6.2 Coal characterization

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6.2.0 ABSTRACT

A serie of fourteen coal types are characterized concerning char and volatile properties. The analytical model presented in chapter 6.1, describing the conversion of porous particles was used to interpret results of batchwise char combustion experiments in a small scale fluidized bed reactor. The analytical nature of the model made it possible to calculate four char dependent combustion parameters simultaneously from a set of experiments by numerical optimization techniques. The four combustion parameters are E, the true activation energy, m the true reaction order in oxygen, I and J. The latter two are newly defined parameters taking into account; the pre-exponential factor, the internal surface area of the particles and the effective pore diffusion coefficient. The evolution of the pore structure during combustion is included in the model. The four combustion parameters are simultaneously, experimentally determined for fourteen coal types of varying rank. This study of char characterization is inspired by fluidized bed combustion of coal, however because of the use of a complete, analytical single porous particle conversion model its applications extend to all forms of coal combustion or indeed any porous particle conversion process.

Volatile properties are investigated qualitatively based on chemical analysis and batch wise small scale combustion experiments.

6.2.1 Introduction

Characterizing char combustion properties by experimentally determining the kinetic expression is hindered by two phenomena originating from the natural porous structure of chars. Firstly, the pore structure is unpredictable and hard to describe quantitavely. Secondly, the pore structure will change during the occurring conversion reactions. These phenomena lead to uncertainties concerning the quantification of the effective diffusion coefficient and the internal reaction surface area to be used in the model equations. The reaction regime is hard to predict and up to now a priori assumptions have been nessecary to interpret experimental combustion data.

In this research use is made of the single particle model needing no a priori assumptions concerning combustion regime or diffusion coefficient. This single particle model for char combustion is described in chapter 6.1 by Brem^{1,2,3}. This model is used for char characterization to interpret results of batch wise char combustion experiments in a small scale fluidized bed.

Fourteen different types of coal have been used for this char characterization program.

6.2.2 Application of the single particle model

The processes to be described, in order to model the combustion of a porous char particle are:

- Heat and mass transfer through the external gas film surrounding the particle.
- Mass transfer through the pores of the particle.
- Chemical reaction kinetics for the surface reaction occurring on both external and internal areas.

Due care has been taken to model the temperature of the particle and the effects from the change in pore structure resulting from conversion.

The single particle model is used for char characterisation by interpretation of experiments of batch wise char combustion in a small scale fluidized bed. The particle model describes the conversion of a porous partical in a gaseous atmosphere as a composite solution for the two limiting cases of kinetic controlled combustion and mass transfer limiting combustion. The time t needed to achieve carbon conversion X, conform to equation 6.1.29 is:

$$t = (t_1(X)^2 + t_2(X)^2)^{\frac{1}{2}}$$
(6.2.1)

 $t_1(X)$, the time needed for conversion X when combustion occurs in the kinetically controlled regime is conform equation 6.1.18.

 $t_2(X)$, the time needed for conversion X when combustion occurs in the mass transfer controlled regime, can be written conform equation 6.1.27.

6.2.3 Overview of model parameters

The presented char combustion model contains a number of model parameters that can be classified in two categories;

parameters depending on coal properties

- parameters depending on process conditions or reactor design.

When the model is used to calculate the time t(X) necessary for char particles to reach a certain degree of conversion X, using eq.(6.2.1) and enthalpy equation (6.1.10), a number of model parameters are to be quantified. These parameters can be found in table 1.

TABLE 1: Model parameters depending on char properties respectively process and reactor design

| Model parameters depending on the | char properties: | and reactor design: | ess conditions |
|---------------------------------------|--------------------|--|---------------------------|
| activation energy E | 0 | external mass transfer coefficient k_d | * (Prins ⁴) |
| reaction order in oxygen m | 0 | external heat transfer coefficient h | * (Prins ⁵) |
| reaction constant I | 0 | stoichiometric reaction coefficient a | #* (Arthur ⁶) |
| boundary layer constant J | 0 | reduced attrition loss S* | #o |
| diameter char particle d _n | # | bed temperature T _b | # |
| porosity particle ϵ . | #o | oxygen concentration C ₄ | # |
| apparent density $\rho_{\rm c}$ | #o | minimum fluidization velocity umf | * (Yates ⁷) |
| carbon concentration C _s | # | superficial fluidization velocity u | # |
| • | | diameter bed particles | # |
| | | minimum fluidization voidage | * (Yates ⁷) |
| * Reliable data can be found for the | ese parameters in | the literature, | |
| # Parameters to be determined by y | vell established m | easurements methods | |

o Parameters requiring detailed analysis and experiments to quantify.

