

CHARACTERIZATION OF BIOMASS USED IN THERMAL PROCESSES WITH REGARD TO THE KINETIC PROPERTIES

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1 INTRODUCTION

The energetic use of biomass plays currently from ecological and economic reasons an increasing role. This results for some biomasses, for example wood originating fuels to a strong demand and respective market prices. Plant operators are therefore forced to develop new fuel sources and fuels. For fuel substitution in currently operating plants there has to be a number of aspects to be considered. A safe and preferably comprehensive characterization of biomass in view of the chemical, calorific, mechanic and reaction kinetic characteristics is the background focus of this paper.

2 CHARACTERISTICS OF FUELS

Fuel characteristics play an important role for the characterization of fossil and biogenic fuels. At this juncture, as for the fossil fuels it has to be differentiated between the chemical, calorific, mechanical and reaction kinetic characteristics [1, 2, 3, 4]. For this classification the borders are partly not fixed e.g. the ash composition is clearly a chemical characteristic but has a direct influence on the ash melting behavior which is classified here under mechanical characteristics.

2.1 Chemical Characteristics of Biomass

The chemical characteristics of a fuel are defined from its composition. The known methods of proximate analysis [5] and ultimate analysis [6] are also used for the characterization of biomass.

2.2 Calorific Characteristics of Biomass

An important parameter for the characterization of a fuel is the calorific value. It is determined [7], respectively calculated from different empirical equations [1].

The ignition behavior of a biomass fuel depends significantly from the amount of the volatile matter. The ratio of C/H and C/O of the fuel indicates an important statement about the expected amount of the volatile matter and gives also information about the combustion behavior. The knowledge is important for the appropriate design of the reactor chamber and respectively about the consequences of a fuel change.

2.3 Mechanical Characteristics of Biomass

Mechanical characteristics like grindability play an important role for the untreated materials. Long fiber stalk originating biomass like hay or straw and also flax and hemp often show poor grindability. In contrast the wood originating biomasses are mostly unproblematic. This is also valid for biomass chars, so that the technical design of the grinding process has to consider the partly strong ignitability of the coal particles. This results from the surface of the biomass chars, which means from the porosity and surface morphology of the particles. The surface areas of biomass are quite different. BET-experiments have shown that for some biomasses the surface differs of the factor 10 at the same process conditions.

From the chemical characteristics of the ash composition, the ash melting behavior can be derived. This is classified here under mechanical characteristics, since through the melting behavior of the fuel ash the softening and agglomeration behavior of the ashes changes, so it can restrict the application of certain biomasses.

2.4 Reaction Kinetic Characteristics

Reaction kinetic properties include ignition, combustion respective burnout behavior, slagging and fouling behavior, the latter are important concerning the corrosion behavior of deposits. Normally reaction kinetic properties of fuels are investigated experimentally in thermal-balances, drop tube reactors or ignition reactors. For this the chemical composition and volatile matter of the fuels play an important role.

3 CLASSIFICATION OF THE PROCESSES

Solid fuels like biomass go through the following processes during thermal conversion: drying, pyrolysis, gasification and residual burnout. Thermal process conditions like atmosphere, process temperature and residence time determine in combination with the different apparatuses (e.g. grate furnace, combustion chamber, fluidized bed combustion) the operation of the processes. For characterization of fuels, also for biomass, process conditions must be considered for the kinetic classification of thermal processes.

Fuel	Dust	Grain	Scrap
Temperature	middle → high		
λ-Value	Pyrolysis / Gasification / Combustion		
Time of Exposure	ms	s → min	min → h
Type / Examples	- Dust Firing - Entrained Flow Gasification*	- Fluidized Bed Combustion / Gasification - Shaft Gasification	- Rotary Kiln Pyrolysis - Shaft Combustion - Grate Combustion

* fuel preparation necessary

Table 1: Classification of different thermal processes.

Especially for reaction kinetic considerations there is a difference between slow processes (e.g. combustion in a grate furnace) and fast processes (e.g. entrained flow gasification, circular fluidized bed and pulverized firing). In Table 1 a classification of the various processes is made.

From this background this paper focuses especially on the determination of kinetic parameters for slow inert thermal processes using a thermal-balance (TGA) at low heating rates and for fast processes using a drop tube reactor (DTR) at high heating rates.

4 EXPERIMENTAL METHODS OF FUEL CHARACTERISATION FOR DIFFERENT THERMAL PROCESSES

4.1 Slow Thermal Processes – Investigations in a TGA

Due to the relatively slow heating rates in a TGA, slow thermal processes can be well understood and investigated. Here the solid bed processes of pyrolysis, gasification and combustion as well as rotary kiln, screw reactor processes and the technical thermo balance [8] have to be mentioned.

