MEASUREMENT AND MODELLING OF THE PYROLYSIS GAS COMPOSITION OF NATURAL WOOD AND WASTE WOOD

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Abstract

In this study, the pyrolysis products of natural wood samples and waste wood are compared and an adequate kinetic model calculation is provided.

The pyrolysis of natural beech wood, birch wood and of waste wood was investigated by thermogravimetric analysis (TGA) at heating rates between 1 and 50 K/min. Some representative product gases were measured quantitatively by FTIR spectroscopy in case of beech wood and waste wood, and by microGC in case of birch wood.

Kinetic model calculations were performed using a novel 7-step reaction model. The model considers permanent gas, tar and char formation from the wood pseudocomponents as well as a condensed phase intermediate metaplast. The stoichiometric coefficients of the decomposition products are calculated automatically which greatly facilitates the investigation of the model sensitivity to input parameters. The rate constants of the decomposition reactions were fitted to the measured DTG curves until good agreement for the decay of the solid mass and, vice versa, for the total amount of gas release was obtained. Next, the elemental compositions of the tar, char and metaplast species were adjusted to obtain good agreement with the measured release of permanent gases.

The measured gas phase product distributions for the two hardwoods were comparable and could well be recalculated with the kinetic model. The waste wood was found to decompose qualitatively into the same gas phase products like natural wood, but in addition, nitrogen containing species (HNCO and NH_3) were identified which probably arise from non-natural ingredients like aminoplast.

1- INTRODUCTION

Pyrolysis is defined to be a thermal decomposition process in the absence of oxidizing species and gasifying media. The pyrolysis of biomass like wood, straw and agricultural residues may be viewed as a stand-alone process for the production of valuable chemicals or secondary fuels with higher energy density. Moreover, pyrolysis is also understood to be the first chemical conversion process during the combustion and gasification of biomass. Despite continuous efforts, a complete experimental characterization of biomass pyrolysis products has not yet been achieved and the reported data show a large scattering [1]. In particular, it has been observed that the retrieval of kinetic data from the measurements is not trivial [2] and, there are no generally accepted model calculations available to date [3,4]. Since there is no experimental basis for detailed kinetic pyrolysis models, a variety of global reaction models has been developed previously [3,5,6]. From these studies it appears that (i) a precise modelling of thermogravimetric data requires a multi-component representation of the solid material (DAEM model [6]) and (ii) an adequate modelling of the volatile compounds may require a very large gas phase kinetic data base [7]. However, even the very complex models will still be phenomenological approximations to the real process. Therefore, a compromise between oversimplified and oversophisticated modelling is sought in this paper.

In the experimental part, two natural wood samples, beech and birch, were investigated by thermogravimetric analysis with quantitative, time resolved determination of some key species released. As further comparison, some experiments were performed on waste wood. The experiments were carried out under conditions of negligible tar decomposition, hence they can be described by a reaction model in which permanent gases, water vapor, tar and char appear as final products. The 7-step model used here is an extension of earlier model developments [8,9]. It employs tar and char species of variable elemental compositions.

2- MATERIALS AND METHODS

Experimental procedure
All wood samples were tested for elemental and proximate analyses. Small amounts of beech wood or waste wood (~ 10 mg) and somewhat larger amounts of birch wood (~ 200 mg) were heated in Netzsch thermoanalyzers (series STA 449) under nitrogen atmosphere at constant heating rates between 1 and 50 K/min. The evolving pyrolysis gases were analyzed:

a) by FTIR (Bruker, Tensor 27) in case of beech wood and waste wood; here, CO, CO_2 and CH_4 were determined quantitatively using calibration standards [10];

b) by microGC (Inficon, 3000 microGC) in case of birch wood; here, the tar and water free gas composition was analyzed for CO, CO_2, CH_4, C_2- and C_3- hydrocarbons and H_2 [11].

The residence time of the pyrolysis gas in the sampling line was only about 50 msec, hence tar decomposition which occurs at time scales above 30 sec was negligible.

