Detailed Investigation of Pollutant Formation in Wood Combustion

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Abstract

In order to investigate the processes of wood combustion, we burn small spherical beech wood samples above a laminar premixed flat flame burner. Temperature and residual oxygen content of the burner exhaust gas can be varied. In this article we describe the temporal mass loss of the samples which acts as a conversion progress indicator and the composition of the pyrolysis gas during the pyrolysis process. We observe strong shot to shot deviations arising from spatial and temporal fluctuations of the pyrolysis rate and the combustion progress. However, correlations of the gas components to each other and principal component analysis suggest that the composition of the pyrolysis gas can be described by only two factors throughout the entire conversion.

Introduction

Wood is a CO_2-neutral fuel. By burning biomass one releases exactly the amount of carbon in the form of CO_2 which this tree assimilated during its lifetime [1]. In Germany, every year there accumulates firewood with an energy potential of $\approx 2.26 \cdot 10^{17}$ Joule [2]. This is equivalent to $\approx 7.7 \cdot 10^9$ kg of mineral coal. By reusing fallow acreage the potential would increase up to $5 \cdot 10^{17}$ Joule, equivalent to $\approx 1.7 \cdot 10^{10}$ kg mineral coal. On the other hand wood develops yet more gas than coal during pyrolysis, leading to a very complicated combustion process. Wood combustion is an interaction of different chemical and physical phenomena and is not yet understood in its whole plentitude. This circumstance and the fact that wood combustion is seldom carried out with expert knowledge (cf. parlour-fireplaces) will give rise to heavy pollutant emissions [3]. This leads consistently to conflicts of interest, especially in densely populated areas . The aim of this work is a detailed investigation of the processes involved in wood combustion.

If wood was a homogeneous fuel, its overall formula would read $C_{42}O_{28}H_{60}$[4]. Wood however is characterized by a very heterogeneous composition (e.g. [5]). The beech wood used for our experiments consists of approximately 21 mass-% lignin, 47 mass-% of cellulose and 26 mass-% of polyose. The rest is built up by fat, terpene (resin) and minerals. *Cellulose* stabilizes the cell walls. It conists of β-D-Glucopyranose as the basic module. These monomers connect to each other by 1-4-bonds and build macro molecules with a degree of cross-linking of about 3000 to 10000. *Lignin* consists of miscellaneous methoxyphenols and −toluenes. By condensation of the methoxyl groups they build a densely meshed amorphous network with a degree of cross-linking of about 5000 to 10000. Lignin ties the cellulose fibrils together and also forms atomic bonds with them.

Wood combustion is an interaction of various phenomena, e.g. heat and mass transfer, chemical reactions, phase change and sorption processes. During pyrolysis 80% of the mass convert to a flammable gas leaving the wood via the pores. The pores themselves get bigger little by little. The pyrolysis needs heat which reaches the inner wood by thermal conduction, thus towards the convection.

Drying: Water is not bound chemically but capillary to the wood [6]. A review of wood drying models is given in [7]. The impact of the water content on transport limitation and the ignition delay is investigated by [8],[9] and [10]. The wooden spheres used in this work have been dried in the desiccator several times and should show minor water content with small change from sample to sample.

Decomposition of wood: In this article the term *pyrolysis* is understood as thermal decomposition independent of temperature, heating rate or gas composition in proximity of the wood. If wood is heated above $\approx 670K$, the solid converts to volatile matters. Van Krevelen [11] postulates a *metaplastic state* as intermediate stage. The polymers are cracked at their weakest bonds. At first they remain in the wood as loose fragments, from which many components volatilize. If these fragments are carried away without delay, they form tar. In the case of a transport limitation the fragments will have enough residence time to build new bonds and to abstract small functional groups, especially OH. Cellulose forms anhydrides which react further to furfural derivates and aliphatic acids. Lignin decomposes by forming its primal metoxyphenols. Depending on the temperature,

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60 to 90% of the original mass decompose during pyrolysis with char as the remainder. Pyrolysis is a strictly temperature controlled process: Tinney [12] burned cylindrical timbers with a diameter of 7mm and observed an excess pressure of 0.3bar, because volatile matter is formed inside the wood. This leads to a convection out of the wood. For this reason oxygen is not able to reach the pyrolysis zone while the pyrolysis is in progress. Temperature is the only way to take influence on the conversion from outside. The papers [13],[5],[14] and [15] describe several pyrolysis models.