For the investigations a thermal-balance TGA/DSC 1 [9] from Mettler Toledo GmbH is used.

It is an apparatus of laboratory scale, with a horizontal balance and furnace combination (Figure 1) in which the sample is heated under different atmospheres (inert to oxidative). Mass change is measured for the respective process conditions in form of a mass loss curve.

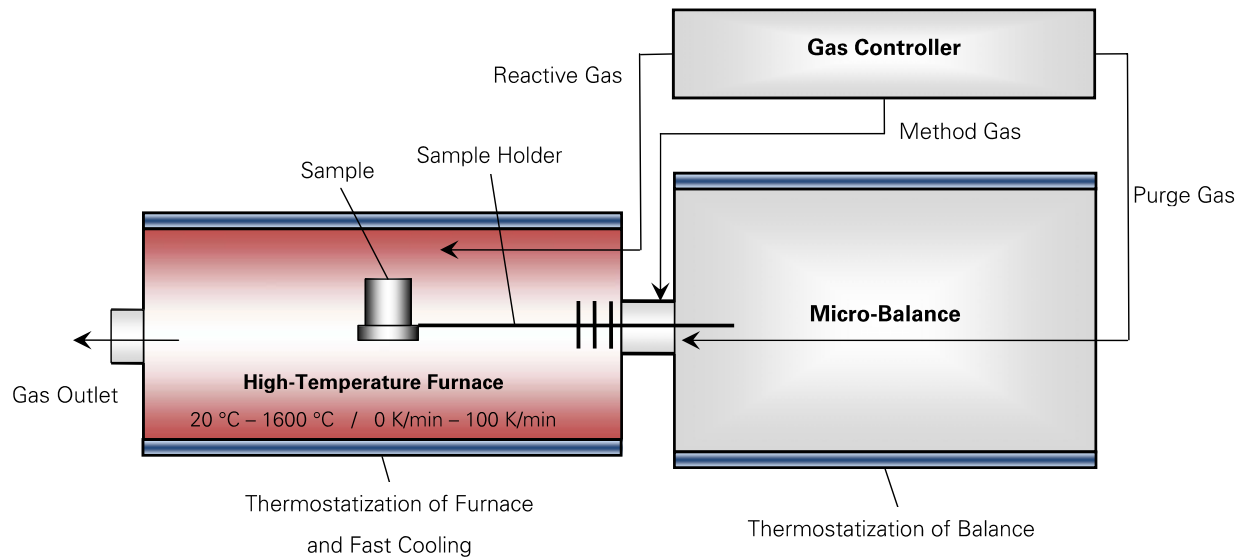


Figure 1: Schematic view of the TGA-Design and function of the Mettler Toledo TGA/DSC 1 used for the examinations of biomass fuels at TU Dresden, Chair of Combustion, Heat- and Mass Transfer.

With this TGA samples of various crucibles with a filling volume up to 900 μl can be heated up to a temperature of 1600 $^{\circ}\text{C}$. The maximum heating rate can be selected from 0 (isothermal operation) until 100 K/min. Beside the information from the heating experiments at different atmospheres information about the solid residues (char, ash) especially the composition and the further thermal behavior can be attained through downstream analysis.

4.2 Fast Thermal Processes – Investigations with a Drop Tube Reactor

Combustion processes run at high heating rates and short residence times. The combustion of biomass e.g. in a pulverized firing can be classified like coal combustion into the two following processes:

- 1. Phase: Pyrolysis (fast release of the volatile matter) and
- 2. Phase: Residual char combustion (heterogeneous oxidation).

The DTR consists of an electrically heated reaction tube, in which a hot reaction gas flows with the same temperature as the reaction tube wall. In the reaction tube the investigated fuel is continually fed, ignited and combusted. The residues and the reaction gases are extracted at different positions of the reaction tube with a sampling probe. The residence time interrelationship with the reaction path and the particle velocity is determined.

In a DTR high temperatures can be realized as in real combustion chambers for steam generation. The gas and tube temperatures and the residence time at the DTR can be controlled. Due to the constant gas and wall temperatures and the laminar gas flow in the reaction tube, the heat and mass transfer processes of fuel particles can be modeled simpler.

The DTR (Figure 2) consists of high temperature resistant steel tube with an internal diameter of 49 mm. The maximum heatable tube length is 2.9 m and the heating is subdivided in 5 heating segments. The segments are individually controlled and can be set up at different temperatures. For every heating segment thermoelements are attached on the tube wall and controlled. The composition of the reaction gases is set up in a gas mixing station. Through the feeding of steam the humidification of the reaction gas is realized. The gas pre-heater serves to regulate the gas temperature before the entry in the reaction tube. With this, the real temperatures in a flame or in a high temperature reactor can be realized up to 1300 $^{\circ}\text{C}$. The fed reaction gas is normally 3 m^3/h (STP). For biomasses which are difficult to combust – the reaction gas amount can be reduced to 2 m^3/h (STP). The fuel particles are dosed at the top part of the reaction tube through a vibration feeder. A small partial flow of the reaction gas is diverted before the gas pre-heater and is

conveyed as purging gas through the feeder. The amount of fuel has to be selected, after the suggestion from FIELD [10] that the O/C mass ratio should not be above 100. The dosed amount varies with the amount of carbon in the fuel and the oxygen in the reaction gas normally between 1g/h up to 4 g/h.

