HYDROTHERMAL BIOMASS GASIFICATION:
A KINETIC MODEL FOR OPTIMIZATION

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In order to optimize the gasification process in supercritical water an improved knowledge of the chemical reaction pathways is necessary. Therefore, experimental studies combined with thermodynamic calculations and kinetic modeling on model compounds as well as with biomass were conducted. From the model compounds, general characteristics of reactions steps could be derived, such as the dependence on temperature, pressure, residence time, heating rates, concentration etc. Selected "key compounds", like phenols, furfurals and organic acids were identified and quantified, which are formed by different and characteristic reaction pathways. They can e. g. be used to compare results from studies with model compounds to those achieved by biomass conversion. From all these results, a simplified reaction mechanism was set up.

The experimental studies shows that not only the composition of the feedstock but also the type of reactor used, influence the gasification results: At high concentrations the CSTR leads to better results than a tubular or batch reactor investigated. This can be explained by an influence of back-mixing on the chemical reaction network. This makes a kinetic description more complex, because the basic chemistry should be the same in both reactor types.

Now a simplified kinetic model for the hydrothermal gasification is developed which reflects the experimentally found properties. This model bases on the key compounds, mentioned above. The model parameters are fitted to the experimental data. The model leads to a deeper understanding of the process and is a tool to explore optimized reaction conditions.

INTRODRUCTION

Use of biomass is of increasing interest to reduce CO_2 emission and the consumption of fossil energy. A particular challenge is to use the so-called wet biomass, i.e. biogenic residues with a water content in excess of 50 % (g/g) and frequently up to above 80 % (g/g). These residues arise in e.g. agriculture, food and beverage industry, and as by-products of many utilization processes that cannot use the whole plant. In hydrothermal gasification, this biomass does not need to be dried with a high expenditure. On the contrary, water is needed in the process as a reactant and reaction medium. Due to the rapid hydrolytic decomposition of carbohydrates and the good solubility of the intermediate products under reaction conditions, high gas yields are reached at comparably small temperatures with a very small formation of undesired products like tars and coke (state of the art: [1]). If hydrogen is the product desired, temperatures of 600 °C or above are required at typically 30 MPa for thermodynamic reasons. The goal is to create a kinetic model to describe the reaction, which includes the knowledge about the process. This will help to optimize the reaction conditions.

This reaction is controlled kinetically, which, for instance, results in the fact that the gas yield decreases with the dry matter fraction that has been observed in most studies in the dry matter range of about 5 – 20 % (g/g) so far (e.g. [2]). Theses studies were conducted in tubular reactors, which means without back-mixing. This decrease was not observed in reactors with back-mixing (CSTR). This was explained by assuming that in the case of back-mixing, late

products can react with early products. Such late product is reactive hydrogen, formed via the water-gas shift reaction:

Water-gas shift reaction: $CO + H_2O \leftrightarrow CO_2 + H_2$
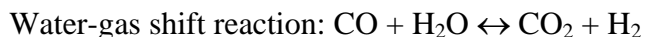
Alkali salts catalyze this reaction. It was observed earlier, that the active hydrogen formed reduces the formation of tar and coke by reacting with reactive compounds, which would polymerize [3-5].

MATERIALS AND METHODS

The experiments were carried out using two different reactors: A spiral tube reactor (6 m long, about 20 mL inner volume, up to 600 °C at 30 MPa, see also [4]), and a continuous stirred tank reactor (about 190 mL inner volume, up to 600 °C, 100 MPa, see e.g. [5]). They do not only differ in the reaction times achieved, but also in back-mixing and heating rates.

To build up a model, a procedure must be found to create the kinetic equations. A simple global degradation equation is not useful, because it would not be possible to describe a CSTR and a tubular reactor with the same basic kinetics. According to the experimental results the tubular reactor need a kinetic description with a negative and the CSTR with a positive reaction order in respect of the feedstock concentration. This is not satisfying from a chemical point of view; it must be in principle the same process! Therefore, the model must be more detailed and has to consist of a couple of single equations. This equation should represent the main reaction pathways, but how can these pathways can be identified?