6.2.4 Measurement of physical and chemical properties of char

The physical property of char particle to know are: the initial apparent density, skeleton density, porosity, and the particle diameter. The chemical property to know is the carbon concentration.

The porosity of a char particle is largely determined by pores larger than 10 μ m. Due to the high porosity in the form of macro pores (diameter 1-100 μ m), the apparent density is hard to measure and therefore calculated from the mass of a known number of particles, assuming spherical particles and a diameter equal to the numerical average of the sizes of upper and lower sieve meshes used.

The skeleton density of char particles can be measured with the use of a pyknometer and methanol with negligible effect of the porosity.

The carbon concentration is derived from the chemical analyses, and the apparent density, see table 2. In order to quantify the remaining parameters, not available in literature it will be necessary to perform combustion experiments.

6.2.5 Experimental set up

To get experimental data relevant to char combustion properties and process conditions, a series of batchwise char combustion experiments are performed in a small scale electrically heated fluidized bed reactor, as can be seen in figure 1.

| | | | COAL AI | AL ANALYSIS (db) CHAR ANALYSIS (db) | | | | | | | | | | | |
|-----------------|-----------|------------|------------|-------------------------------------|------|------|------|------|------------|-----------|------------|------------|-------|-------|-----------------------|
| COAL TYPE | %C | % H | % N | ۲S | 20 | %Ash | %Vol | XC | % H | XN | X S | X D | % Ash | % Vol | Density(app) kg/m3 |
| SophiaJacoba | 82.6 | 2.9 | 1.2 | 2.2 | 1.8 | 9.2 | 5.7 | 85.5 | 0.8 | 1.2 | 1.5 | 1.3 | 9.7 | 0.5 | 1721 |
| Petroleum cokes | 87.9 | 3.6 | 1.1 | 5.5 | 1.5 | 0.3 | 9.6 | 89.8 | 1.0 | 1.3 | 5.4 | 2.2 | 0.3 | 1.7 | 1820 |
| Illawara | 70.6 | 4.0 | 1.2 | 0.4 | 3.3 | 20.4 | 16.1 | 71.Z | 0.2 | 1.2 | 0.4 | 3.2 | 23.8 | 1.7 | 1200 |
| Newlands | 70.8 | 4.2 | 1.4 | 0.7 | 7.2 | 15.7 | 22.6 | 73.7 | 0.3 | 1.4 | 0.3 | 3.4 | 20.8 | 1.7 | 1000 |
| Queens Land | 71.5 | 3.7 | 1.5 | 0.4 | 8.3 | 14.6 | 23.1 | 76.2 | 0.7 | 1.5 | 0.3 | 2.5 | 18.7 | 1.7 | 1000 |
| Ruhr | 73.5 | 4.3 | 1.4 | 0.9 | 5.9 | 13.9 | 23.6 | 77.4 | 0.4 | 1.6 | 0.7 | 2.9 | 17.0 | 1.6 | 920 |
| Gorlovka | 69.8 | 4.3 | 2.1 | 0.5 | 7.7 | 15.6 | 27.7 | 74.1 | 0.3 | 2.1 | 0.4 | 2.3 | 20.9 | 2.5 | 930 |
| Steam Slack | 73.4 | 4.1 | 1.8 | 0.4 | 10.1 | 10.2 | 28.0 | 80.1 | 1.0 | 1.8 | 0.4 | 3.1 | 13.7 | 3.2 | 1200 |
| Polish-10 | 77.3 | 4.6 | 1.4 | 0.7 | 7.9 | 8.1 | 29.2 | 84.2 | 0.5 | 1.4 | 0.6 | 1.0 | 12.3 | 2.1 | 900 |
| ANR | 77.5 | 4.9 | 1.3 | 0.9 | 7.6 | 7.5 | 30.6 | 83.2 | 0.3 | 1.6 | 0.8 | 3.5 | 10.6 | 2.0 | 975 |
| Elzas-Lorraine | 77.0 | 4.8 | 0.9 | 1.2 | 9.2 | 6.6 | 30.9 | 84.2 | 0.3 | 1.1 | 0.9 | 2.9 | 10.6 | 1.9 | 900 |
| West Kentucky | 71.2 | 4.5 | 1.4 | Z.6 | 7.7 | 12.6 | 32.2 | 74.7 | 0.5 | 1.5 | 1.7 | 3.8 | 17.8 | 3.0 | 885 |
| El Cerrejon | 77.4 | 5.1 | 1.4 | 0.8 | 10.3 | 5.0 | 35.2 | 85.4 | 0.3 | 1.8 | 0.4 | 3.5 | 8.6 | 2.0 | 870 |
| Gardanne | 70.2 | 4.4 | 1.6 | 3.9 | 10.7 | 9.1 | 37.8 | 80.9 | 0.3 | 1.7 | 2.9 | 0.1 | 14.1 | 2.3 | 860 |