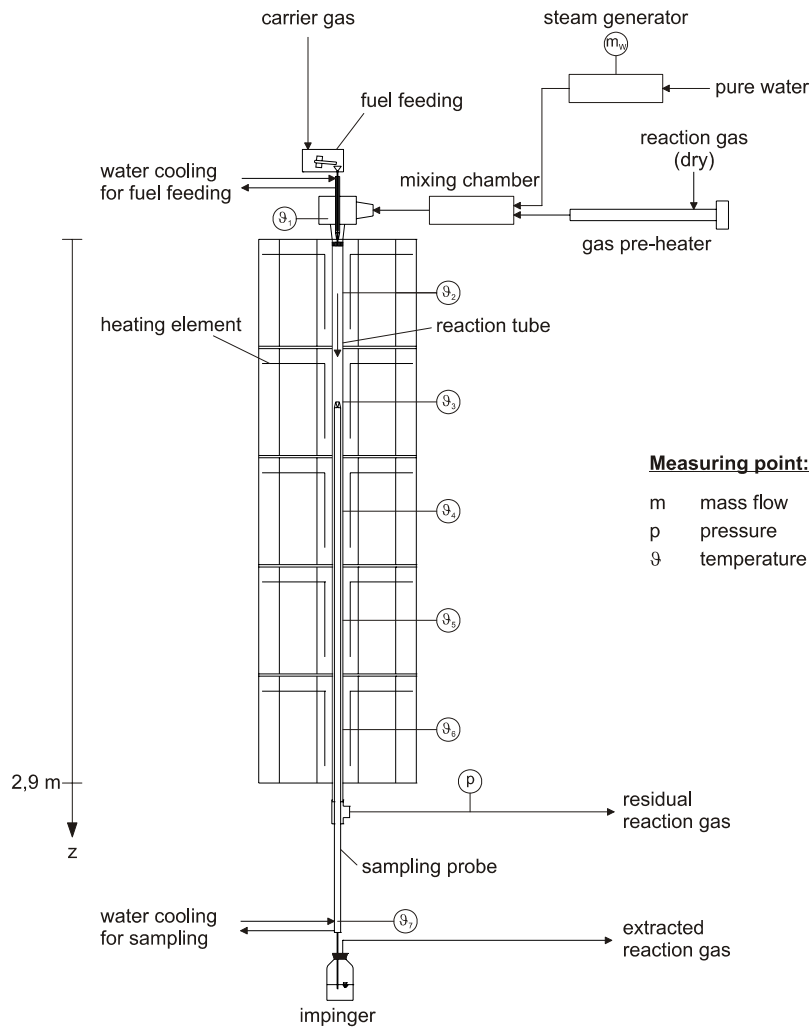


Figure 2: Configuration of the drop tube reactor at TU Dresden, Chair of Combustion, Heat- and Mass Transfer.

The residuals are extracted isokinetically by a water cooled sampling probe. Here the temperature of the sample particles is cooled very fast to a temperature under 300 °C. The actual sample collection occurs in the downstream wet scrubber where the residuals are separated from the reaction gas. The sample is initially dried in the laboratory and the following characteristics are analyzed:

- particle size distribution,
- density,
- proximate analysis (if applicable: the determination of the combustible amount on the thermal-balance for small sample sizes [11]).

5 RESULTS OF THE KINETIC INVESTIGATIONS

5.1 Reaction Kinetic Characteristics from TGA Investigations

For the reaction kinetic investigation from the TGA curves two simple methods according to Kissinger [12, 13] and Ozawa [12, 14] are chosen. The methods are illustrated against each other as a control mechanism. They were developed for the evaluation of dynamic heating curves from thermo-gravimetric investigations in the 1950 and 1960's. They are based on the evaluation of the temperature for maximum material conversion. From that the most solid \rightarrow solid + gas-reactions are described by the equation¹

$$\frac{d\alpha}{dt} = k_{0,v} \cdot f(\alpha) \cdot \exp\left(\frac{-E}{\mathfrak{R} \cdot T}\right) \quad (1).$$