Burnout of the pyrolysis gas: The pyrolysis gas consists of flammable, partly oxygenated components. Usually it inflames near the wood surface. The combustion-induced temperature rise gives a positive feedback to the pyrolysis rate.

Heterogeneous combustion: After the pyrolysis gas convection has decreased to a point where diffusion between char pores and the bulk phase is possible, the heterogeneous combustion of the remaining coke commences. Carbon is dissolved from the solid char grid by OH-radicals and oxydized to CO_2 at a small distance from the char. But the kinetics are not critical for the heterogeneous combustion, rather are the diffusion of the reactands (non-radical species) in the pores of the char and the heat transfer. Whereas the pyrolysis is merely a function of temperature, the heterogeneous combustion is both, temperature and oxygen-concentration controlled.

In order to investigate the mechanisms of pollutant formation in wood combustion and to analyse the emerging pyrolysis gas during the temporal devolution, the following experiment is carried out.

Experimental setup

For our detailed investigation we need an experiment with conditions close to the technical applications, but well defined and constant in time and space. This leads to the experimental setup described below (Figure 1): Spherical beech wood samples with 25mm in diameter and $\approx$5g of mass are burnt. The furnace is replaced by a laminar premixed flat flame burner (120mm in Diameter). The burner is operated on a mixture of N_2, O_2 and CH_4 in adjustable flow rates and provides the wooden sample with hot exhaust gas which can contain an amount of residual oxygen, according to the adjustment of the experiment. Near the sample this oxygen is availiable for reaction. The experiment is carried out within a huge tube (150mm in Diameter) and is thereby protected against leak air. For adjusting the temperature the burner is moved along the axis towards or away from the sample. Perforated plates above the sample (downstreams) normalise the flow and prevent
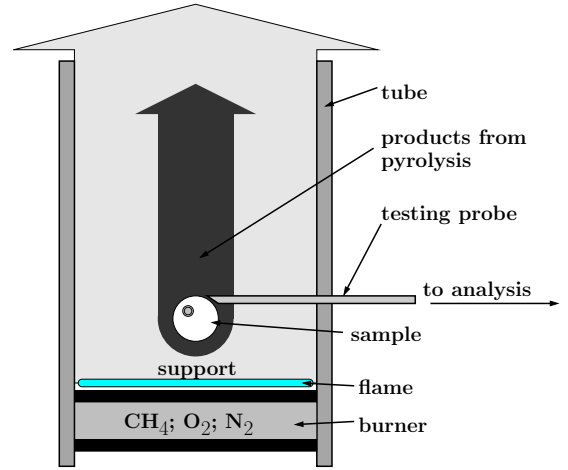
a backflow caused by radial temperature gradients.

Test conditions

The tests are performed at several temperatures (773K, 923K, 1073K) and several oxygen fractions. With a fixed volume flow rate around the sample of $1.2 \cdot 10^{-3} m^3/s$ the following overall mole flows are needed: 1.83mmol/s at 773K, 1.53mmol/s at 923K and 1.32mmol/s at 1073K. Assuming plug-flow this yields a constant velocity of 6.6m/s. At stages with zero oxygen in the burnt support gas, an air-like combination of N_2 and O_2 is mixed stoichiometricaly with methane and burnt in the laminar flat flame. Experiments were also carried out with an overall oxygen surplus of $\frac{1}{8}$mmol/s and $\frac{1}{4}$mmol/s. With the progressive rate of oxygen, the nitrogen rate gets decreased so that the overall flow rate around the sample is maintained. These adjustments give oxygen mole fractions in the burnt support gas of:

