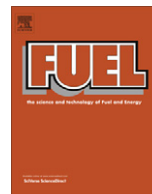




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Gasification kinetics during entrained flow gasification – Part II: Intrinsic char reaction rate and surface area development

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HIGHLIGHTS

- ▶ Char samples are produced at up to 1600 °C and 2.5 MPa.
- ▶ Char is produced above the ash melting temperature in an entrained flow reactor.
- ▶ A significant loss of surface area is measured in the later stages of conversion.
- ▶ The loss is attributed to the melting of mineral matter.
- ▶ The char reaction kinetics with CO₂ and H₂O are measured in a pressurised TGA.

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ABSTRACT

The reaction behaviour of two different coals is analysed in a pressurised entrained flow reactor (PiTER) and a pressurised thermogravimetric analyser (PRETA). The entrained flow reactor is used to produce char samples under conditions relevant to larger scale entrained flow gasifiers, i.e. at temperatures up to 1600 °C and pressures up to 2.5 MPa. The conversion rate of these char samples is measured under defined conditions in the PRETA using CO₂ and H₂O atmospheres.

Furthermore, the development of char surface area during devolatilisation and char gasification is analysed in the PiTER. The initial surface area after devolatilisation is dependent on pressure. In the later stages of conversion a significant loss of surface area is detected. The decrease in surface area is attributed to a melting of mineral matter as the PiTER is operated above the ash melting temperature of the coals. The development of the mass specific surface area during gasification cannot be described by the Random Pore Model probably because of the ash melting, but by an empirical correlation.

The surface area data are combined with the thermogravimetric analysis to derive the intrinsic reaction rates at the char surface. The intrinsic rate is modelled by nth order and Langmuir–Hinshelwood rate equations. The temperature influence on the char–CO₂ reaction can be described by an activation energy of 200 kJ/mol, and on the char–H₂O reaction by an activation energy of 212 kJ/mol. The activation energy is found to be independent of the char preparation conditions, whereas the pre-exponential factor significantly decreases for a higher heat treatment severity of the char sample.

The model equations can be used to predict the intrinsic gasification behaviour in the absence of mass transport limitations.

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1. Introduction

The conversion rate of solid fuels under entrained flow operating conditions is a critical issue for the design of gasifiers and the selection of suitable fuels. Several reaction processes occur simultaneously and/or consecutively within the hot reaction zone. In order to evaluate the rate of fuel conversion detailed information about the reaction rates of single processes is required. Although

operating conditions and fuel properties have an influence on the rate of these reactions, it is generally observed that devolatilisation, the combustion reactions, and the homogeneous gas reactions are several orders of magnitude faster than the heterogeneous char gasification. At the high temperature within an entrained flow gasifier, devolatilisation (including particle heat up) occurs in a time interval of tenth or hundreds of milliseconds depending mainly on temperature [1–3]. Although not much kinetic data on volatiles combustion are available, it is clearly established that these homogeneous reactions are much faster than the heterogeneous char gasification reactions [4]. Similar to volatiles combustion, the other homogeneous reactions in the gas phase are very fast. Therefore,

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the local gas composition in the reactor at high temperature can be described by chemical equilibrium [5]. Homogeneous reactions do not determine the overall reaction rate. Compared with fast devolatilisation and volatiles combustion, the heterogeneous char reactions with O₂, CO₂, H₂O, and H₂ are much slower. Amongst the heterogeneous reaction, char combustion with O₂ is several orders of magnitudes faster than gasification by CO₂ and H₂O [6–8]. Therefore, oxygen is consumed instantly and the combustion does not limit the overall conversion rate in the gasifier. In contrast, the methanation reaction (C + 2H₂ → CH₄) is very slow and only makes a marginal contribution to char conversion [9]. Consequently, the char gasification by CO₂ and H₂O limits the overall fuel conversion. The rates of both reactions at entrained flow operation conditions are similar [8] and both have to be considered to describe the char conversion. In the sequence of all reactions, the heterogeneous char reactions with CO₂ and H₂O are the rate-determining step in entrained flow gasification. Fundamental knowledge of the rates of these reactions is important for the design and optimisation of gasification reactors by numerical simulation approaches and for the selection of suitable fuels (coal and biomass) for gasification.

As the reaction of char with CO₂ and H₂O occurs at the microporous char surface, both the available surface area for reaction and the chemical reactivity (intrinsic reactivity) of the surface area influence the heterogeneous reaction rates. During devolatilisation a porous char structure is formed with a large internal surface area, typically above 100 m²/g [10]. At the high reaction temperatures within a gasifier the char gasification might be influenced by mass transfer limitations within the porous structure, i.e. the chemical surface reaction is so fast that the reactants CO₂ and H₂O do not reach the char particle centre. In this case, a gas concentration gradient is built up and the available surface for reaction is reduced. However, as the mass transport limitation only partly influences the char conversion, the internal surface area of char is still a very important reaction parameter.

