MEASUREMENT OF BEECH WOOD PYROLYSIS KINETICS IN A FLUIDIZED BED REACTOR

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Abstract
Detailed experimental data for pyrolysis kinetics of pulverized solid fuels at high heating rates for temperatures below 1000 K is essential for the validation of reaction mechanisms in complex pyrolysis network models. The present study demonstrates the capability of a fluidized bed reactor setup to provide experimental data in the temperature range from 523 to 973 K carried out with pulverized beech wood. A comparison with simple 1- and 2-step models has shown plausible results.

Introduction
For the simulation of pulverized fuel boilers, modeling of devolatilization behavior plays an important role to describe ignition, volatile combustion and pollutant formation. With increasing computational power, typically used single first order models are replaced with more complex models e.g. network models like Chemical Percolation Devolatilization (CPD), Flashchain or Functional-Group, Depolymerization, Vaporization, Cross-linking Model (FG-DVC). Necessary validation data for those models are typically provided by drop tube reactors (DTR) at high temperatures and high particle heating rates. A fluidized bed reactor (FBR) is capable to extend the validation data set to lower temperatures in combination with high particle heating rates. Furthermore, a continuous analysis of the reaction products like in the FBR allows for more data points than the analysis at discrete time steps in the DTR. The higher number of data points is helpful to prove the plausibility of possible reaction mechanisms in network models. The present study demonstrates the capability of an FBR to determine pyrolysis kinetics in the temperature region from 523 to 973 K.

Experimental Setup
For determination of pyrolysis kinetic data, a small-scale fluidized bed reactor with a diameter of $d = 55$ mm is used. Reactor temperature is controlled with an electrical heated furnace around the reactor (see Figure 1). The main part of the reactor consists of two axial Al_2O_3 pipes, mounted in a stainless steel reactor head. The annular gap between the pipes serves as heat up zone for the fluidizing gas

flow (150–300 slph N_2 depending on temperature), while the inner part encloses the fluidized bed consisting of Al_2O_3 particles ($d_{50} = 116$ μm).

Gas flush injection
Fuel lock
Fuel feed pipe
Exhaust gas to FTIR spectrometer
Thermocouple tube
Sealings
Feed-gas
l=750
Ceramic packing
Fluidized bed
Distributor
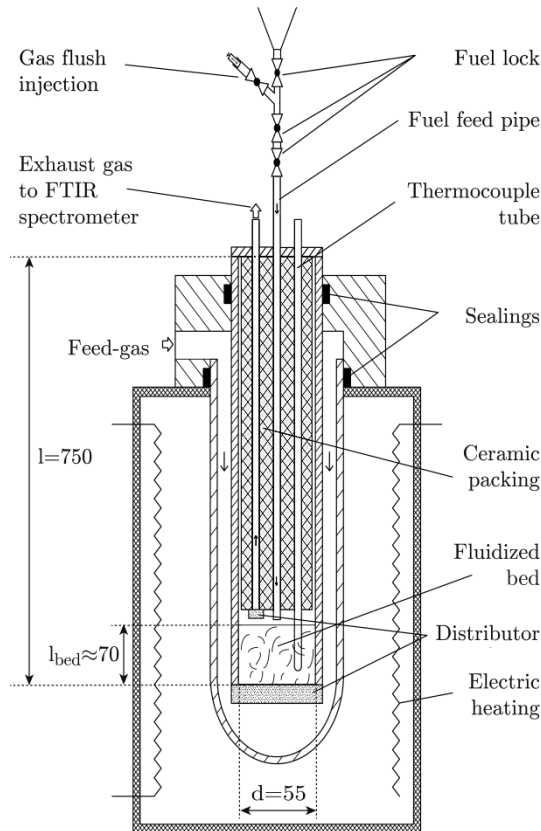$l_{bed} \approx 70$
Electric heating
d=55

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

Fuel samples (15–50 mg depending on temperature) are supplied to the reactor in batches. Particle transport from the fuel lock to the bed is forced with a gas flush from (10 ml N_2) to achieve fast heating rates of approximately 10^4 K/s [1]. Product gases are captured just above the bed and then transported to an FTIR spectrometer. The sampling line is heated to 453 K to avoid condensation of H_2O and tar components. The ceramic packing reduces dead volume, while the distributor in front of the gas sampling line allows for higher volume flows without particle entrainment. Both increase the gas exchange rate, which was identified to be the limiting factor in the determination of reaction rates of solid fuel particles [2]. Time dependent gas concentrations $c_i(t)$ are measured with an Agilent Cary 670 FTIR spectrometer, which analyzes in the wavenumber range from 600 to 6500 cm^{-1}, a spectral resolution of 4 cm^{-1} and a sampling frequency of 10 Hz. More detail on construction, operation and error analysis is given elsewhere [1–3].

For the present investigation pulverized and pre-dried beech wood particles from a sieving mesh size of 125–160 μm are used. Corresponding results from proximate and ultimate analysis are given in Table 1.