O2-surplus\T	773K	923K	1073K
0mmol/s	0vol%	0 vol%	0vol%
$\frac{1}{8}$mmol/s	6.7vol%	7.9vol%	9.1vol%
$\frac{1}{4}$mmol/s	13.3vol%	15.8vol%	18.2vol%

Temporal mass loss

As it will become obvious beneath, the Pyrolysis gas concentration depends on the time the sample has spent above the support flame. As a measure for the conversion of the wood its mass loss is appropriate. At first the wooden ball is weighed together with a beaker of water, then the sample is inserted into the support gas. After a certain time the test is stopped and the sample is quenched in the water. Difference weight to the initial state gives the mass which the wood has lost until the moment of quenching. The rate devolutions of all
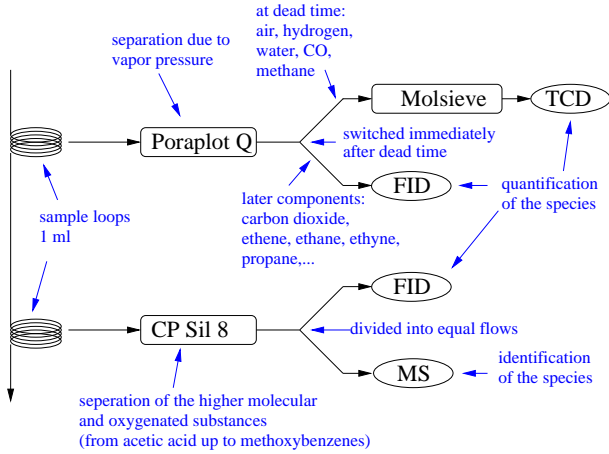
FIGURE 2: Setup for detection of the pyrolysis gas components

FIGURE 3: temporal development of carbon monoxide @ 773K; no Rest-O_2 (Total amount of gas per analysis: ≈ 25000 nmol)

tests begin and end at zero and pass one single maximum between . The curves differ in two criteria:

Cumulative converted mass: The conversion did not reach 100% at any of the experiments. Instead of that, it approaches a value between 75 and 95%. Along with oxygen concentration the total conversion value increases. The heat release of the pyrolysis gas burnout seems to enhance the heterogeneous combustion, otherwise a total conversion of 100% would be possible.

Duration: The duration of the wood conversion ranges from 4 up to 12 minutes. At the absence of residual oxygen an increase in temperature decreases the conversion time from 12 to seven minutes. At experiments with ignited states we were not able to detect a drop in conversion time by increasing the temperature. The duration is $4\frac{1}{2}$ minutes. Other authors who burn smaller samples observe a distinct rise in conversion rate at comparable conditions ([6],[4] and [14]).

Measuring setup for the gas components

A small gas flow is taken directly from the surface of the wood by a probe. This gas mixture is separated into its single components and quantitized by two gas chromatographs. The sample gas gets into the GCs in the following way: It passes two sample loops consecutively ($1cm^3$, 473K, 1bar, dead time from wooden sample to the last of the loops $\approx$16s). At measurement time two 6-port valves are switched inserting the sample loops into the carrier gas flows of the GCs. Figure 2 shows the column assembly used for this experiment.