The influence of operating conditions on the char gasification with CO₂ and H₂O is described by model equations, whereby nth order Arrhenius type equations [7,11–13] and Langmuir–Hinshelwood–Hougen–Watson (LHHW) approaches [14–17] are widely used. The most important parameter that influences the reaction rate is the conversion temperature. Its influence is usually described by the activation energy.

In the absence of mass transport limitations, the reaction rate can be analysed in thermogravimetric analysers (TGA) due to their controlled experimental conditions. Despite similar reaction conditions in the TGAs and similar fuels, a large range of activation energies is reported in the literature. In nth order rate equations, the activation energy ranges from 133 kJ/mol [18] to 250 kJ/mol [19] for the char–CO₂ reaction, and from 37 kJ/mol [20] to 237 kJ/mol [17] for the char–H₂O reaction. The value of the activation energy seems to be strongly dependent on the parent fuel and the char preparation conditions. Rosenberg et al. [21] compared properties of chars sampled from experimental setups (flow reactors, muffle furnace, full-scale pulverised combustion boiler). They showed that chars that are produced above a threshold temperature of around 1300 °C in a flow reactor were similar to the chars from the full-scale application whereas chars produced at lower temperature were significantly different.

The objective of this study is the analysis of intrinsic reaction rates of char samples that are produced at conditions relevant to high temperature entrained flow gasifiers. The devolatilisation behaviour and the effects of char deactivation at high temperature have already been shown [3].

The measurement of intrinsic reaction rates is not a novel approach and several publications can be found on this topic (e.g. [11,17,18]). However, the analysis of the influence of a very high temperature (up to 1600 °C under pressurised conditions) on char

reactivity is considered to be novel. At this high temperature the melting of mineral matter might occur which is expected to influence char reactivity and specific surface area. Both parameters are analysed in this paper at temperatures above the ash melting temperature which has a high relevance for industrial scale entrained flow gasifiers.

Furthermore, the kinetic model derived here will be combined with kinetic models for devolatilisation, char deactivation, and gas diffusion in the third part of the paper series [22]. The model development together with the validation of these models using experimental data will enable the description of fuel conversion at high temperature and high pressure and the design and optimisation of entrained flow gasifiers based on kinetic data.

2. Experimental methods

2.1. Fuel preparation

The internal char surface evolution and the char conversion rate of two different coals are analysed. The proximate and ultimate analysis of these coals is shown in Table 1. The fuel preparation procedure is given in Ref. [3].

2.2. Entrained flow reactor

Fuel gasification at high temperature is studied in the pressurised high temperature entrained flow reactor (PiTER). The facility is designed to study gasification reactions at operation conditions relevant to industrial scale entrained flow reactors. The reactor can be operated at a maximum temperature of 1800 °C and a maximum pressure of 5.0 MPa with a defined gas mixture (N₂, H₂, O₂, CO₂, C₃H₈) and a highly controllable fuel feed rate from 0.2 kg/h to 5.0 kg/h. The main reaction tube has an inner diameter of 70 mm and a length of 2.3 m.

Char and gas samples are taken from the hot reaction tube through a stainless steel probe that is cooled with water or tempered with oil. This probe is inserted at the bottom of the pressure vessel and can be moved upwards into the reaction tube. By adjusting the height of the sampling probe char and gas samples are taken at different stages of conversion. The variation of the gas flow rate in the reaction tube and the movement of the sampling probe enable residence times in the range 0.5–3 s. More information about the PiTER can be found in a previous publication [3].

2.3. Thermogravimetric analysis

The reaction rates of chars that are collected from the PiTER are studied in the pressurised thermogravimetric analyser (PRETA). The facility is designed, built up and commissioned in cooperation with the company Linseis GmbH in Selb, Germany. The PRETA can

Table 1
Fuel properties.

	Coal R	Coal A
<i>Proximate analysis (wt%, dry)</i>		
Ash content	5.5	11.2
Volatile matter content	52.7	41.3
<i>Ultimate analysis (wt%, daf)</i>		
Carbon	67.8	78.3
Hydrogen	5.2	5.3
Nitrogen	0.8	1.6
Sulphur	0.8	0.9
<i>Ash melting (reducing atmosphere)</i>		
Deformation temperature (°C)	1210	1164
Flow temperature (°C)	1263	1378

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