Since for reaction kinetic investigations of fuels in a TGA the heating process has a dynamic character, the heating rate must be considered in contrary for investigations in a DTR where the process is regarded as isothermal. This is shown by the equation

$$T = T_0 + \beta \cdot (t - t_0) \quad (2).$$

After application and conversion in the equation according to Kissinger this results to

$$\ln\left(\frac{\beta}{T_{max,Peak}^2}\right) = -\frac{E}{\mathfrak{R} \cdot T_{max,Peak}} + \ln\left(\frac{k_{0,v} \cdot \mathfrak{R}}{E}\right) + \ln[n \cdot (1 - \alpha)^{n-1}] \quad (3).$$

Considering the reaction approximately as a reaction of 1st order, the last term becomes zero. In this case it is valid:

$$\ln\left(\frac{\beta}{T_{max,Peak}^2}\right) = -\frac{E}{\mathfrak{R} \cdot T_{max,Peak}} + \ln\left(\frac{k_{0,v} \cdot \mathfrak{R}}{E}\right) \quad (4).$$

The equation postulated by Ozawa is also based on the equation (1) and (2), but another solution equation is used. Solving the equation from Ozawa, one attains the following equation (5)

$$\ln \beta = \ln\left[\frac{k_{0,v} \cdot E}{\mathfrak{R} \cdot g(\alpha)}\right] + \ln p(x) \quad (5).$$

$p(x) = p\left(\frac{E}{\mathfrak{R} \cdot T}\right)$ can be solved after the approximate approach from Doyle [15], respectively from a revised approach according to Doyle [16].

The equations (4) and (5) are illustrated in a linear equation and evaluated, as $\ln\left(\frac{\beta}{T_{max,Peak}^2}\right)$

respectively $\ln \beta$ is plotted against $\frac{1}{T_{max,Peak}}$.

Evaluation of results from the TGA Experiments

An example of wood shavings from pinewood is analyzed for the above mentioned equations for the determination of the kinetic parameters of activation energy E and the pre-exponential factor $k_{0,v}$.

The initial weight is carried out in crucibles from Al_2O_3 with a filling volume of 70 μ l. The heating occurs for all samples from 35 °C to 800 °C under nitrogen atmosphere with heating rates of 5 K/min, 15 K/min, 25 K/min, 35 K/min und 45 K/min.

¹ adapted with regard to pyrolysis conditions (devolatilization)

TG Curves of Pyrolyzed Wood Shavings from Pinewood

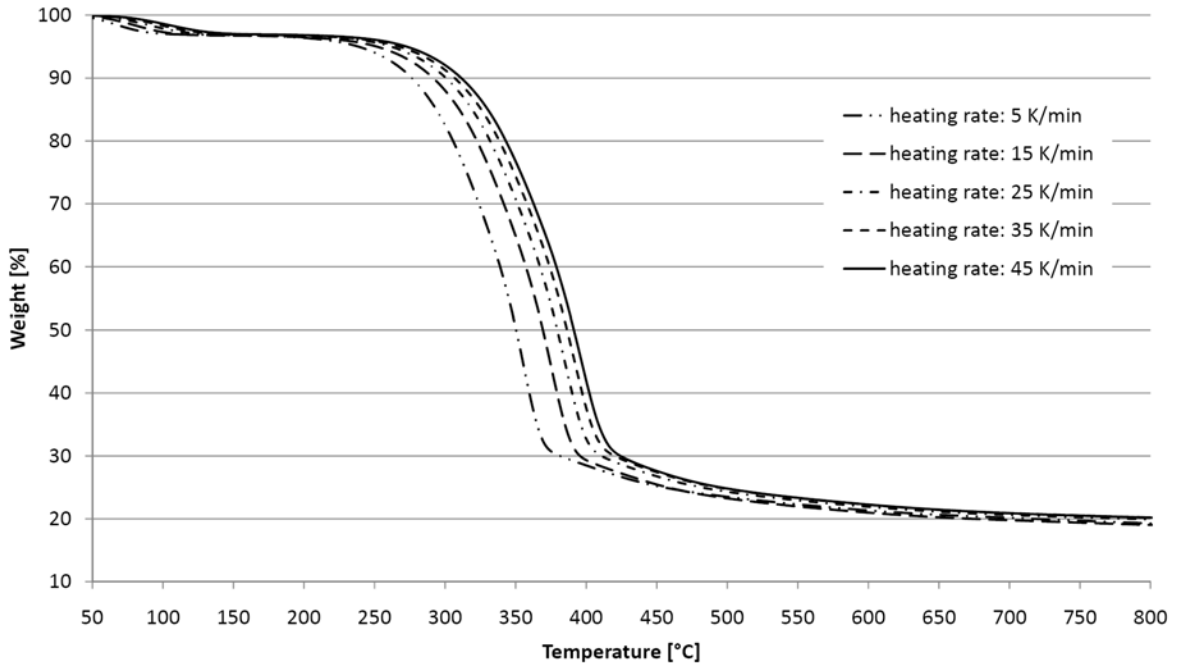


Figure 3: TG curves of wood shavings from pinewood at different heating rates from 5 K/min to 45 K/min under a nitrogen atmosphere.