Temporal evolution of the main products

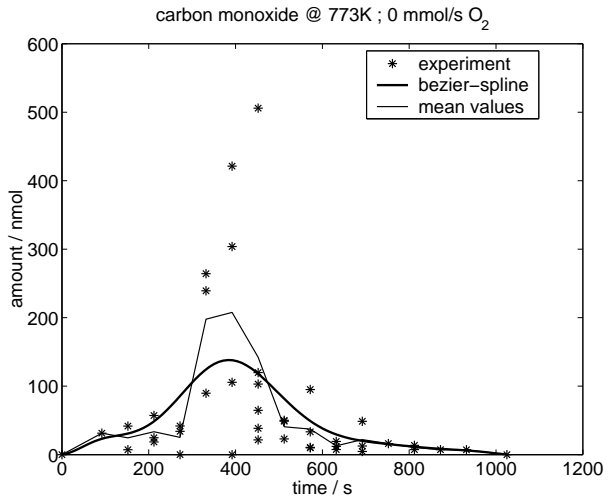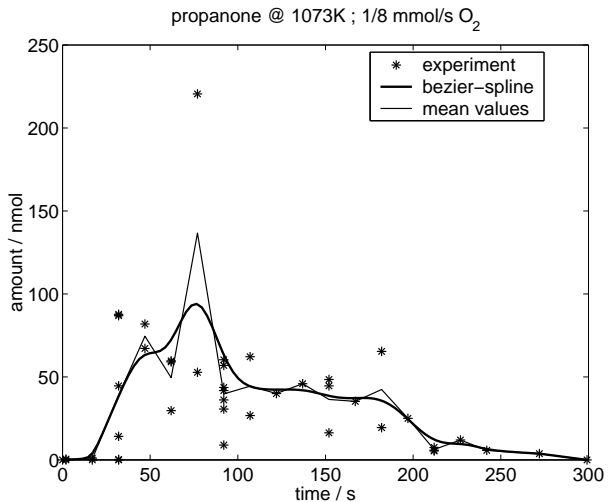With the above described setup we were able to detect about 200 different pyrolysis gas compo-

FIGURE 4: temporal development of propanone @ 1073K; $\frac{1}{8}$mmol/s residual-O_2 (Total amount of gas per analysis: ≈ 25000 nmol)

nents ranging from CO to naphtalene. Only the 35 main species will be discussed in this paper. Figures 3 and 4 show the time evolution of two species concentrations at different test conditions. The concentrations of all species begin and end at zero and pass through a single maximum but the values fluctuate very heavily from shot to shot. A contant flow is diverged through the sample capillary. Not only pure pyrolysis gas gets analysed but also a considerable amount of flat flame support gas, in particular at time stages where the pyrolysis rate is low. The support gas fraction can be defined by the drop of molecular nitrogen compared to the reference measurement without the
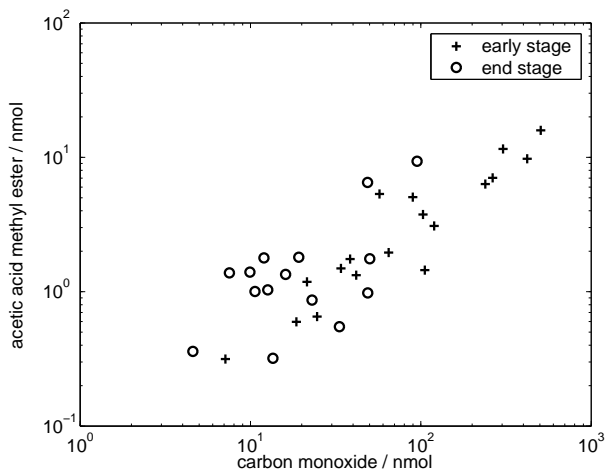
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FIGURE 5: Correlations of acetic acid methyl ester to CO @ 773K, no O_2.
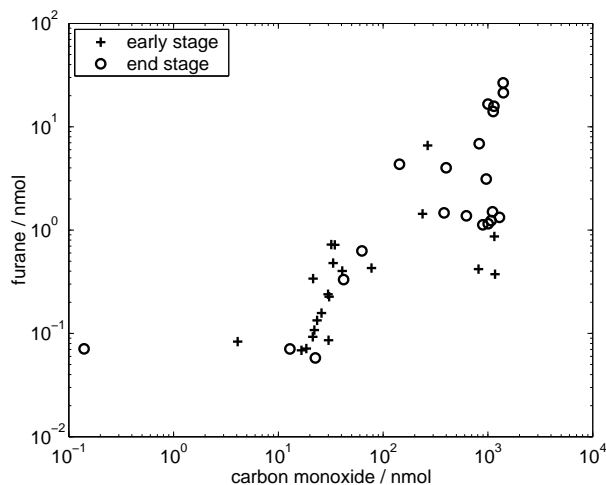