TABLE 2: Chemical analysis on dry basis of coal and char and char apparant density



FIGURE 1: Experimental fluidized bed reactor

Small scale fluidized bed reactor

The quartz-glass reactor with a diameter of 100 mm is placed in an electric oven at a constant, thermostatically controlled temperature. The fluidization gas is preheated and enters the bed through a porous plate, designed to give an optimal distribution of the gas. The fluidization gas consists of an adjustable mixture of oxygen and nitrogen. The off gas from the reactor is sampled at 28 cm above the reactor distribution plate. The sample gas is cooled instantaneously and filtered and distributed over gas analyzers measuring CO, CO_2 , O_2 , C_xH_y . Each 2 seconds, data from the gas sample unit and analyzers.

Char used for experiments

Char used for the experiments is produced from coal by pyrolysis under nitrogen at 850°C in a 100 mm diameter reactor. 50 gram coal, diameter fraction 2-6 mm, is pyrolized on a removable grate in the reactor. After 10 minutes the grate with char is placed into a second reactor at ambient temperature to cool down in a nitrogen atmosphere. Finally, the char is broken and sieved to various diameter fractions used for the experiments.

6.2.6 Char combustion experiments

For each of the fourteen coal types 24 experiments are done with narrow sieve fractions of char. Bed temperature, inlet oxygen concentration and diameter fraction of char are varied over ranges to be found in table 3. For every combustion experiment gas analyzer data were collected and numerically processed concerning carbon conversion. The time necessary to reach 90% conversion (t_{90}) was derived from the calculated conversion versus time function. The experiments could be repeated within 3% of the measured t_{90} . Times for 90% conversion for different types of char are presented in figure 2, showing the influence of char properties.

TABLE 3: Char combustion experiments

| | Bed temperature: | 600-950 °C |
|---------|--|---|
| | Particle diameter: | 0.4-2.0 mm |
| | Batch size: | 1.25-2.25 g |
| | O _{2 in} | 2.5-10 % |
| Further | fluidized bed conditions: | : |
| Further | fluidized bed conditions: Bed material: | : sand |
| Further | fluidized bed conditions: Bed material: d _v : | : sand 0.63-0.80 mm |
| Further | fluidized bed conditions: Bed material: d _p : u _m : | : sand 0.63-0.80 mm 0.15 m/s (850 °C) |
| Further | fluidized bed conditions: Bed material: d _p : u _m : u _f : | sand 0.63-0.80 mm 0.15 m/s (850 °C) 0.3 m/s (850 °C) |



FIGURE 2: Time for 90% conversion for different types of char

6.2.7 Reactor modeling of experimental fluidized bed

Before using the mathematical model for single porous particle combustion to determine the char combustion parameters from the experimental results, an adequate description of the behaviour of the small scale reactor used for the experiments should be given.

The small scale reactor behaviour is investigated experimentally and the results are reported by van der Honing⁸. It can be stated that with the insights gained from reported experiments it is possible to formulate a simple reactor model comprising:

- single gas phase,
- plug flow,
- perfect solids mixing,
- no in-bed CO-combustion.

