

# BIOMASS CARBONIZATION: ROTARY KILN EXPERIMENTS AND REACTION MODELING

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## Introduction

Rotary kilns are well suited for carbonization of heterogeneous materials like biomass. Experimental results achieved with a set-up for rotary kiln pyrolysis of 1 kg/h of biomass are reported in [4]. Mathematical modeling is performed by solving the mass and energy balance. Crucial for the success of theoretical models is the validity of the submodels concerning thermodynamic properties and the description of the reactions taking place. This paper will focus on the latter topic.

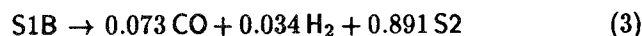
## Experimental

The experimental work with the rotary kiln equipment includes maize pyrolysis in the temperature range of 440 °C up to 800 °C with different solids and volatiles residence times. In order to evaluate the processes in the bulk phase separately from gas phase reactions and the influence of heat and mass transfer, further experiments are performed in a thermobalance coupled to an evolved gas analysis system. The special design of the thermobalance allows large samples (3 g) and a fairly low residence time of volatiles in the heated zone (< 2 s). With this TG/EGA set-up pyrolysis of coarse particles can be investigated under conditions similar to those in the bulk phase in the rotary kiln. Experiments are performed with heating rates  $\kappa$  from 3 K/min up to 20 K/min in order to remain within the kinetically controlled region. The mass, the temperature directly underneath the sample, the gas flow rate, and the concentrations of CO<sub>2</sub>, CO, CH<sub>4</sub>, and H<sub>2</sub>, are monitored continuously, which yields experimental reaction rates.

## Model

Although it is known that pyrolysis proceeds in a complex mechanism including competitive and consecutive intra-particle reactions the overall process is often treated as one single step reaction [1, 2]. The first of both ways employs too many parameters to determine by experiments, the second cannot describe peaks at different temperatures. A suitable formal reaction scheme for the description of the reactions in the bulk phase is shown in eqs. 1-3. It consists of a primary reaction followed by the degradation of the primary solid in two parallel reactions. Since the amount of gas does not depend significantly on the heating rate for heating

rates of more than 10 K/min the second step can be described by independent reactions.



The elemental composition of the primary solid product S1 is taken from the product of the 440 °C rotary kiln pyrolysis, the ultimate analysis of the solid product in the thermobalance describes S2. The term L denotes all matter which is not detected separately, i.e. water and C<sub>2+</sub> compounds. Its composition is determined by fulfilling the elemental balance for the TG experiment. S1A and S1B are fractions of S1 (0.4 and 0.6). The mass stoichiometric coefficients are determined by solving the system of linear equations given by the elemental balance for each reaction. The mass balance for each species  $i$  yields, neglecting transfer influence and assuming first order kinetics with an Arrhenius-type approach for the reaction rate coefficient:

$$r_{w,i} = \frac{d \frac{m_i}{m_{\text{BM},0}}}{dt} = \sum_{j=1}^3 \Psi_{j,i} k_{0,j} \exp\left(-\frac{E_{A,j}}{RT}\right) \frac{m_{j,e}}{m_{\text{BM},0}} \quad (4)$$

$\Psi_{j,i}$  denotes the mass stoichiometric coefficient of the species  $i$  in reaction  $j$ ,  $m_{j,e}$  the mass of the educt in reaction  $j$ . The kinetic parameters  $k_{0,j}$  and  $E_{A,j}$  are determined by minimizing the expression

$$\text{MSE}_j = \sum_n \left( \ln k_{\text{exp},j,n} - \ln k_{0,j} + \frac{E_{A,j}}{RT_n} \right)^2 \quad (5)$$

following [3]. The experimental rate coefficient for each reaction  $j$ ,  $k_{\text{exp},j,n}$ , is determined at several temperatures  $T_n$  from the DTG signal and the concentrations of CH<sub>4</sub> and H<sub>2</sub> according to eq. 4. The comparison of the model and the experimental results is shown in figs. 1 and 2. Taking into account that the shoulder of the first peak is not included in the model, the fit is well acceptable. It is important to note that the formal kinetic parameters are determined from an experiment with  $\kappa = 10$  K/min and compared to the experiment with  $\kappa = 20$  K/min to show that the dependence on  $\kappa$  is covered by the model. The extrapolation of the results of the model to higher heating rates is necessary