FIGURE 7: Correlation of furane to CO @ 773K, $\frac{1}{4}$mmol/s
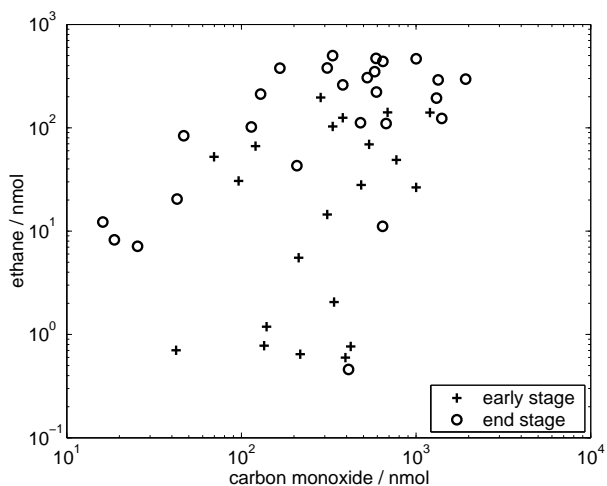

FIGURE 6: Correlation of ethane to CO @ 1073K, no O_2

wooden sample. At our experiments the support gas fraction spreads from 0% to 100% although most of the tests happen at about 70 to 90%. These values were approved by mixing a small amount of neon to the support gas and comparing the drop in concentration compared to reference measurements. (All results presented here are not adjusted to the support gas fraction) These shot to shot fluctuations origin particulary from two phenomena: Pyrolysis gas is exhausted mainly along the pores. Because of the change in shape during the pyrolysis phase it was not possible to adjust the sample properly according to the pore direction. Temporal and spatial fluctuations in the gas exhaust rate of the sample can also be held responsible for the fluctuations in analysis gas concentration. The averaged amounts of the single components make up the following order: Carbon monoxide, propanone, butene, methane,

ethane, furfural, ethyne, butyne, 2-methyl-furane, ethene, methyl-vinyl-ketone, 2,6-dimethoxy-phenol and many more. Benzene which is mentioned to be a main product in many works (e.g.[16]) is a minor product in our tests ranging three orders of magnitude below carbon monoxide. Acetic acid, Water and Hydrogen can not be analysed quantitatively with the existing experimental setup.

Correlation of the species with CO

A method of interpreting the data without the influence of the scatter is to plot one species versus another. If they undergo the same fluctuations of the support gas fraction they should correlate very well. We choose carbon monoxide as the reference substance because of its large concentration and beeing one of the more inert components. At 773K, with no residual O_2, all investigated species show good correlation to CO (exemplified in figure 5). Acetic acid methyl ester, all alkanes and alkenes as far as C4, short oxygenated substances as e.g. propargyl alcohol and furane as cellulose decomposition product and many other species correlate very well to CO ($\rho = 1.0\ldots0.65$). Most of the remaining investigated substances, e.g. benzene, toluene, lignign monomers as 3,4,5-trimethoxytoluene and vanillin correlate little with CO ($\rho = -0.2\ldots+0.2$). These are also the substances that are formed in small concentrations. If the temperature is increased in the case of zero oxygen around the sample, the correlations get less sharp in general (Figure 6). At an increase in residual oxygen concentration from 0 to $\frac{1}{8}$mmol/s — maintaining 773K or 923K for the time being — the results do not change. Further temperature increase at $\frac{1}{8}$mmol/s residual oxygen

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leads to a significant deviation of the results. Albeit some smaller species (Methane and C2) correlate very well, all components above C2 (and ethyne) show the following behavior: At most of the measuerements they correlate well to CO, too. But at some experiments of those with a maximum concentration of CO, the concentration of the correlated species drops to almost zero. Further increase of oxygen to $\frac{1}{4}$mmol/s enforces this behaviour, even at 773K (e.g. Figure 7). This effect was always present at conditions on which the pyrolysis gas inflamed shortly after leaving the wood. It might be attributed to the progress of the combustion: Higher hydrocarbons decompose very quickly whereas the oxidation of CO and CH_4 is slower ([17]).