Overall kinetics
It is a common feature of thermal decomposition and pyrolysis processes that the major decomposition temperature T_D increases with increasing heating rate β. According to an earlier analysis by Kissinger [12], the measured values $T_D = f(\beta)$ can be used to derive the Arrhenius parameters k_0 and E_a (pre-exponential factor and activation energy) for the decomposition process according to eq. (1):

$$\log \frac{\beta}{T_D^2} = \log \frac{R \cdot k_0}{E_a} - 0.4343 \cdot \frac{E_a}{R \, T_D} \qquad (1)$$

where R is the universal gas constant. In a strict sense, this equation holds only for a single component which decomposes according to a single first order reaction. However, eq. (1) is often applied to polymeric materials and multiple reaction systems as well. In biomass pyrolysis, both cellulose and lignin contribute to the major decomposition peak. Hence the derived kinetic parameters may reflect the different concentrations of these species and are difficult to interpret. Further, T_D does not depend very strongly on β. A change of β by a factor of 10 results in a change of T_D by 30 - 50 K. Therefore, the determination of k_0 and E_a may readily become erroneous due to the required extrapolation procedure.

Note also that eq. (1) refers to the thermally thin regime, where the pyrolysis is under kinetic control. Eq. (1) is less applicable to large particles with internal temperature gradients.

Model development

In the model calculation, the biomass is assumed to be composed of cellulose $(C_6H_{10}O_5)_n$, hemicellulose $(C_5H_8O_4)_n$ and lignin $(C_{10}H_{10}O_4)_n$. In the decomposition equations, only the monomers of these pseudocomponents are used. Each of the monomers decomposes in two parallel reactions which differ by the gas phase $tar_{(g)}$ and the metaplast $tar_{(l, s)}$ products:

$$\text{pseudocomponent} \longrightarrow \alpha_1 \, tar_{(g)} + \beta_1 \, CO_2 + \gamma_1 \, CO + \delta_1 \, H_2 + \varepsilon_1 \, H_2O + \zeta_1 \, CH_4 + \eta_1 \, char_{(s)} \quad (2.a)$$
$$\longrightarrow \alpha_2 \, tar_{(l, s)} + \beta_2 \, CO_2 + \gamma_2 \, CO + \delta_2 \, H_2 + \varepsilon_2 \, H_2O + \zeta_2 \, CH_4 + \eta_2 \, char_{(s)} \quad (2.b)$$

The inclusion of a metaplast intermediate is well known from other models [3,7]. In the present model, the nature of the metaplast is not strictly defined. It may be a high boiling liquid or a solid intermediate or a mixture thereof. The decomposition of the metaplast is assumed to occur according to eq. (2.a). The first requirement for the set of reaction equations is their agreement with the measured DTG curves which represent the mass loss rate of the condensed phase and the associated increase of the total amount of volatiles. The gas composition results from the stoichiometric coefficients α - η, which are calculated automatically by the model. A variation of the gross elemental composition of $tar_{(g)}$, $tar_{(l, s)}$ and/or $char_{(s)}$ results in a change of the calculated gas composition. This provides a means of iterative refinement of the model results.

3- RESULTS AND DISCUSSION

The proximate and ultimate analyses of the three wood samples [10,11] are given in Table 1.

	Prox. Analysis (as received, [wt.-%])				Ultimate Analysis (dry, ash free, [wt.-%])				
	Moisture	Ash	Fix C	Volatiles	C	H	O	N	S
beech	6.1	0.24	18.63	75.03	49.57	6.08	44.14	0.21	-
birch	8.2	0.8	13.2	85.9	47.6	6.9	45.3	0.1	0.1
waste	8.8	1.56	25.29	64.35	51.34	5.84	41.87	0.95	-

Table 1: Composition of the wood samples.

From these analyses, it is obvious that beech wood and birch wood have similar compositions. The waste wood contains a notably high amount of nitrogen.