As biomass is a complex mixture of variable composition, it is difficult to identify individual reaction paths of the reaction network. For this reason, experiments with model substances, e.g. glucose, were carried out first (among others [3-9]). Key substances, usually typical intermediate products, were allocated to each reaction path identified as "indicators" (Fig. 1). With the help of these key substances, the same reaction paths could also be found in the conversion of biomass. Changed concentrations of key substances reflect a changed selectivity of the corresponding reaction path, e.g. due to salts [10]. The model biomass used was a mixture of carrots and potatoes (for more detailed information, see [11]).
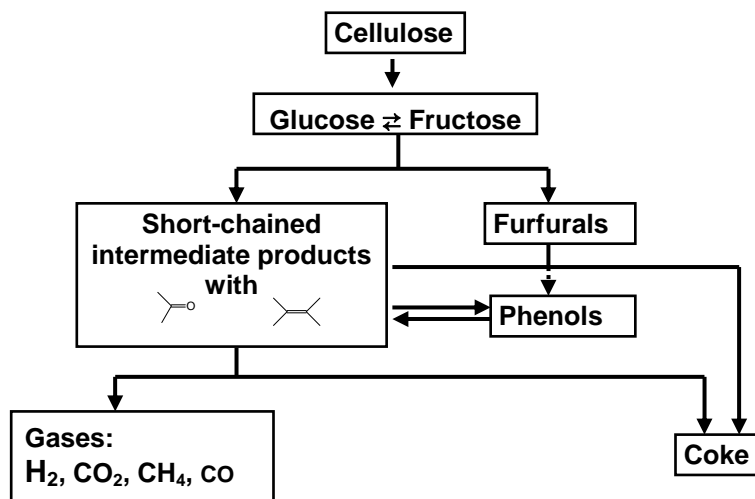
Figure 1: Simplified reaction network, consisting of key substances and based on cellulose

The reaction network shown in Fig. 1 does not include the effect of back-mixing, which enables the reaction of active hydrogen with early intermediates and reducing tar and coke formation. To include this in the reaction scheme an "artificial" reaction is included. This is the reaction of hydrogen with the short-chained intermediates to other, less reactive short-chained intermediates. These hydrogenated, less reactive intermediates are able to react further to gases, but they are not able to react to compounds of higher molecular weight (Figure 2).
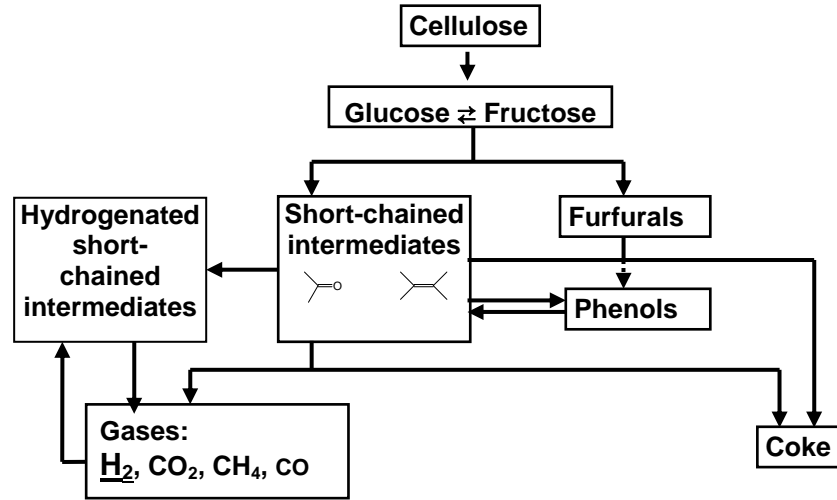
Figure 2: Simplified reaction network, including the reaction of the late product hydrogen with intermediates.

It is reasonable to assume that degradation reactions like gas formation process a low reaction order. It is also reasonable that polymerization show a higher reaction order; for the phenol formation, a reaction order near two was found experimentally [5]. For the model the reactor order for phenols formation was set to two, the reaction order for the polymerization to coke was set two three and all others were set to one. Basing on these assumptions, the reaction network shown in Figure 2 and stoichiometric limitations, a system of kinetic equations are built up (Table 1).

Table 1: Kinetic model of the tubular reactor (p=25 MPa).

d(y1)/d(t) = -k1*y1
d(y2)/d(t) = k1*y1+k2*y3-(k3+k4+k15)*y2
d(y3)/d(t) = k3*y2-(k2+k3)*y3
d(y4)/d(t) = k5*y3-(k6+k7)*y4
d(y5)/d(t) = 1/3*k9*y6^2-(k10+k11)*y5
d(y6)/d(t) = 3*k4*y2+3*k6*y4+3*k10*y5+2*k16*y13-k8*y6^3*k9*y6^2+k12*y6-
        (k13+k14)*y6
d(y7)/d(t) = 0.5*k7*y4+1/6*k8*y6^3+0.5*k11*y5
d(y8)/d(t) = 2*k12*y6+3*k17*y9+k19*y10*y14+2*k16*y13-k18*y10*y8-
        20*y11*y8+3*k21*y12-k23*y6*y8
d(y9)/d(t) = k13*y6+k18*y10*y8+k22*y12-k17*y9
d(y10)/d(t) =2*k12*y6+k17*y9+k20*y11*y8+2*k21*y12+(k18*y8+k19*y14)*y10
d(y11)/d(t) = k19*y10*y14-k20*y11*y8+k15*y2
d(y12)/d(t) = k23*y6*y8-(k21+k22)*y12
d(y13)/d(t) = k15*y2-k16*y13
d(y14)/d(t) = 3*k5*y3+(6*k8+3*k9)*y12+k18*y10*y8+k20*y8*y11-k19*y10*y14

y: concentration of the key compound

with: $k = k_0 * \exp(EA/RT)$ for all k.
k_0: Ahrrenius factor
EA: Activation energy
T: Temperature (K)
R: Gas constant