Principal component analysis

Instead of investigating single correlations a principal component analysis can be carried out: For this purpose we write the results of the main components in a matrix X (n by m). The n lines denote the several measurements at a single set of testing conditions. The m columns denote the different species that were acquired together at each shot in m-tupels. The correlation matrix R reads:

$$R = \frac{1}{n-1} \cdot Z^T \cdot Z \qquad ; \qquad z_{ij} = \frac{x_{ij} - x_j^{mean}}{s_j}$$

In an m-dimensional space this complies to a linear estimator with the mean values of the gas components as the point of origin. The eigenvectors of R are called the factors. They are always linearly independent. Those factors belonging to the largest eigenvalues hold most of the estimator information whereas the factors belonging to small eigenvalues only deal with the scattering. In this way the data are described with the aid of few factors. Note, that the factorial analysis is only a tool for visualising the abundance of the data. We presumed a strict linear coherence between the sets of species which was not definitly apparent from the correlation plots. Especially our results cover several orders of magnitude. In the case of slow conversion at 773K, no residual oxygen (Figure 8) the most important factor holds already 41% of information. The three most important factors together account for approximately 70%. Carbon monoxide, alkanes and alliphatic components as well as furane are adressed by the first factor. All aromatic species, propane and the higher molecular oxygenated substances appear hardly at this first factor. The second factor shows the opposite behavior: It only deals with the aromatic species. A third factor adds a further degree of freedom to propane. We have shown in the previous section that all factors appearing on the first factor also
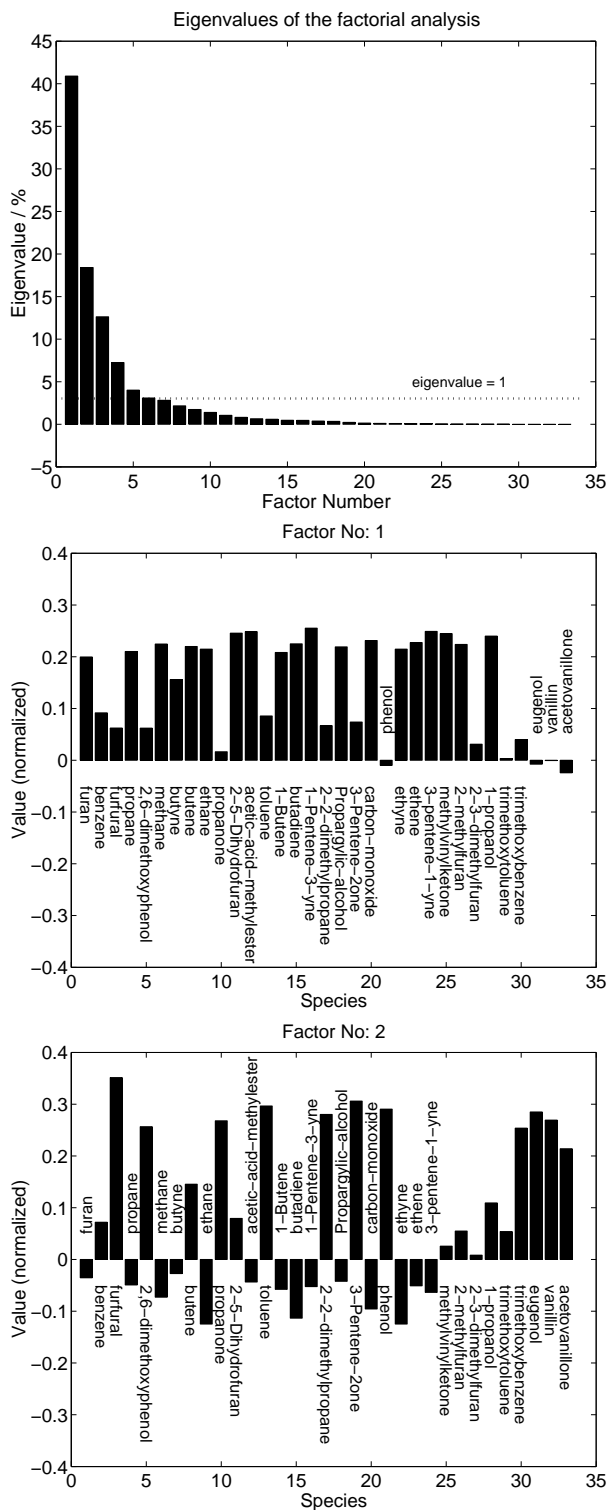