The TG and DTG curves were published elsewhere [10,13]. Here we report only the kinetic analysis by plotting $\log(\beta/T_D^2)$ vs. $1/T_D$ for beech wood and birch wood as shown in Fig. 1.
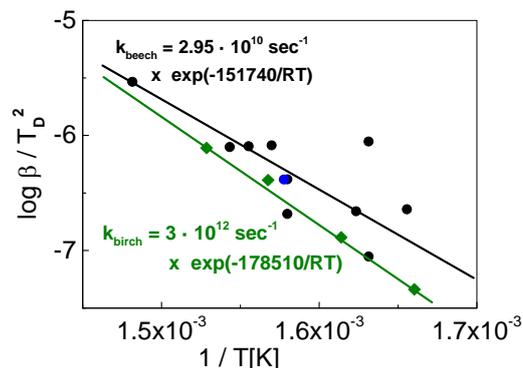

Figure 1: Kissinger plots of beech wood and birch wood pyrolysis (● beech, from refs 14–18;
● beech, this work; ◆ birch, this work; E_a [J/mol]).

Despite the close chemical composition of beech wood and birch wood, their thermal stability is somewhat different. According to the above overall rate constants, the half-life times are 2 min for beech wood and 3.6 min for birch wood at 350 °C.

During beech wood and waste wood pyrolysis, FTIR spectra were recorded for qualitative and quantitative gas analysis. Example spectra are shown in Fig. 2 for a temperature which is close to the major decomposition peak at $\beta = 10$ K/min. The absorption peaks of CO and CO_2 are clearly visible, as are the absorption bands of alcohols, aldehydes, acids and phenols. A weak absorption by pyrolysis water is seen. CH_4 is not yet visible at this temperature.
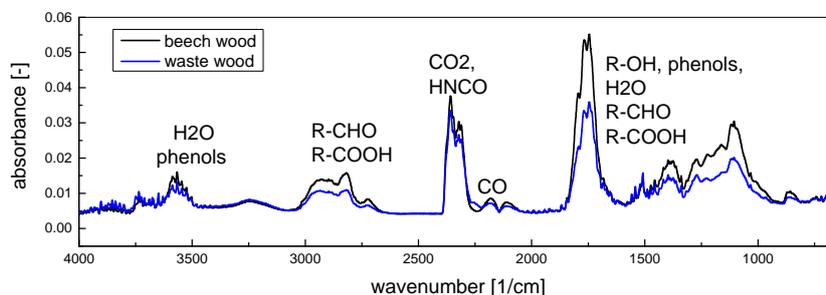

Figure 2: FTIR spectra of pyrolysis gas from beech wood and waste wood (T = 355 ±5 °C).

The absorption bands of isocyanic acid (HNCO) are located between the CO_2 and CO peaks [19] and become visible after subtraction. HNCO was detected only in the waste wood spectra. The maximum absorbance occurred around 270 °C. Figs. 3.a and 3.b show the temperature dependence of measured HNCO spectra and of the integral band intensity.
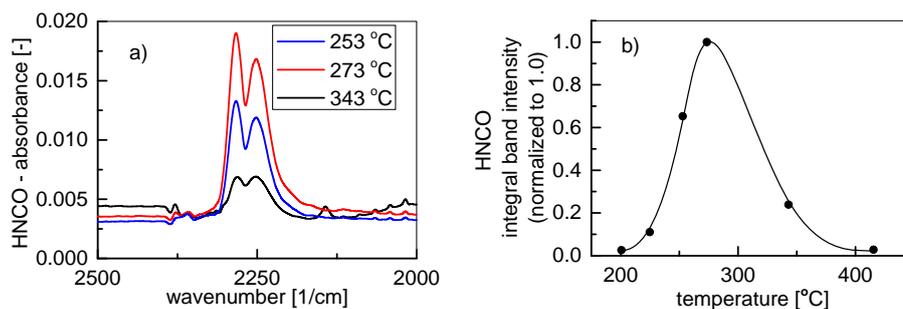

Figure 3: HNCO spectra and band intensity during the pyrolysis of waste wood.

Simultaneously with HNCO, ammonia was detected in the FTIR spectra, with characteristic absorption bands around 966 and 930 cm^{-1}. It appears probable that HNCO and NH_3 originate from monomeric or weakly crosslinked aminoplasts which are used as adhesives in wood panels [20,21]. Taking into account an overall composition of $C_6H_5ON_5$ for the aminoplast and comparing the ultimate analyses of beech wood and waste wood, the amount of amino-plast in the waste wood can be estimated to be up to 5 wt.-% [10].