6.2.8 Definition of experimental parameters

The mathematical combustion model needs several experimental input parameters. Some of these can be measured straightforwardly others might need some simple or more complicated calculations from raw experimental data. The less trivial parameters will be discussed in this section.

Combustion time and conversion

The time (t_{90}) necessary to reach conversion X=0.9 during a combustion experiment is based upon the flue gas, composition measured. This time is reached after 90% of the total carbon measured in the flue gases, has passed the sampling probe.

Oxygen concentration

A value for the average oxygen concentration experienced by burning char particles has to be determined. During the combustion of a batch of char particles in the small scale fluidized bed the oxygen concentration in the bed, will change continuously in time and place. Assuming plug flow and an apparent first order reaction in oxygen, certainly applicable for external mass transfer limited combustion, the effective oxygen concentration in the bed, O_{2eff} can be characterized by the so-called logarithmic oxygen concentration, which is still a function of time t, defined as:

$$O_{2eff} = \frac{O_{2in} - O_{2out}(t)}{\ln[O_{2in}/O_{2out}]}$$
(6.2.2)

Slow combustion experiments at low bed temperatures can be treated similar, because the calculated values only show a small deviation from the appropriate average, even though the real or apparent order might differ from unity. This is because inlet and outlet oxygen concentrations are almost equal for the low combustion rates during these experiments.

The instantaneous combustion rate is used as a weight factor to define the effective mean oxygen concentration over the duration of a char combustion experiment. The instantaneous combustion rate, dm/dt is a function of the measured oxygen concentration: $dm/dt \approx O_{2in} - O_{2out}(t)$. The effective mean oxygen concentration is defined as:

$$\overline{O_{2eff}} = \frac{\int_{0}^{\tau} \frac{dm}{dt} dt}{\int_{0}^{\tau} \frac{1}{O_{2eff}} \frac{dm}{dt} dt} = \frac{\int_{0}^{\tau} [O_{2in} - O_{2out}(t)] dt}{\int_{0}^{\tau} \frac{1}{O_{2eff}} \frac{dm}{dt} dt} = \frac{\int_{0}^{\tau} [O_{2in} - O_{2out}(t)] dt}{\int_{0}^{\tau} \frac{O_{2in} - O_{2out}(t)}{O_{2eff}(t)} dt}$$
(6.2.3)

 O_{2in} is the present constant oxygen concentration of the fluidization gas and $O_{2out}(t)$ is the measured instantaneous flue gas oxygen concentration.

With definitions 6.2.2 and 6.2.3 one effective time-average oxygen concentration for each experiment can be calculated.

Stoichiometric reaction coefficient a

The stoichiometric coefficient a of the reaction is the number of moles of oxygen used for the conversion of one mole carbon:

$$(1+n) C + (1+n/2) O_2 \rightarrow nCO + CO_2$$
(6.2.4)

where n is the CO/CO_2 ratio at the particle. Then the stoichiometric coefficient a is:

$$a = \frac{1 + n/2}{1 + n} \quad (molO_2/molC) \tag{6.2.5}$$

The correlation of Arthur⁶ for the CO/CO_2 ratio at the particle is preferred to measurements. Experimental CO concentration data agree for experiments at temperatures up to 700°C. Above this temperature additional CO oxidation occurs in the freeboard leading to underestimation of the CO/CO_2 ratio.

Attrition

The attrition of char in the bed leads to the production of small char fragments that will be elutriated from the reactor. The attrition related parameter in the model is the reduced attrition loss S^* . The value of this parameter depends both on char properties and process conditions. The value of the reduced attrition loss is derived from the char combustion experiments.

$$S^* = \frac{m_0 - m_{out}}{m_0} \tag{6.2.6}$$

with: m_{out} the total carbon measured in the flue gases, and m_0 the initial carbon mass calculated from mass of batch charge and chemical analysis of char.