The previous Figure 3 shows the TGA curves for the respective heating rate. The mass loss which occurs due to the drying is clear to note for all the 5 heating rates. Remarkable to note is that the vaporization at high heating rates ends later as for slower heating rates. From about 200 °C the first pyrolysis step can be noted, and depending on the heating rate it is completed between 360 °C and 425 °C.

DTG Curves of Pyrolyzed Wood Shavings from Pinewood

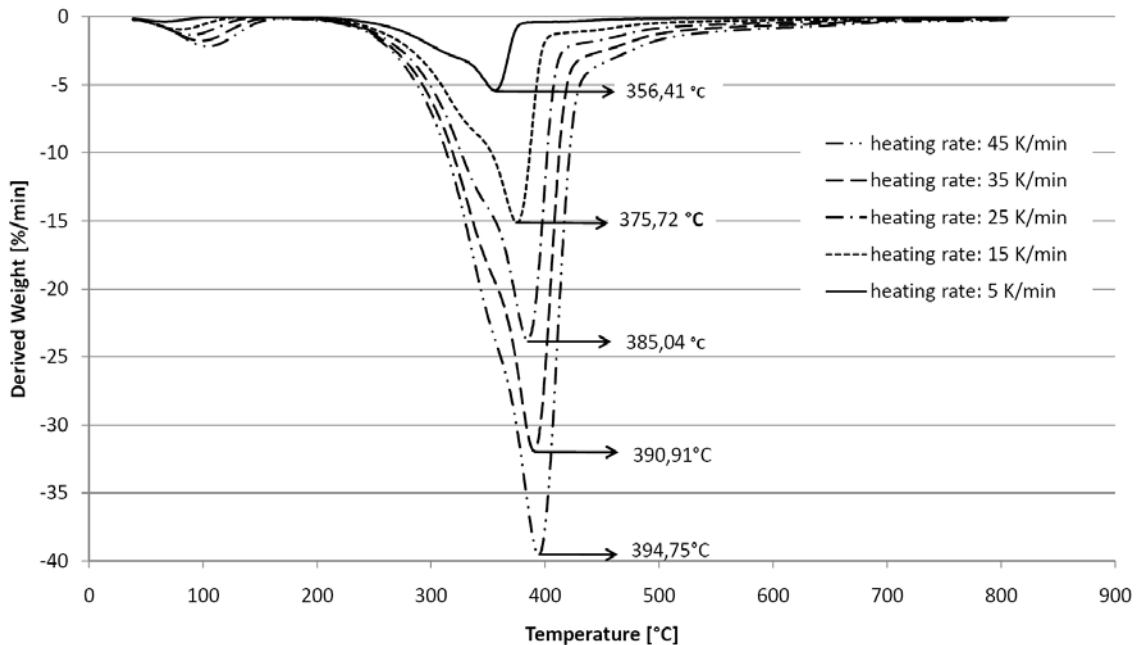


Figure 4: DTG curves of wood shavings from pinewood at different heating rates from 5 K/min to 45 K/min with the respective peak temperatures used for the kinetic evaluation.

At this point already 70 % of the original mass has been converted, hence a large amount of the volatile matter has been pyrolyzed.

The degasification of the second pyrolysis step progresses basically flatter and slower and at 700 °C it approaches gradually to constant mass.

The previous Figure 4 shows the first derivation of the mass loss curve, that is the devolatilization rate of the process. Clearly at the left side of Figure 4 the influence of the increase in heating rate for drying of the material can be noted. The peak is shifted at higher heating rates to higher temperatures. In the central part of the diagram it can be noted, how fast the pyrolysis progresses for the single heating rates. At lower heating rates the pyrolysis progresses with lower conversion rates than at higher heating rates. From the DTA-curves the peak-maximum-temperature for the kinetic evaluation based on Kissinger and Ozawa are determined [12].

