COMPARISON OF DIFFERENT DIAGNOSTIC TECHNIQUES FOR THE ASSESSMENT OF COAL PYROLYSIS RATE

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Abstract and Introduction

Simulation of fluidized bed combustion by commercial tools such as Barracuda or other CFD codes requires suitable kinetic models. Notably in fluidized bed reactors pyrolysis takes place with high heating rate in the temperature range of 800–900 °C and with coarse particle sizes (up to 10 mm). Therefore, intrinsic kinetics must be combined with modeling of heat and mass transfer.

Intrinsic kinetics can be obtained by conventional TGA analysis at low heating rate (2–20 K/min) and with small particle size (in the order of 100 μm). Recently a fluidized bed reactor purposely designed for operation with small particle size in combination with FTIR gas analysis has been used in Aachen to measure pyrolysis kinetics with high particle heating rate compatible with fluidized bed conditions [1]. Another innovative method to assess the rates of pyrolysis under fluidized bed conditions has been proposed by Solimene [2] in Naples and relies on the measurement of time resolved pressure.

In the present work these different methodologies have been used for a German bituminous coal "Auguste Victoria" to obtain pyrolysis behavior over a broad range of operating conditions. Results show that for the two fluidized bed test rigs, using larger particle sizes, transport limitations become important. As expected, for this regime the reactions rates become lower the larger the particle size.

Experimental description

The work was carried out on a German bituminous coal "Auguste Victoria" (AV). Ultimate and proximate analysis are reported in Table 1 and ash analysis in Table 2. The experimental conditions are given in Table 3.

Table 1. Coal analysis

Ultimate Analysis [wt.-%, dry]	
Carbon	79.36
Hydrogen	4.81
Nitrogen	1.85
Sulphur	1.08
Oxygen (Rest)	5.37
Proximate [wt.-%, raw]	
Ash	7.29
Volatile Matter	27.01
Fixed Carbon (Rest)	62.46
Moisture	3.24
Calorific Analysis [MJ/kg, dry]	
LHV	31.2

Table 2. Ash analysis

Ash	[wt.-%] of ash
SiO_2	51.0
Al_2O_3	27.3
Fe_2O_3	8.7
CaO	2.2
MgO	1.1
SrO	0.09
BaO	0.14
Na_2O	1.28
K_2O	4.7
MnO	0.04
TiO_2	1.1
SO_3	1.78
P_2O_5	0.61

Table 3. Experimental conditions of different tests

Reactor	Particle size range [μm]	Temperature [°C]
Fluidized bed with FTIR gas analysis	125–160	500; 600; 700; 800
Fluidized bed with pressure measurement	200–600; 600–850; 1,000–1,400; 1,400–2,800	700; 750; 800; 850
TGA	94–112	up to 850

TGA
TGA experiments were carried out in a Netzsch STA 409 CD thermo balance in a flow of nitrogen of 250 ml/min. Before the pyrolysis tests the samples of about 20 mg were dehumidified in the TGA for 10 min at 100 °C. Afterwards the samples were heated up to 850 °C with constant heating rates of 2, 5, 10 and 20 K/min. The samples were finally held at 850 °C for additional 30 min.
Mass loss data has been worked out to calculate:

conversion degree $f(t) = \frac{m_0 - m(t)}{m_0 - m_{Char}}$ and conversion rate $R = \frac{df}{dt}$.

Fig. 1 compares the pyrolysis rate profile obtained from mass loss with the results of gas analysis. It can be observed that the main peak of mass loss (indicated by arrow 1 in Fig. 1) is not balanced by the net release rate of CH_4, CO, CO_2 and H_2. The difference in mass loss rate and net gas release rate can be traced back to the