Figs. 4.a and 4.b show the measured quantitative release rates of CO, CO_2 and CH_4 during the pyrolysis of beech wood and waste wood. The pattern of the release rates was found to be very well correlated to the DTG curves for CO_2, less well for CO and poorly for CH_4. Moreover, CH_4 was detectable from ~ 350 °C only and showed two release peaks close to 400 °C and 550 °C. This suggests that parts of the CH_4 may be formed by secondary pyrolysis reactions, e.g. from metaplast intermediates.
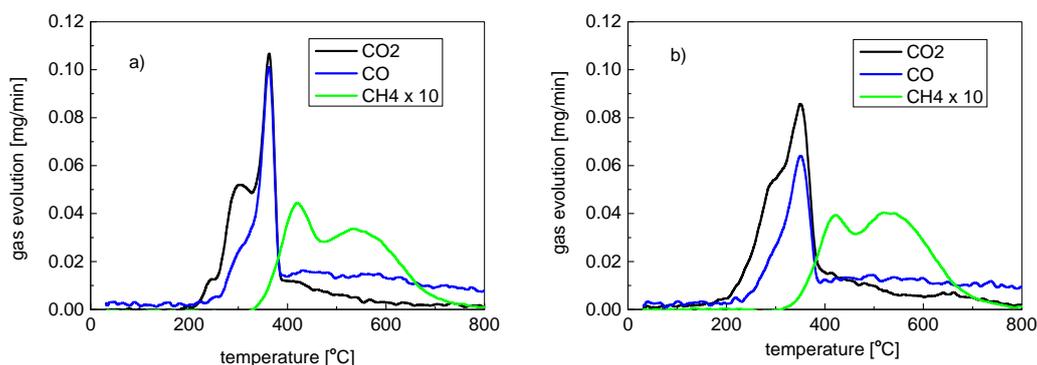

Figure 4: Pyrolysis gas evolution from a) beech wood and b) waste wood.

The model calculation was performed for the natural beech wood sample and the comparison between experiment and model calculation is shown in Fig. 5. The model correctly predicts the gas evolution to be well, moderately and poorly correlated to the total mass loss (DTG).

The release of CO is reproduced quantitatively by the model, but the predicted amount of CO_2 is roughly twice as high as the measured one. Note, however, that a ratio of $CO_2 : CO \approx 2$ is quite typical in low temperature pyrolysis [1]. From this point of view, the calculated release of CO_2 appears to be in good agreement with previous findings, but the experimental results appear to be close to the lower end of previous results. Methane (like other hydrocarbons) is difficult to simulate numerically. The present model calculation reproduces the total amount of released CH_4 quite well, but the calculated methane formation is between 250 and 450 °C, i.e. starting and finishing earlier than measured experimentally.
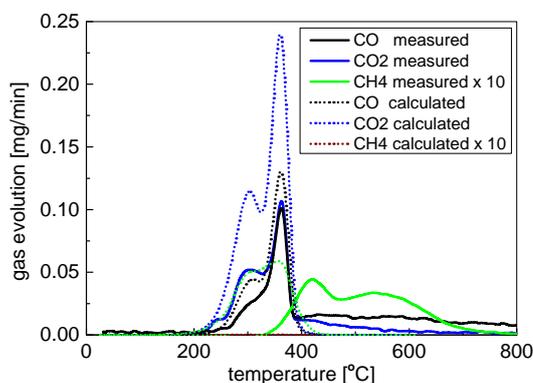

Figure 5: Comparison of measured and calculated pyrolysis gas evolution from beech wood.

4- CONCLUSIONS

Although quite similar in chemical composition, the thermal degradation of beech wood and birch wood was found to be significantly different. The pyrolysis gas composition of beech wood and waste wood was found to be similar, but waste wood releases significant amounts of isocyanic acid and ammonia which probably originate from adhesives. Quantitative data were presented for the release of CO, CO_2 and CH_4. By model calculation, the CO release is simulated in good agreement with the experimental findings. The calculated release of CO_2 is in good agreement with previous literature data, but is approximately twice as high as the measured release. The calculated amount of methane formation during pyrolysis agrees well with the measurements, but the methane formation is calculated to occur too early during the pyrolysis process.

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