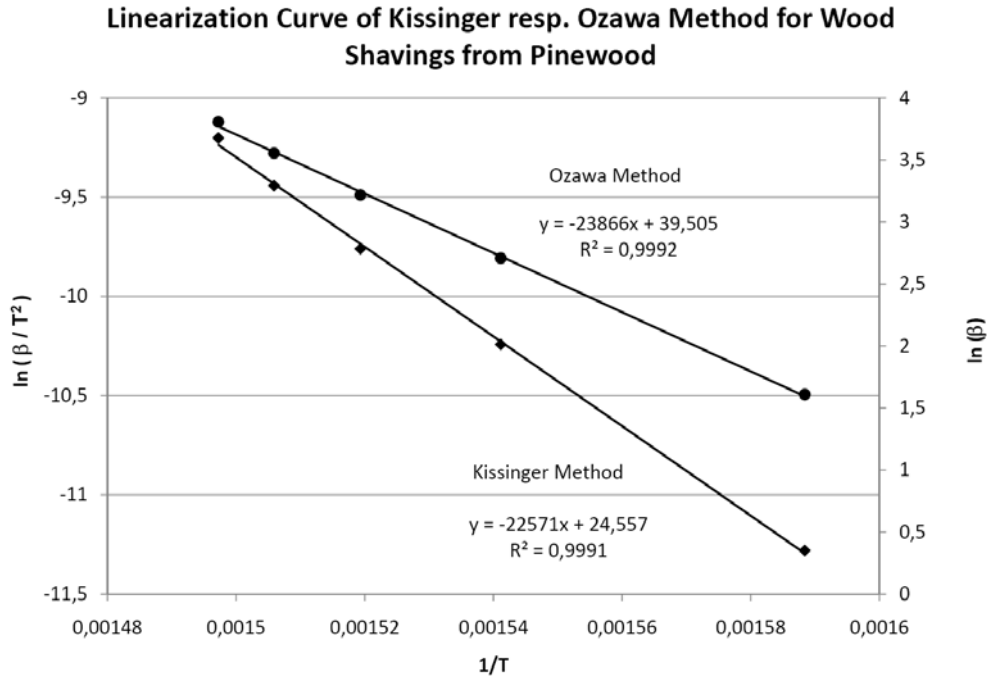


Figure 5: Linearization slope according to the Kissinger and Ozawa Method for wood shavings from pinewood.

In Figure 5, the linearization line of the value $\ln\left(\frac{\beta}{T_{max,Peak}^2}\right)$ for the method from Kissinger and also

$\ln\beta$ for the method from Ozawa is plotted against $\frac{1}{T_{max,Peak}}$. The coefficient of determination R^2

for both methods shows a very good correlation of the measured values of approximately 1.

The evaluation of equation (4) shows an apparent activation energy for the wood shavings after Kissinger of $E = 187.66$ kJ/mol from the gradient of the line and an pre-exponential factor of $k_{0,V} = 34.58$ 1/s.

From the method from Ozawa the apparent activation energy E calculated from the line gradient is 188.69 kJ/mol and the pre-exponential factor $k_{0,V}$ is 34.39 1/s.

The correlation between both methods is very good and the difference between the results is about 1 kJ/mol for the activation energy. From the revised equation of Dolye by Junmeng et. al [16] the values of the apparent activation energy are more closer to each other. The difference between the two methods according to Kissinger and Ozawa is only 0.95 kJ/mol. Also with this approach the difference between the pre-exponential factors from Kissinger and Ozawa can be reduced.

Kinetic investigations with the commercial Star^e-Software from Mettler-Toledo [9] are based on the equation for model free kinetic. Until a devolatilization level of approximately 90 % the investigations show a relatively constant mean activation energy of 188.74 kJ/mol.

5.2 Reaction Kinetic Characteristics from Drop Tube Reactor Investigations

Under steam production conditions that means for single particle combustion at a high heating rate, the main influencing parameters for the combustion process are independently varied from each other. For example these are oxygen concentration in the reaction gas, the reaction gas temperature and the residence time.

The principle of reaction kinetic investigation is based on, that the reaction path dependency (i.e. time combustion behavior) has to be quantitatively determined for fuels with a fixed particle distribution under defined physical-chemical conditions. The variation of the reaction path z occurs from the insertion point of the sampling probe.

From the proximate analysis of the investigated biomass the composition can be summarized as follows:

$$\xi_{H,B} + \xi_{V,B} + \xi_{C,B} + \xi_{A,B} = 1 \quad (6).$$

The unburnt fraction $u(z)$ along the reaction path are evaluated from the dry ash amount $\xi_{A,B,d}$ of the biomass, from the mass of the residuals m_R and from the ash amount in the residuals $m_{A,R}$. This method is referred to as ash-as-tracer method.

$$u(z) = \frac{\xi_{A,B,d}}{1 - \xi_{A,B,d}} \cdot \frac{1 - \xi_{A,R}(z)}{\xi_{A,R}(z)} \quad (7).$$

During the burnout in the reaction tube, the mass, the diameter and the density of the fuel particle are changed. In order to determine the kinetic parameters a combustion model has to be considered. A combustion model is a complex, mathematical description of the development of a fuel particle in the reaction zone. In this case the combustion model is based on a cell model. More information about the used combustion model is found in literature [11, 17, 18, 19, 20].