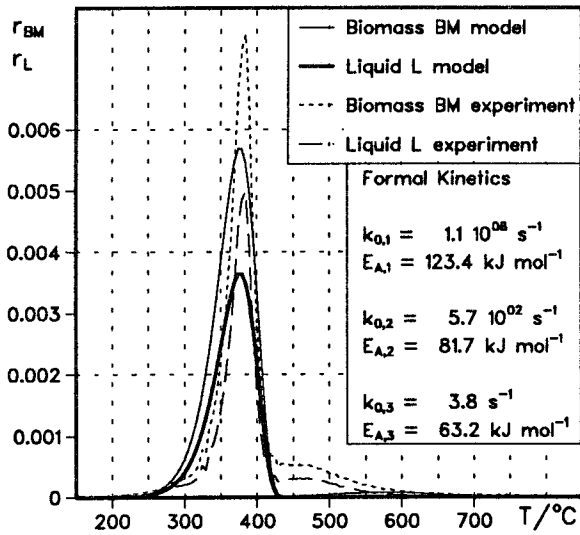


Figure 1: Reaction rate of the formation of L and decomposition of biomass for  $\kappa = 20$  K/min

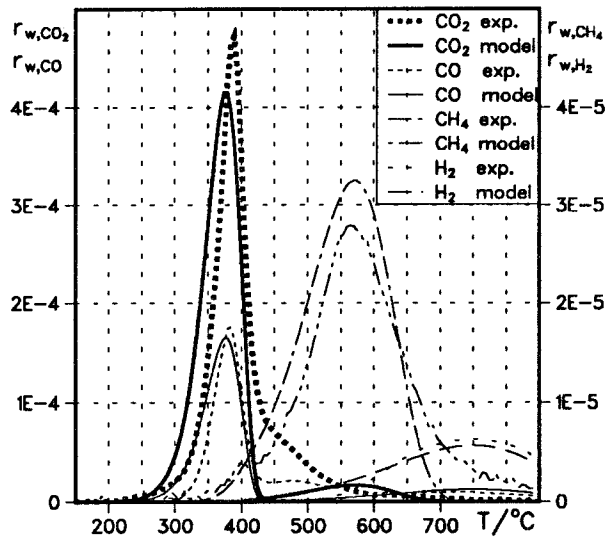


Figure 2: Reaction rate of the formation of gases for  $\kappa = 20$  K/min

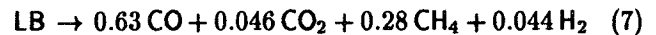
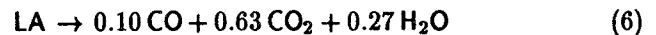
because the rotary kiln  $\kappa$  is in the order of magnitude of 100 K/min where heat transfer limitations prohibit kinetic evaluation.

Rotary kiln pyrolysis yields, even at a temperature of 440 °C, much more gas than the thermoanalysis. This is a consequence of secondary reactions in the gas phase. The amount of gas formed in the gas phase varies with temperature and volatiles residence time in a different way for CO<sub>2</sub> and CO. The ratio of CH<sub>4</sub> and H<sub>2</sub> formation does not vary significantly. Whereas CO<sub>2</sub> is formed mainly at lower temperatures, the yield of the

Table 1: Elemental composition of solids and summed matter on water, ash and nitrogen free basis

	BM	S1	S2	L	LA	LB
c	0.475	0.826	0.892	0.360	0.215	0.493
h	0.059	0.043	0.010	0.075	0.030	0.114
o	0.467	0.130	0.099	0.565	0.755	0.393

other gases increases drastically at high temperatures. For this reason the sum of not detected substances L is now split into two fractions LA and LB. LA accounts for 49% of the mass of L and decomposes already at low temperature, LB is the more stable fraction. For the elemental compositions, which are determined by the sum of the products of the following reaction scheme, see table 1.



Coupling the bulk and the gas phase reaction schemes it is possible to model the pyrolysis of biomass in a rotary kiln and other processes with moderate heating rate, dense bulk phase, long residence times and poor gas solid contact, where mainly homogeneous reactions occur. It should be mentioned that this model may not yield the best fit to experimental data in a mathematical sense, but strictly obeys the physicochemical condition of a fulfilled elemental balance for each element at any time.

## Conclusions

The formation of gaseous, liquid and solid products of biomass pyrolysis under the conditions of a rotary kiln can be modeled with a set of three reactions in the bulk phase and two secondary homogeneous gas phase reactions. The given set of formal kinetic parameters for the bulk phase reactions describes the shift of the peak towards higher temperature with increasing heating rate as well as the total formation of the gases. Mass stoichiometric coefficients for all involved reactions are determined from experimental results and elemental balances. Further work will cover the introduction of the presented formal kinetics into the rotary kiln model.

## References

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