formation of heavier volatile compounds in the main stage of pyrolysis (primary pyrolysis) not detected by the gas analyzers. At higher temperature a second and modest event of pyrolysis (indicated by arrow 2 in Fig. 1), which can be regarded as a secondary pyrolysis stage, occurs with formation of CH_4, CO_2 and H_2. Here, the release of heavier volatiles seems to be negligible because mass loss rate and net release rate of CH_4, CO, CO_2 and H_2 match well with each other.
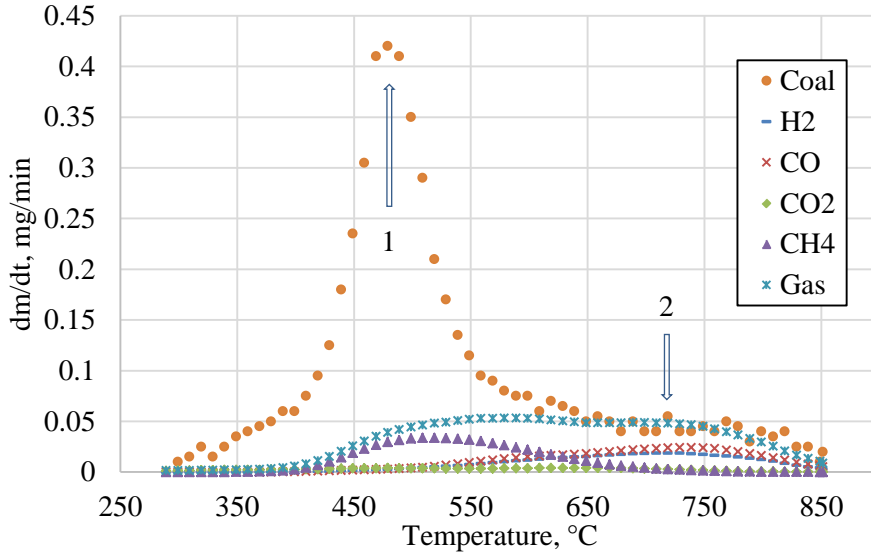

Figure 1. Mass loss rate of coal compared to measured species in the TG

Primary pyrolysis has been modeled by a power law kinetic expression:

$$R = \frac{df}{dt} = k_0 \exp\left(\frac{E_a}{R_u T}\right) \cdot (1 - f)^n \tag{1}$$

The kinetic parameters obtained by Kissinger [3] and Friedman [4] methods are reported in Table 4:

Table 4. Kinetic data from TG analysis

	E_A/R_u [K]	k_0 [1/s]	n
Primary pyrolysis	2.9E+04	1.4E+15	6.8

Naples' fluidized bed with pressure measurement
Experiments have been carried out in a 17 mm inner diameter fluidized bed reactor (Figure 2, left) described in detail in [2]. A high-precision piezo resistive electronic pressure transducer has been used to measure the pressure increase due to released gases.
Quartz sand with a size range of 300–400 μm was used as bed material with an inventory of 13 g, which corresponds to a static bed height of about 40 mm.

The nitrogen gas flow for all experiments was 39.2 l_N/h, which corresponds to a superficial velocity of 0.18 m/s at 850 °C. The batch-wise fuel mass fed into the reactor is about 50 mg. Typical heating rates are in the order of 10^4 K/s.

Assuming ideal gas law, the mass balance on the nitrogen and volatiles leads to

$$V_R \frac{dP}{dt} + K_P P(P - P_{ATM}) = R_G T_R \left(\frac{\dot{m}_0}{M_{gas}} + \frac{\dot{m}_v(t)}{M_{vol}} \right), \tag{2}$$

where V_R is the reactor volume, $\dot{m}_0$ is the mass flow rate of the nitrogen and $\dot{m}_{vol}(t)$ is the mass flow rate of the emitted volatiles. M_{gas} is the molar mass of nitrogen and M_{vol} the molar mass of the volatiles. K_P is the linear constant between flowrate and pressure difference in the reactor to the surrounding [2]. Equation 2 can be solved for $\frac{\dot{m}_v(t)}{M_{vol}}$, the molar mass flow of the volatiles, based on the measurement data. A typical result is shown in Fig. 2, right. The negative values for molar mass flow occur for the moment in time when the coal is added to the reactor. These negative values are excluded from further data analysis.