The mass change of the volatile matter during pyrolysis can be described by the 1st order Arrhenius Equation

$$\frac{dm_V}{dt} = -k_V \cdot m_V \quad (8),$$

$$k_V = k_{0,V} \cdot \exp\left(\frac{-E_V}{\mathfrak{R} \cdot T_{P,m}}\right) \quad (9).$$

The material conversion of the residual char combustion can be formulated through the Arrhenius Equation. The apparent reaction rate coefficient in this case is referred on the surface of all particles

$$\frac{dm_C}{dt} = -N_p \cdot A_{P,S} \cdot k_C \quad (10).$$

Since the carbon conversion is dependent on oxygen concentration, it is therefore included in the determination of the apparent reaction rate coefficient.

$$k_C = k_{0,C} \cdot p_{O_2,S}^n \cdot \exp\left(\frac{-E_C}{\mathfrak{R} \cdot T_{P,m}}\right) \quad (11).$$

In the equation (10) N_p represents the number of the particles before combustion

$$N_p = \frac{m_B}{m_P} = \frac{m_B}{\rho_{P,0} \cdot \frac{1}{6} \cdot \pi \cdot d_{P,0}^3} \quad (12).$$

With the exponent n for the oxygen partial pressure on the particle surface the apparent reaction order of the residual char combustion can be considered. For the residual char combustion a single layer model with carbon monoxide as the only reaction product is taken. The further oxidation of the carbon monoxide occurs in the reaction gas. The progression of the unburnt fraction along the reaction path can be calculated by the following equation

$$u(z) = \frac{m_{V,B}(z) + m_{C,B}(z)}{m_{V,B,0} + m_{C,B,0}} \quad (13).$$

In the combustion model it is assumed that the residual char combustion occurs simultaneously with the pyrolysis of the volatile matter.

In real plants, fuels with a defined particle distribution are applied into combustion units. If the accurate kinetic data are needed for the applied fuels, the particle size distribution has to be considered for investigations in DTR. The particle size distribution can be interpreted in the combustion model with various fractions i and the respective amount of mass ξ_i . The unburnt fraction of the respective size class in a cell are simultaneously calculated in the combustion model and summed together.

$$m_V(z) = \sum \xi_i \cdot m_{V,i}(z) \quad (14),$$

$$m_C(z) = \sum \xi_i \cdot m_{C,i}(z) \quad (15).$$

From that it results for the total unburnt fraction

$$u(z) = \frac{m_V(z) + m_C(z)}{m_{V,0} + m_{C,0}} = \frac{\sum \xi_i \cdot [m_{V,i}(z) + m_{C,i}(z)]}{m_{V,0} + m_{C,0}} = \sum \xi_i \cdot u_i(z) \quad (16).$$

With the combustion model the reaction progress of the fuel particle in the DTR can be closely reproduced. The aimed kinetic data like pre-exponential factors ($k_{0,V}$ and $k_{0,C}$) and the activation energies (E_V and E_C) are given in the model as known values.

The kinetic parameters of the pyrolysis are firstly determined, whereby the fuel in the DTR with an inert gas atmosphere (e.g nitrogen) is investigated. The same combustion model without considering the residual char combustion is used here. The progression of the unburnt fraction is calculated with an estimated band of parameter pairs. The burnout curve which is calculated with the given parameter combination is compared point wise to the measured values. If for a fuel sample various burntout curves at different process conditions are taken, then the deviation of a burntout curve at any chosen measuring point can be given as:

$$f_{j,k,l} = u_{k,l,measured}(z) - u_{j,k,l,calculated}(z) \quad (17),$$

whereby the indices j , k and l are respectively for the parameter combinations, burnout curve and the measuring point number indicator. For every parameter pair, an average standard deviation is made, in which all the calculated curves are compared to the experimental measurement points

$$f_j = \sqrt{\frac{1}{k_{max} \cdot l_{max}} \sum_k \sum_l f_{j,k,l}^2} \quad (18).$$

The parameter combination which leads to the smallest standard deviation is chosen as the result. Analogous, the reaction kinetic parameters for the residual char combustion with the known pyrolysis parameters will be calculated.

In Figure 6 the calculated burnout curves and the measured values at the DTR for lignite is shown. The measured reaction path is 1,3 m. The respective particle residence time is about 0,4 s. With the apparent reaction order of $n = 1$ and the parameter pair for pyrolysis of $k_{0,V} = 0,8 \cdot 10^6$ 1/s and $E_V = 104$ kJ/mol, the parameter pair $k_{0,C} = 3,5$ g/(m²·s·Pa) und $E_C = 60$ kJ/mol for the residual char combustion is determined.