| CHAR TYPE | E/R | m | I | J | k _a | D_{eff} |
|-----------------|-------|------|----------------------|-----|----------------------|----------------------|
| Sophia Jacoba | 22300 | 0 | 1.26 10° | 22 | <1 10 ⁻⁷ | 3.7 10-7 |
| Petroleum Cokes | 12270 | 0.23 | 0.44 10 ⁷ | 2.3 | 1.5 10-7 | 1.1 10-6 |
| Illawara | 17250 | 0.75 | 0.11 1010 | 138 | 2 10 ⁻⁷ | 1.8 10-5 |
| Newlands | 14800 | 0.72 | 0.97 10 ⁸ | 52 | 2.0 10.7 | 2.7 10-5 |
| Queensland* | 11100 | 0.22 | 1.00 105 | 0.5 | 3.6 10 ⁻⁷ | 2.5 10-6 |
| Ruhr | 14800 | 0.59 | 0.20 108 | 21 | 3.0 10-7 | 2.2 10-5 |
| Gorlovka | 14300 | 0.74 | 0.39 10 ⁸ | 25 | 3.9 10 ⁻⁷ | 1.6 10-5 |
| Steam Slack | 9400 | 0.49 | 0.15 106 | 2.7 | 4.0 10-7 | 4.9 10 ⁻⁵ |
| Polish 10 | 14900 | 0.74 | 0.81 10 ⁸ | 52 | 3.0 10-7 | 3.4 10-5 |
| ANR | 17860 | 0.70 | 1.28 109 | 123 | 3.4 10-7 | 1.2 10-5 |
| Elzas-Lorraine | 13150 | 0.67 | 0.80 107 | 14 | 3.3 10-7 | 2.4 10-5 |
| West Kentucky | 14200 | 0.64 | 0.19 10 ⁸ | 25 | 2.3 10-7 | 3.4 10-5 |
| El Cerrejon | 11700 | 0.67 | 0.26 107 | 13 | 4.8 10 ⁻⁷ | 6.5 10 ⁻⁵ |
| Gardanne | 12100 | 0.73 | 0.57 107 | 11 | 5.9 10 ⁻⁷ | 2.1 10-5 |

TABLE 4: Results for char combustion parameters

• = based on a limited experimental program

6.2.9 Calculation of char combustion parameters E, m, I, J and k_a

The four model parameters E, m, I and J are calculated for each char type by using the model (eqs.(6.2.1) and (6.1.10)) to interpret the experimental results of the 24 char combustion experiments. The procedure used is schematically shown in figure 3.

With the use of a numerical optimization technique, based on the Simplex method, solutions are calculated for E, m, I and J so that calculated burn-out times agree as closely as possible to measured burn-out times. To start the optimization program initial values for E, m, I and J are chosen. As this choice is completely free, no assumptions have to be made concerning combustion regime or reaction order in oxygen.



FIGURE 3: Schematic of the calculation procedure

For the total set of 24 experiments the times for 90% conversion are calculated. A criterion σ used to compare the calculated and measured times t₉₀, is defined as follows:

$$\sigma = \left[\frac{\sum_{i=1}^{n} (1 - \frac{\tau_c}{\tau_m})^2}{n}\right]^{1/2}$$
(6.2.7)

with t_c and t_m being respectively the calculated and measured times for 90% conversion. n is the number of experiments for each char type. The calculation of the model parameters E, m, I and J results for the different type of chars in values listed in table 4.

Finally, for modeling the char combustion in a FBC the attrition constant k_a is still required. The attrition constant k_a can be calculated from the reduced attrition loss S^{*} derived from the experiments. Continuing combustion of the fines resulting from attrition is thus neglected. Using combustion parameters from table 4 it can be shown that this is allowed for most coal types for temperatures up to 800°C, assuming that the residence

time in the reactor of these fines is of the order of a second. An empirical correlation for the attrition constant as suggested by Arena et al⁹ is of the form:

$$k_a \approx \frac{S^*}{(u - u_{mf}) \frac{6}{d_p} 1.87 t_{90}}$$
 (6.2.8)

where u_f is the superficial fluidization velocity and d_p is the initial char particle diameter. The factor 1.87 results from a correction to account for the time necessary to reach 100% combustion, being the true residence time of the char particles in the fluidized bed.

Experimental results in this research include values for S^* for a range of t_{90} resulting from different bed temperatures. The effect from varying excess gas velocities is not incorporated in the experimental program. Its effect however has been extensively studied by authors mentioned above. From the experimental results and eq. 6.2.8 it is possible to calculate k_a for the different coal types. The results can be found in table 4 and agree well with values found by Arena⁹.