FIGURE 8: Eigenvalues and the two most important factors @ 773K, no O_2

show good correlation whereas all those substances showing few correlation appear on the second factor. These results suggest a description of the pyrolysis gas composition as a sum of one lignin-
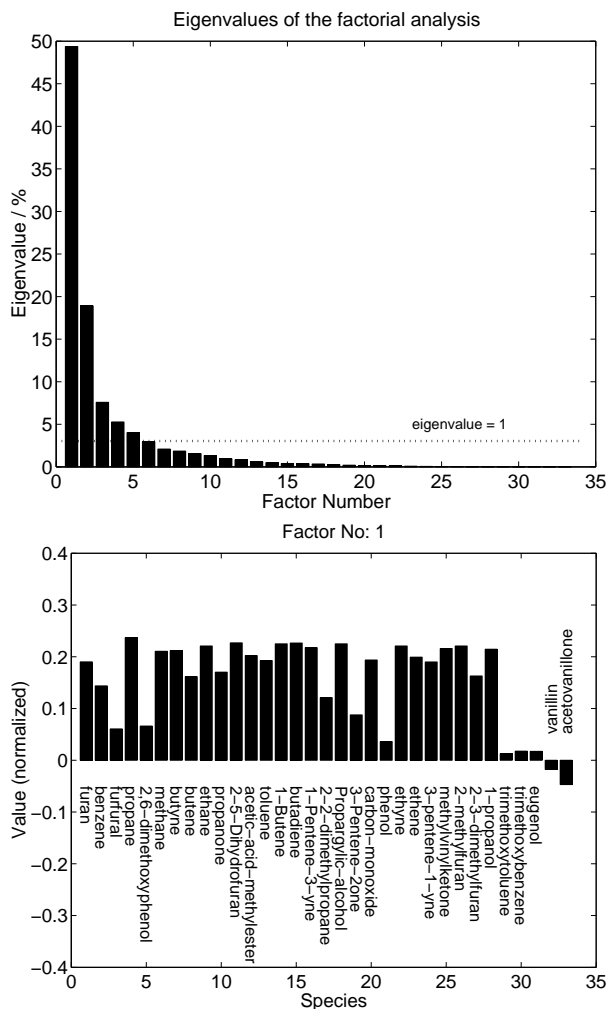
FIGURE 9: Eigenvalues and the most important factor @ 1073K, $\frac{1}{8}$mmol/s O$_2$

factor and one cellulose-factor or rather as a sum of one factor dealing with fast pyrolysis yielding aromatic and higher molecular substances, and another factor describing the decomposition of the wood into small substances at long residence times. These results do not change significantly neighter by increasing the temperatur nor by adding oxygen to the support gas, e.g. figure 9 at 1073K, $\frac{1}{8}$mmol/s residual O$_2$. At these conditions the first factor holds 50% of all the information. Even propanone is accounted to the first factor in the usual extend at 1073K, $\frac{1}{8}$mmol/s O$_2$. Solely the vector components pointing towards the lignin monomers tend to some smaller values. Again the second important factor points towards these species.

Conclusion

The rate of the gases emitted by the wooden sample undergoes large temporal or spatial fluctuations. Uncertainties are the stochastic mixture between pyrolysis gas and support gas, the fluctuating pyrolysis rate and the progress of pyrolysis gas burnout. Examinations in generalized coordinates (principal component analysis and correlations to CO) however show that it is possible to describe the composition of the pyrolysis gas with the aid of two factors. An extension of the correlation analysis to the non-linear case will be subject of future work.

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