The first reaction is the hydrolysis of cellulose. The second is the formation glucose and the reaction of glucose to fructose and other products. The third is the formation of fructose from glucose and its reaction, and so on. All together fourteen key compounds were used. The kinetic constants k are defined to follow Ahrrenius behavior. This model was included in a MATLAB program [12]. Here the kinetic parameters (Ahrrenius factor, and activation energy) were fitted to the experimental data.

RESULTS

Beside the key compounds chosen for the reaction network also sum parameters like the DOC (dissolved organic carbon) value can be calculated. This value is measured and in the model calculation, it is the sum of all soluble compounds. Figure 3 shows the comparison of experimental and calculated model data. These are preliminary results, because some key compounds e.g. the CO content is not well described by the model up to now. In fact, the calculated CO content is some orders of magnitude to low. In other words: The system shifts too much to the equilibrium value [13]. The water-gas shift equilibrium is implemented by considering the forward and reverse reaction.

Anyway, the first results show that the model in principle is able to describe the reaction. Further optimization of the kinetic parameters is in progress. Likely, the model has to be changed concerning the reaction pathways connected with the water-gas shift reaction.
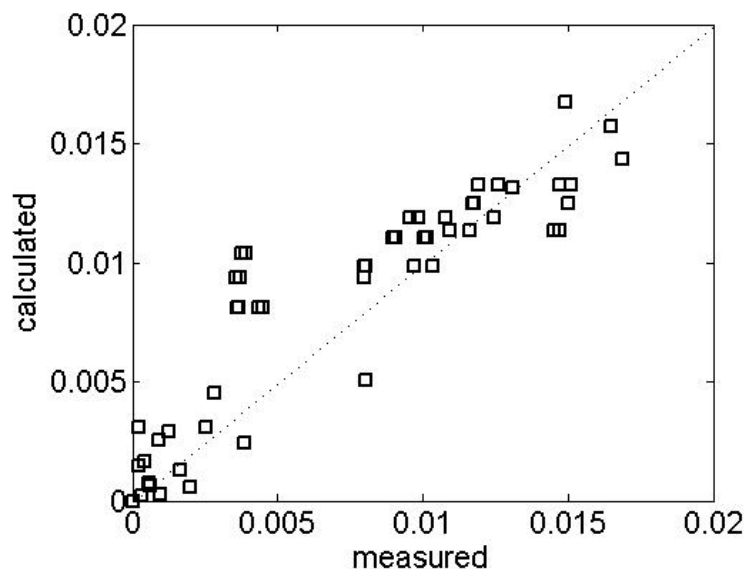
Figure 3: Comparison of measured and calculated TOC amounts, given ppm.

The calculations for the tubular reactor show the same concentration dependence as found experimentally: The relative gas yield decreases with the initial concentration (Fig. 4). In the case of the CSTR, the opposite is found experimentally and in the calculation results (not shown here).
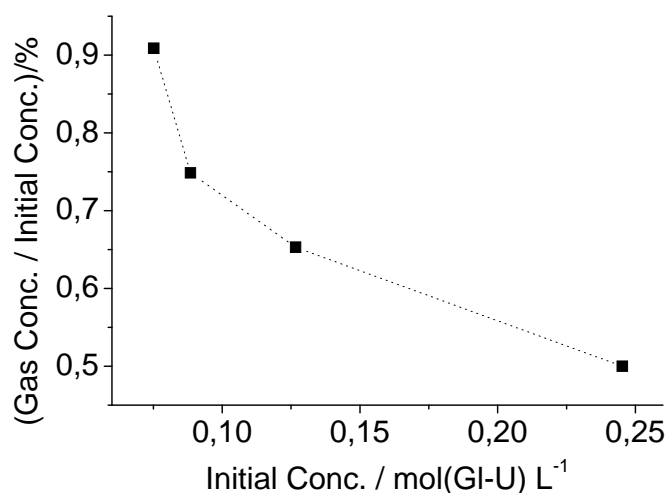
Figure 4: Calculated concentration dependence in a tubular reactor (500 °C, 25 MPa). The initial concentration is given as number of glucose units per litre.

CONCLUSION

The basic properties of the hydrothermal biomass gasification can also be found in the experimental results. In addition, the model can predict important measurable values like the DOC content. Anyway, the model is not good enough to be used for process optimization. Here further work on the model development is necessary.

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