 1553 K. Gaseous reaction products are captured just above the fluidized bed by an exhaust pipe. A ceramic filter, which is mounted to the lower pipe end, prevents entrainment of small particles. The exhaust gas is fed into the FTIR-gas analyzer through a sampling line and a filter. A Gaset DX-2000 FTIR spectrometer is employed for real-time gas analysis, sampling at 0.56 Hz. More detail on construction, operation and error analysis is given elsewhere [2–4].

In this work a biogenic char made from beech wood chips pyrolyzed in a screw reactor under pure nitrogen atmosphere with a residence time of 5 minutes at 773 K is investigated. Table 1 gives an overview of the proximate and ultimate analysis results for the fuel: The char mainly consists of carbon (> 80 wt.-%) with a remaining volatile content of 23.3 wt.-%.

Table 1. Fuel properties based on ultimate and proximate analysis for investigated beech wood char particles (mesh size: 125–160 μm)

Ultimate analysis	C (daf)	H (daf)	N (daf)	S (daf)	O (daf)
	81.2 %	3.3 %	0.3 %	0.0 %	12.1 %
Proximate analysis	Moisture (raw)		Ash (dry)		Volatiles (daf)
	3.6 %		3.1 %		23.3 %

Evaluation procedure

The establishment of kinetic parameters is based on a carbon species balance around the reactor. The dimensionless carbon conversion rate dX/dt can be derived experimentally from the temporal concentrations of the reactor exhaust gas species discharging the reacted carbon from the reactor - namely CO_2 and CO (cf. eq. 1). It can also be computed by a model approach, which can be interpreted using the characteristic reaction rate r_0 as an adjustable fit-parameter (cf. eq. 2). This characteristic reaction rate is determined iteratively by fitting the model prediction to the experimental data. A detailed overview of all steps of the employed evaluation routine is given in [4].

$$\frac{dX_{\text{exp}}}{dt} = \frac{M_c}{m_c} \cdot \Delta C \cdot \dot{n}_{\text{out}} \quad (1)$$

$$\frac{dX_{\text{mod}}}{dt} = (1 - X) \cdot r_0 \quad (2)$$

Where M_c is the molar weight of carbon and m_c represents the total captured carbon mass in the exhaust gas flow. The molar change in carbon due to reaction is symbolized by ΔC and the molar gas flow leaving the reactor by \dot{n}_{out} . Depending on the type of experiment conducted (CO_2 , H_2O or $\text{CO}_2/\text{H}_2\text{O}$ gasification) the balance yields different expressions for both of the factors \dot{n}_{out} and ΔC (cf. [3]).

Results

Three sets of experiments have been conducted under different gas atmospheres:

1. 20 vol.-% CO_2 in N_2
2. 20 vol.-% H_2O in N_2
3. 20 vol.-% H_2O + 20 vol.-% CO_2 in N_2

For all three sets, temperature has been varied from 800 °C to 1000 °C. Reacting conditions regarding temperature, particle size and reactant partial pressure have been chosen to ensure that particles react under regime I, which means that no significant mass transfer limitations (e.g. pore diffusion or external diffusion) are expected. After performing the evaluation routine described above, the determined characteristic reaction rate r_0 is plotted against the reciprocal temperature in Figure 2. Marker symbols specify the mean value of at least 5 repeated single measurements with error bars showing their standard deviation. The diagram exhibits linear profiles for all three reaction types, indicating that in the investigated range of temperature a typical exponential temperature dependency is found.

Focusing first on the experiments conducted in environments containing either CO_2 or H_2O (blue triangles, black squares) ratios of both reactions are close to unity ($r_{\text{H}_2\text{O}}/r_{\text{CO}_2} = 0.95$) at 800 °C. With increasing temperature rates start to diverge, reaching a ratio of $r_{\text{H}_2\text{O}}/r_{\text{CO}_2} = 1.56$ at 1000 °C. This trend is due the higher activation energy of the H_2O gasification reaction compared to CO_2 gasification, which is directly proportional to the slope of the continuous black line. The calculated activation energies are $E_{\text{A,H}_2\text{O}} = 230$ kJ/mol and $E_{\text{A,CO}_2} = 202$ kJ/mol.