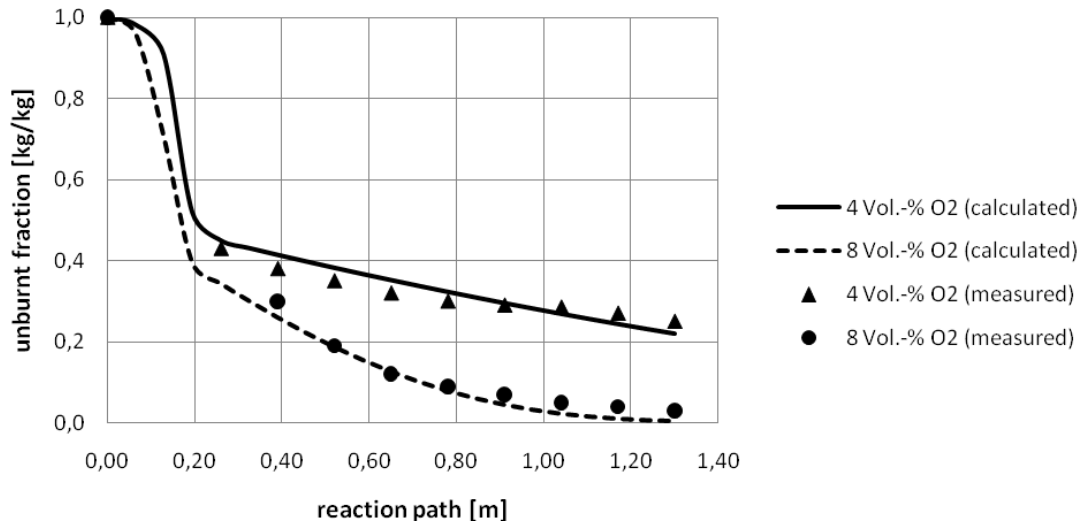


Figure 6: Comparison of the evaluated burnout curves with the measured values (Lignite, 125-160 μm at 900 $^{\circ}\text{C}$).

6 CONCLUSIONS AND FUTURE OUTLOOK

Two parameters have a large influence on pyrolysis of biomass. On the one hand process temperature plays a role and on the other hand the heating rate too. At higher process end temperatures the devolatilization level is higher and at high heating rates the state of a constant mass is reached earlier, that means the pyrolysis process is faster. Simultaneously at low heating rates the pyrolysis steps are completed at lower temperature levels. With higher heating rates the absolute maximum of the pyrolysis is shifted to higher temperatures.

With an exemplarily chosen biomass – wood shavings from pinewood – it is shown through the use of simple reaction kinetic methods that the apparent activation energy and the pre-exponential factor can be evaluated from a series of pyrolysis measurements with different heating rates in TGA. It can be noted that the reaction kinetic parameters for the degasification are only dependent on the heating rate, an influence from process end temperature cannot be seen. From both used methods according to Kissinger and Ozawa only small differences can be noted. This result has been confirmed by a software-based analysis using the method of model free kinetics.

The combustion of biomass particles at high heating rates (10^4 - 10^5 K/s) and short residence times (up to 2 s) can be simulated in DTR. Through the burnout curves it can be seen that the pyrolysis occurred very fast whilst the residual char combustion progressed slower. Investigating the influence of the reaction temperature on the burnout, it is ascertained that through increasing the temperature a defined burnout can be achieved in shorter residence time. The burnout rate increases with the decrease in the particle size of the fuel. Burnout can be increased by an increase of the oxygen concentration in the reaction gas. With an appropriate combustion model for the DTR, the reaction kinetic data of the pyrolysis and the residual char combustion of the used fuel can be attained. Particle size distribution is also considered.

The attained values can be applied in reaction models for the respective reactor and process types to obtain a higher accuracy for pre-calculations at the design and modification of thermal processes.

7 SYMBOLS

α	conversion, [-]		Indexes
β	heating rate, [K/min]	A	ash
ξ	mass fraction, [kg/kg]	B	fuel or biomass
\mathfrak{R}	gas constant, 8,314 [J/(mol·K)]	C	char (fixed carbon)
A	area, [m ²]	d	dry
E	activation energy, [J/mol]	H	humidity
$k_{0,C}$	pre-exponential factor of residual char combustion, [kg/(m ² ·s·Pa ⁿ)]	m	mean
$k_{0,V}$	pre-exponential factor of pyrolysis, [1/s]	max	maximum
k_C	coefficient of reaction rate of the residual char combustion, [kg/(m ² ·s)]	O_2	oxygen
k_V	coefficient of reaction rate of the pyrolysis, [1/s]	P	particle
m	mass, [kg]	R	residue
n	reaction order, [-]	S	surface
N_p	number of particles, [-]	V	volatiles
p	pressure, [Pa]		
t	time, [s]		Abbreviations
T	absolute temperature, [K]	DTR	drop tube reactor
u	unburnt fraction, [kg/kg]	TGA	thermal-balance
z	reaction path, [m]	STP	standard temperature and pressure

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