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

Ultimate analysis	C (daf)	H (daf)	N (daf)	S (daf)	O (daf)
	48.83 %	5.64 %	0.23 %	0.02 %	45.24 %
Proximate analysis	Moisture (raw)		Ash (dry)		Volatiles (daf)
	7.28 %		0.36 %		85.34 %

Evaluation and Modeling
In the first step of the evaluation procedure for determining pyrolysis kinetic parameters, the experimentally derived rate of released gases $dY_{Gas,exp}/dt$ is calculated according to equation (1) from the measured FTIR gas concentrations c_i of 21 different gas species (including CO, CO_2, $C_xH_yO_z$, SO_2 and NO_x). Concentration of H_2O was ignored to avoid interferences with underlying drying processes.

$$\frac{dY_{Gas,exp}}{dt} = \frac{\rho_{N_2} \cdot \dot{V}_{N_2}}{m_F \cdot M_{N_2}} \cdot \frac{\sum_{i=1}^{n} c_i \cdot M_i}{1 - \sum_{i=1}^{n} c_i} \tag{1}$$

Herein m_F is the injected fuel mass, $\dot{V}_{N_2}$ the fluidizing volume flow of nitrogen, ρ_{N_2} the density and M_i the molar mass of each measured species.
In the second step, the experimentally derived gas release rate $dY_{Gas,exp}/dt$ is approximated with a model derived one. In the present study, two different model approaches are presented, a 1-step model and a 2-step model. Characteristic parameters of both models are evaluated by the method of least squares. Effects of gas transportation and mixing in reactor and sampling line have been considered with a convolution transfer function as described in detail in [3].
In the 1-step model, the rate of released gases during pyrolysis is captured with

$$\frac{dY_{Gas}}{dt} = r \cdot \left[Y_{Solid}(t) - Y_{Solid,\infty}\right], \tag{2}$$

where r is the characteristic reaction rate and Y_{Solid} represents the mass fraction of solid material, unconsidering the chemical transformation process from coal to char. $Y_{Solid,\infty}$ is the final char yield after pyrolysis is completed. Amount of solid material can be calculated from a coupled integration of equation (2) and a mass balance (equation (3)) with the assumption, that all released volatiles are captured in the gas phase:

$$Y_{\text{Solid}}(t) = 1 - Y_{\text{Gas}}(t) \tag{3}$$

In the 2-step model, primary and secondary pyrolysis reactions are considered in the model formation. During primary pyrolysis, the model assumes the release of gaseous products ($Y_{\text{Gas,prim}}$) as well as tar (Y_{Tar}). Fraction of released tar from the overall amount of released volatiles is given by the factor f_{Tar}. Corresponding rate equations are given by equation (4) and (5).

$$\frac{dY_{\text{Gas,prim}}}{dt} = (1 - f_{\text{Tar}}) \cdot r_{\text{prim}} \cdot \left[Y_{\text{Solid}}(t) - Y_{\text{Solid},\infty}\right] \tag{4}$$

$$\frac{dY_{\text{Tar}}}{dt} = f_{\text{Tar}} \cdot r_{\text{prim}} \cdot \left[Y_{\text{Solid}}(t) - Y_{\text{Solid},\infty}\right] - r_{\text{sec}} \cdot Y_{\text{Tar}} \tag{5}$$

Despite the formation of tar, also decomposition during secondary pyrolysis with the reaction rate r_{sec} is considered in the last term of equation (5). The decomposed tar reacts into secondary gas $Y_{\text{Gas,sec}}$ according to equation (6).

$$\frac{dY_{\text{Gas,sec}}}{dt} = r_{\text{sec}} \cdot Y_{\text{Tar}} \tag{6}$$

For the comparison with experimental data, primary and secondary gas release rates are summed, as there is no possibility to distinguish between primary and secondary gas species during the experimental evaluation.

$$\frac{dY_{\text{Gas}}}{dt} = \frac{dY_{\text{Gas,prim}}}{dt} + \frac{dY_{\text{Gas,sec}}}{dt} \tag{7}$$

Analogous to equation (3), yield of remaining solid is calculated via a mass balance:

$$Y_{\text{Solid}}(t) = 1 - Y_{\text{Gas}}(t) - Y_{\text{Tar}}(t) \tag{8}$$

Results

Figure 2 gives a comparison between the experimentally derived gas release rate $dY_{\text{Gas,exp}}/dt$ (dots) and the two model derived fitted curves for 1- and 2-step model. Data corresponds to a single batch experiment at 873 K. Both models can capture the overall profile. Especially the maximum peak height is almost identical to the experimental values. Offside the peak, different behaviors of the two models are observable. While the 2-step model captures the experimental curve for all times very well, the 1-step model shows deviations in particular on the falling edge of the profile. Further investigations are thus only performed with the 2-step model.
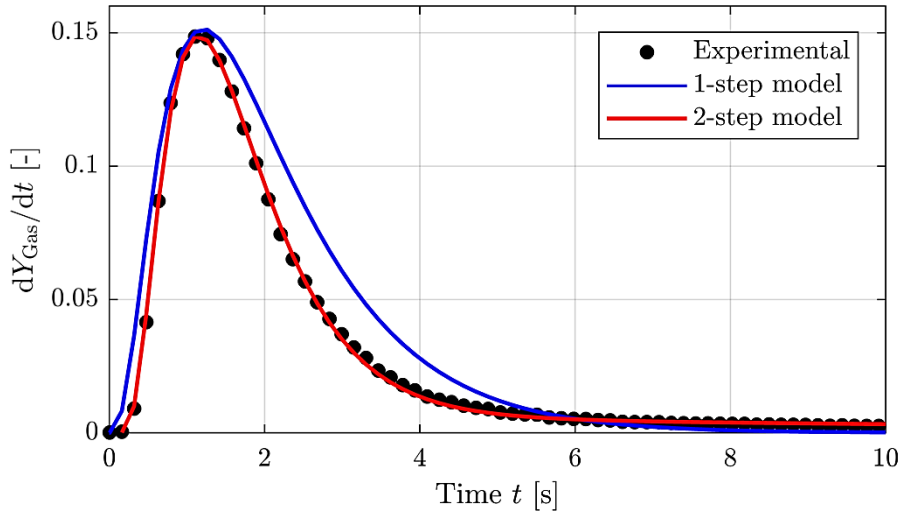
Figure 2. Comparison of experimentally derived gas release rate and corresponding model fit for 1- and 2-step model (single experiment at 873 K)

The above shown 2-step model curve is based on the following parameter set: $r_{\text{prim}} = 1.656 \text{ s}^{-1}$, $r_{\text{sec}} = 0.0575 \text{ s}^{-1}$, $f_{\text{Tar}} = 0.235$ and $Y_{\text{Solid},\infty} = 0.629$. Analogous, parameter sets are derived via least squares fits for all investigated temperatures from 523 K to 1473 K. Figure 3 shows an Arrhenius diagram, where the primary reaction rate r_{prim} is plotted over inverse temperature. Two main aspects are observable. In the low temperature region below $\approx$973 K, the reaction rate shows a linear trend according to an Arrhenius law

$$r = A \cdot \exp\left(-\frac{E_a}{\mathcal{R}T}\right), \tag{9}$$

where A is the pre-exponential factor, E_a the activation energy, $\mathcal{R}$ the universal gas constant and T the temperature. For the investigated beech wood, $E_a = 48.74 \text{ kJ/mol}$ and $A = 1.27 \cdot 10^3 \text{ s}^{-1}$ are found as kinetic parameters. In the high temperature range, detection limit of the reactor has been reached as it was theoretically predicted in [2].

Conclusion

The study has shown that the small-scale fluidized bed reactor is capable to derive pyrolysis kinetic parameters in the temperature range from 523 to 973 K. For the exemplary chosen beech wood, a 2-step model including primary and secondary pyrolysis reactions was well suited to capture the experimentally derived gas release. Furthermore, the fitted parameters show consistent behavior within the investigated temperature range.
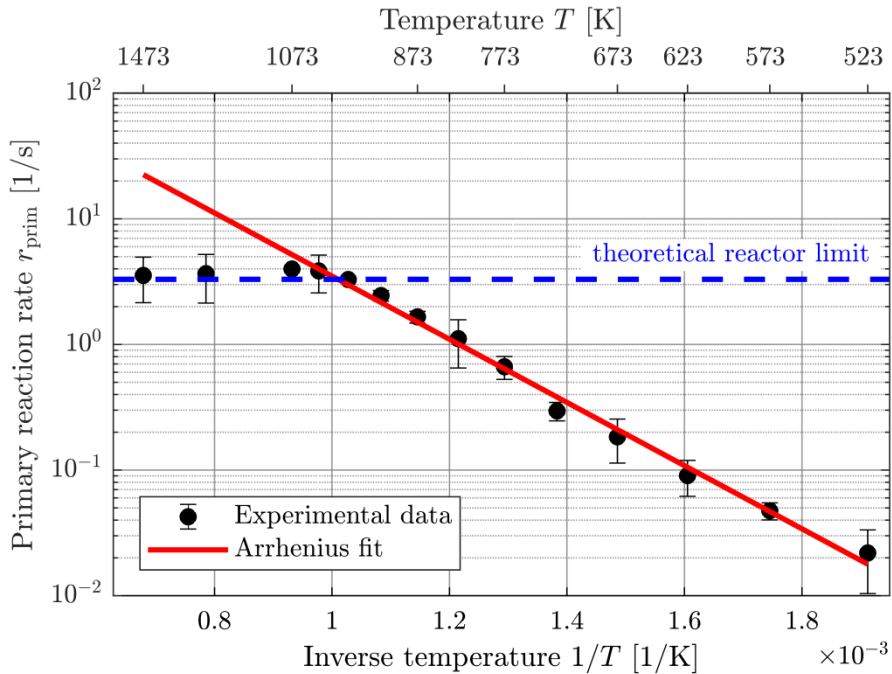
Figure 3. Arrhenius diagram for primary reaction rate

References
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