Comparing the determined rates in mixtures of CO_2 and H_2O (red circles) to the two single reactions it can be concluded that the rates in mixed atmospheres clearly lie above the others for low temperatures ($T < 900$ °C) and are in between them for higher temperatures ($T > 900$ °C). Furthermore, the rates in mixed atmospheres are lower than the sum of the two individual reactions for the investigated conditions, leaving no evidence for an additive reaction mechanism (cf. dashed line in

Figure 2). This finding suggests a competitive behavior between the two reactions. However, an extrapolation of the continuous lines in Figure 2 suggest, that an additive behavior of the rates might be observable for even lower temperatures at around 700 °C. The slope of the mixed gasification reaction is almost identical to the one of CO₂ gasification which leads to a similar activation energy of $E_{A,mix} = 196$ kJ/mol.

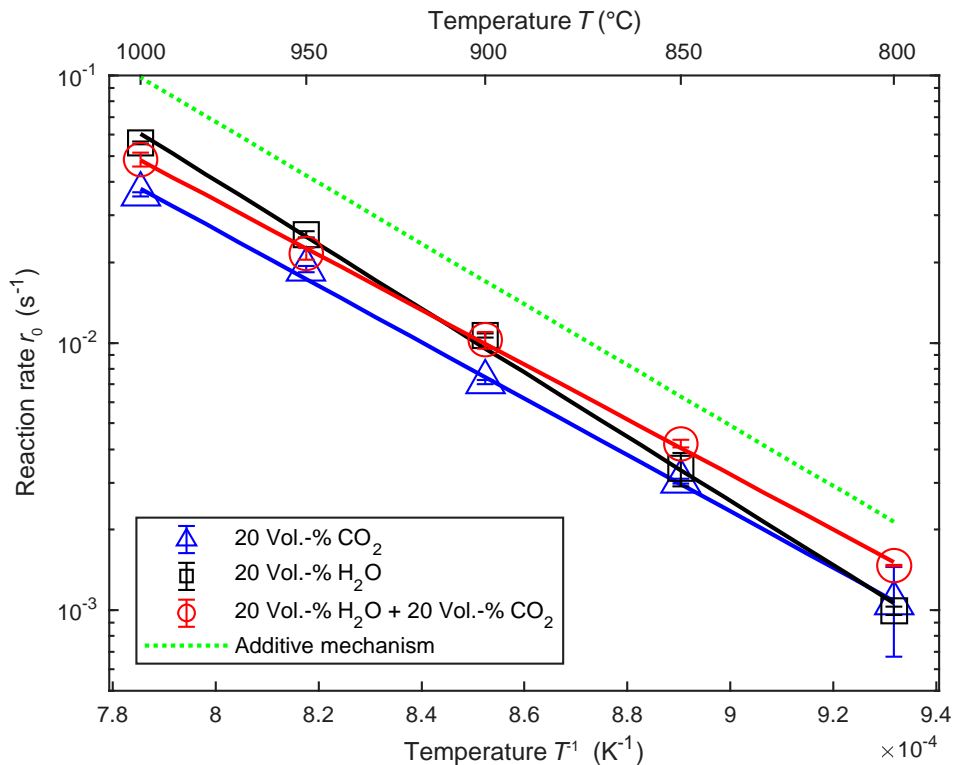


Figure 2. Reaction rates of biochar particles measured under different gas atmospheres in the fluidized bed reactor plotted against reciprocal temperature. Symbols give mean values of repeated experiments, continuous lines represent linear regressions.

Conclusions

This study has investigated the gasification of biochar particles and has underlined an inhibitive/competitive reaction mechanism regarding the reactivity in mixtures of CO₂ and H₂O. It has been shown that rates in mixtures of both reacting gases are above the two single reactions for low temperatures ($T < 900$ °C) and are in corridor between the two reactions at higher temperatures ($T > 900$ °C).

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