6.2.10 Discussion

The essentially new approach of this model lies in the definition and the use of I and J describing the effects of the pore structure and its evolution in respectively the chemical kinetics controlled and the pore diffusion controlled combustion regimes. The model calculations for 90% conversion times of char batches agree very well with experimental data.

The model's accuracy in describing experimental burn-out times is expressed by the value σ from eq. 6.2.7. Values for σ are between 0.1-0.2 for all types of char. This value includes any experimental inaccuracy.

Although the mathematical model does not need the effective diffusion coefficient it is possible to estimate it from I and J. It is thus possible to compare results presented here with those available in the literature. Using eqs. (6.1.19) and (6.1.28) and the observation that D(S) and A(S) are of unity order it follows that:

$$D_{eff} = \frac{J^2}{I} \tag{6.2.9}$$

The calculated effective pore diffusion coefficients presented in table 4 show that D_{eff} is around 10⁻⁵ m²/s for most types of char. This is of order of magnitude of molecular diffusion through a network of macro-pores. The lower effective diffusion coefficient found for the anthracite Sophia Jacoba points to fewer macro-pores, for which case the slower Knudsen diffusion will become the limiting transport mechanism. Experiments show that for high temperature burn-out time becomes independent of the type of char used, (see figure 2). This is not due to combustion limited by external mass transfer, but

more likely by similar macropore diffusion. Calculated values for the Biot number $Biot=R_0k_d/D_{e,0}$, expressing the ratio of external mass transfer and pore diffusion, for experiments with Thiele number $\phi > > 1$ confirm the limiting effect for high temperature experiments of pore diffusion, rather than external mass transfer.

The range of activation energies found in this study agrees well with work done by Field^{10,11} and Tseng and Edgar^{12,13}. Smith¹⁴ made an inventory of experimental work from several research workers and found after processing an average activation energy of 179kJ/mol compared to an average of 110kJ/mol determined in this research. The difference can be attributed to the small diffusion coefficient assumed by Smith resulting from a mono sized pore structure where Knudsen diffusion becomes the rate limiting phenomenon. It is suggested that many combustion experiments used for Smith's review article were actually performed in the kinetically controlled combustion regime. In the present study interpretation will lead to activation energies of approximately half of those resulting from Smith's interpretation.

6.2.11 Volatile characterization

Volatile properties are investigated qualitatively by a series of batch wise coal combustion experiments in the small scale reactor as described in paragraph 6.2.5 and presented in figure 1. The volatiles of coal are investigated on:

- volatile content and analysis
- devolatilization time
- Sulphur and nitrogen reduction during volatiles combustion

Volatile content and analysis

Compared to the volatile content obtained from the proximate analysis of coal the true amount of volatiles releasing at combustion of coal under fluidized bed conditions is less. This is caused by the relative low fluidized bed temperature of 850°C compared to 1000°C for the proximate analysis test.

The true volatile content of coal for fluidized bed combustion conditions can be estimated from the differences of the proximate volatile analysis of coal and char. The chemical analysis of volatile matter can be derived from coal and char analysis by use

The chemical analysis of volatile matter can be derived from coal and char analysis by use of the equation 6.2.10.

$$CHONS_{vol.} = \frac{CHONS_{coal} - (1 - fraction vol.) CHONS_{char}}{fraction vol.}$$
(6.2.10)

Devolatilization time

The devolatilization time of coal is studied by batch wise combustion experiments of narrow sieved diameter fractions of coal in a small scale fluidized bed reactor as presented in figure 2. In literature different definitions are used for the devolatization time which result in different measured times. Here we used the gas analyzer to measure the CO₂ and C_xH_y concentration profile during burn off. The devolatization time is defined as 95% of

the cumulative C_xH_y amount measured in the flue gases.

For different diameter fractions the devolatilization time of coal is measured at conditions of 850°C and 15% inlet oxygen in the experimental fluidized bed and presented in table 5.