The rate of pyrolysis has been calculated as $0.95/t_{95}$, where t_{95} is the time required to attain 95 % devolatilization. Further details on data analysis can be found in [2].
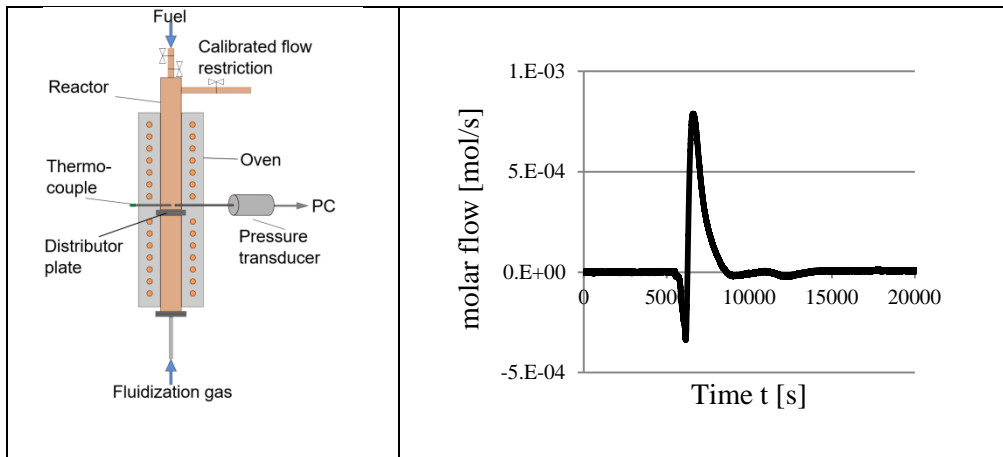

Figure 2. Scheme of the fluidized bed reactor (left) and molar mass flow rate of volatiles based on results of pressure measurements (right)

Aachen's fluidized bed with FTIR gas analysis

A small-scale fluidized bed reactor (Fig. 3, left) with a diameter of $d = 55$ mm was used, which is described in detail in [1]. Al_2O_3 particles (d_{50}=116 µm) are used as bed material with a static bed height of about 70 mm. Volume flow was 300 l_N/h, which corresponds to a superficial velocity of 0.16 m/s at 800 °C. Fuel samples (30 mg at 400 °C and 15 mg at 500 to 800 °C) were supplied to the reactor in batches. Particle transport from the fuel lock to the bed was forced with a gas flush (10 ml N_2) to achieve fast heating rates of approximately 10^4 K/s [1].
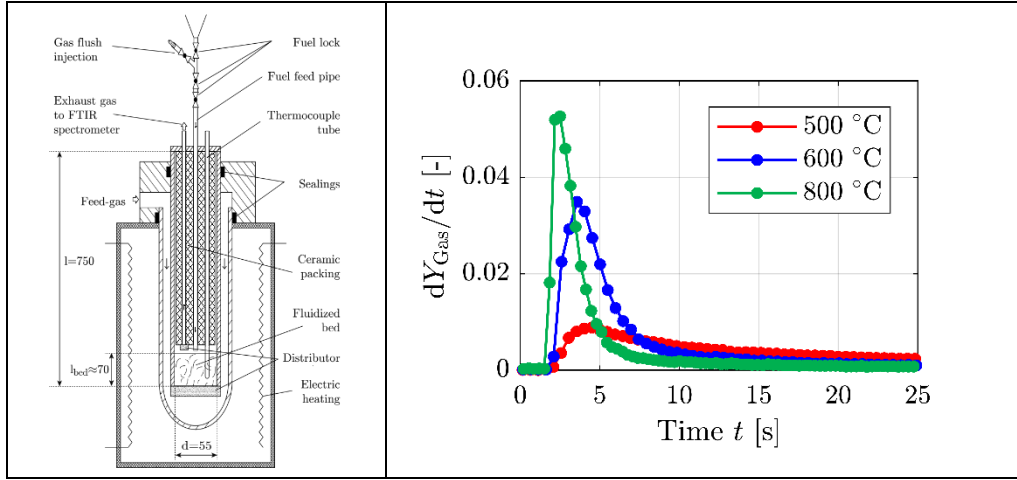
Figure 3. Scheme of the fluidized bed reactor (dimensions in mm) (left) and mass release rate of volatiles based on gas analysis (right)

Product gases were captured just above the bed and then transported to an FTIR spectrometer. The sampling line was heated to 453 K to avoid condensation of H_2O and tar components. Time dependent gas concentrations $c_i(t)$ were measured with an Agilent Cary 670 FTIR spectrometer and a sampling frequency of 10 Hz. More detail on construction, operation and error analysis is given elsewhere [1,5].