A well known empirical expression for the devolatilization time t, is given by Pillai¹⁷:

$$t_{v} = 10 \left[\frac{1048}{T_{b}} \right]^{3.8} d^{0.75 \left[\frac{T_{b}}{1048} \right]}$$
(6.2.11)

where T_b is the bed temperature [K] and d_p is the particle diameter [m].

| diameter coal | devolatilization | devolatilization |
|---------------|-------------------|------------------------|
| fraction (mm) | time measured (s) | time theory Pillai (s) |
| 0.4 - 0.5 | - | 4 |
| 0.8 - 1.0 | 7 | 7 |
| 1.7 - 2.0 | 10 | 12 |
| 2.3 - 2.8 | 12 | 16 |
| 4.0 - 4.75 | 20 | 25 |

TABLE 5: Experimental result and theory for the devolatilization time

The measured t_v are about 20% less than followed from the expression of Pillai¹⁷ which can be declared by differences in the measurements definitions.

For types of coal of different rank the t_v is almost the same. For coal particle smaller than 1 mm combustion of volatiles and char occurs simultaneously, which made it hard to measure t_v based on flue gas analysis.

Volatile combustion

The combustion of volatiles occurs either in the bed or in the freeboard. The combustion rate at bed temperatures of 850° C depends on the rate of mixing of volatiles and oxygen. Combustion of volatiles is made visible experimentally in a small scale flat fluidized bed made of quarts glass. At a temperature range between $800 - 900^{\circ}$ C the volatiles combust in the bubbles above a critical diameter. At higher temperatures the volatiles start burning in the dense phase.

Sulphur and nitrogen reduction

Flue gas analysis of batch wise combustion of diameter fractions of coal lead to the following conlusions for sulphur and nitrogen reduction:

Volatiles show much higher sulpher concentrations compared to char. Sulphur released during the devolatilization reacts mainly to SO_2 as determined by flue gas analysis. Natural reduction of sulphur is limited the sulphur originated from char.

Volatiles and char of one type of coal contain about equal nitrogen concentrations. (see also table 2). During combustion of coal the reduction processes are about the same for nitrogen released from either char or volatiles.

List of symbols

- molar stoichiometric coefficient of combustion, [-] а non dimensionalized specific internal area, [-] Α internal area per unit volume char. [m⁻¹] A, pre-exponential factor in kinetic rate expression, [kmol^{1-m}m^{3m-2}s⁻¹] A₀ Bi Biot number for mass transfer, [-] C_A oxygen concentration, [kmol m⁻³] particle carbon concentration, [kmol m⁻³] Cs effective pore diffusion coefficient, [m²s⁻¹] Deff d_p particle diameter, [m] Ē true activation energy for char combustion [kJ kmol⁻¹] external heat transfer coefficient, [kW m⁻²K⁻¹] h reaction constant, [kmol1-mm3m-2s-1] I boundary layer constant, [kmol^{0.5(1-m)}m^{0.5(3m-1)}s⁻¹] J k, attrition constant, [-] external mass transfer coefficient, [m s⁻¹] k, reaction rate constant, [kmol^{1-m}m^{3m-2}s⁻¹] k. true reaction order in oxygen, [-] m number of experiments, [-], n $[CO]/[CO_2]$ ratio, [-] n time-averaged effective oxygen concentration, [kmol m⁻³] O_{2eff} O_{2in} inlet oxygen concentration, [kmol m⁻³] O_{2out} instantaneous outlet oxygen concentration, [kmol m⁻³] gas constant, [kJ kmol⁻¹K⁻¹] R R₀ initial char particle radius, [m] S critical non-dimensionalized particle carbon concentration for which attrition occurs, [-] time, [s] t t, devolatilization time [s] $T_{\boldsymbol{b}}$ bed temperature, [K] time necessary to reach conversion X, [s] t(X)time necessary to reach 90% conversion, [s] too superficial fluidization velocity, [m s⁻¹] u_f minimum fluidization velocity, [m s⁻¹] u_{mf} X conversion. [-] conversion determined from flue gas analysis, total carbon measured in flue gas is X_m defined as 100% conversion, [-] char particle porosity, [-] ϵ_{s} apparent char particle density, [kg m⁻³] ρ, Thiele number based on initial parameters, [-] ф
- $\tau_{\rm c}$ time calculated by model to reach certain conversion, [s]
- $\tau_{\rm m}$ time measured experimentally to reach certain conversion, [s]
- σ criterium, [-]

subscripts

- 0 referring to initial value
- 1 chemical kinetics controlled ($\phi << 1$)
- 2 mass transfer controlled ($\phi >> 1$)
- ∞ value far removed from particle

6.2.12 References

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