FTIR gas concentrations c_i of 21 different gas species (including CO, CO_2, $C_xH_yO_z$, SO_2 and NO_x) have been worked out to obtain:

$$\frac{dY_{Gas,exp}}{dt} = \frac{\rho_{N_2} \cdot \dot{V}_{N_2}}{m_F \cdot M_{N_2}} \cdot \frac{\sum_{i=1}^{n} c_i(t) \cdot M_i}{1 - \sum_{i=1}^{n} c_i(t)} \tag{3}$$

Herein m_F is the injected fuel mass, $\dot{V}_{N_2}$ the fluidizing volume flow of nitrogen, ρ_{N_2} the density and M_i the molar mass of each measured species. Results for dY_{Gas}/dt at 500, 600 and 800 °C are depicted in Fig. 3 (right). Reaction rate is derived by fitting the experimental results to a 2-step model including primary and secondary pyrolysis. Details about underlying equations can be found in [5].

Comparison of the data and Summary

Results for reaction rate R obtained with the different techniques are compared in the Arrhenius plot of Fig. 4. Note that the reaction kinetics measured in Aachen from FTIR analysis refer to particle size of 125–160 μm, intermediate between the size used in the TGA (94–112 μm) and in the fluidized bed experiments carried out in Naples (200-2,800 μm). Around 900 K Aachen results are in good agreement with the ones obtained from TGA and allow stretching the Arrhenius plot up to 1000 K. At still higher temperature the slope of the Arrhenius plot decreases suggesting the onset of heat transfer limitation. The pressure-based rates measured

in Naples' fluidized bed were obtained with larger particles size. Here pyrolysis rate appears lower the larger the particle size, confirming the dominance of heat transfer limitations on the rate of pyrolysis. However, the rates are consistent with the Aachen data, keeping in mind the lower particle size used for the Aachen FTIR experiments.
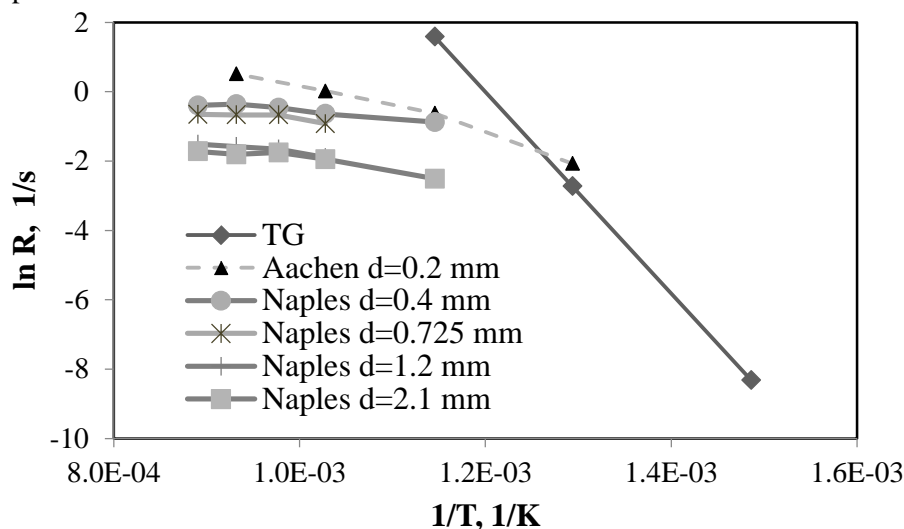

Figure 4. Evaluated reaction rate for the tests in an Arrhenius plot

Acknowledgement

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