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Full Length Article

Experimental investigations on lignite char gasification kinetics using a pressurized drop tube reactor

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ABSTRACT

A novel pressurized drop tube test facility, named KIVAN, for the investigation of heterogeneous gasification reactions under elevated pressures is presented. Facility configuration and possibilities of experimental test procedures are explained. The gasification behavior of a lignite char is investigated at a pressure of 21 bar. The effects of gasification temperature (1173–1323 K) and partial pressure of CO_2 (5.25–15.75 bar) on the carbon conversion are determined. The measured temperature and concentration profiles inside the reactor, the settling velocity of the particles and the flow conditions along the reaction tube are used to determine kinetic parameters of the Boudouard reaction. Data on the char structural changes depending on the carbon conversion is provided and it is suitable for detailed numerical modeling of gasification processes. The determined kinetic parameters of the Boudouard reaction under these conditions are: activation energy 162 kJ·mol^{-1}, reaction order 0.36 and pre-exponential factor 3.26·10^{5} s^{-1} bar^{-036}.

1. Introduction

Partial oxidation and gasification of hydrocarbons such as oil, natural gas and coal are the most important processes for the generation of syngas required for the production of chemicals. Coal remains as one of the most important feedstock in the chemical industry due to its wide availability and stable price compared to its alternatives [1].

The heterogeneous reactions of the coal-char after pyrolysis are one of the more complex steps in the whole gasification process and one of its limiting steps. Many studies have been carried out on with the aim of deriving kinetic parameters for these reactions or obtain data necessary for CFD modelling [2–14], but the data produced by different equipment remains difficult to compare and the characteristics of the experimental equipment are rarely taken into account in the kinetic evaluations.

The aim of this research is to investigate the heterogeneous gasification reactions in a pressurized drop tube reactor considering the temperature and concentration profiles under process conditions as accurately as possible.

The first experimental results obtained using a new pressurized drop tube reactor are shown. In addition, the change of physical char structure parameters are measured to support the kinetic evaluation based on Random Pore Model (RPM) and the whole dataset is provided for further activities in terms of CFD modelling and validation.

Drop tube (DTR) and pressurized drop tube reactors (PDTR) are often used for the kinetic investigation of combustion, pyrolysis and gasification processes. DTRs and PDTRs have many advantages: very good heat and mass transfer conditions, possibility of working at higher temperatures than in a thermobalance (TGA) along with high particle heating rate. However, they also have some disadvantages like difficulties taking samples at intermediate points of the reactor or irregularities in the axial temperature profile due to construction limitations.

The non-uniformity in the axial temperature profile and the changes in the gasification agents concentration along the reactor have been noticed by various researchers, but there is a lack of agreement on how to take into account these effect when estimating the kinetic parameters. Data on the changing char properties during the gasification process obtained with drop tube reactors are scarce.

Ahn et al. [2] used a PDTR with three heating zones to study the gasification of char with CO_2 in the temperature range of 1173–1873 K and total pressures up to 15 bar. The particle temperature was considered to be equal to the reactor wall temperature due to the slow rate of the Boudouard reaction. The particle velocity was estimated as the sum of the particle sinking velocity (calculated using the Stokes' equation) and the gas velocity. Carbon conversion was calculated based on the ash tracer method.

Costa et al. [15] measured the combustion kinetics of biomass in a DTR at atmospheric pressure and reactor wall temperatures between

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1223 and 1673 K. The gas temperature was measured at different reactor lengths during operation, showing significant deviations from the set wall temperatures, caused not only by limitations of the heat transfer between reactor walls and gas but also by the highly exothermic nature of the combustion process. The kinetic estimation was based on the set wall temperatures and the mass balance was based on the analysis of the mineral matter of the combustion residues.

Gonzalo-Tirado et al. [16] measured the change in the particle size as function of the carbon conversion at temperatures between 1313 and 1573 K, pointing out that the particle size remains almost constant during the coal conversion for both gasification and combustion processes.

Harris et al. [6], used a pressurized entrained flow reactor to gasify samples of char from sixteen different Australian coals at a temperature range between 1373 and 1773 K (wall temperature) and a pressure of 20 bar. The gasification agent was a mixture containing 2.5% of O_2 and N_2. The ratio O_2/char was changed by varying the char feeding rate. The estimated particle residence time was estimated to be maximum 3 s. The products composition for different O_2/char ratios was shown.

Küster et al. [17] was able to measure the temperature at the surface of lignite and hard coal particles during gasification with CO_2 between 1173 and 1473 K at ambient pressure using a modified TGA reactor with optical ports connected to a thermo-camera. This work also showed that for the studied particle sizes (< 4 mm) there is an important temperature drop on the particle surface caused by the endothermic nature of the Boudouard reaction (up 40 K for lignite and 5 K for hard coal) and that the development of the particle temperature can be linked to the reaction rate.

Lee et al. [18] studied the gasification reactions of four different coals at atmospheric pressure (1373–1773 K) using a DTR with four heating elements made of silicon carbide. They provided gas temperature profiles for different reactor set temperatures, but they used the reactor set temperatures in their kinetic analysis. A constant particle residence time of 4.8 s was used for all evaluations, independently of gas temperature. Ash content in the char and Ar as basis for the mass balance were used. The specific surface area of the char at different conversion degrees was measured for one of their tested coals. The measured values oscillated between 10 and 58 m^2/g.

Monson et al. [19] used a PDTR heated by molybdenum heaters grouped in three heating zones for studying coal combustion. They found significant differences between the reactor wall temperature and the gas temperature inside the reactor. The particle temperature and velocity were measured using two-color pyrometry and particle imaging techniques at pressures up to 10 bar. The measured particle temperature was coupled with the carbon conversion (calculated using mineral content in the char) to estimate the particle reactivity.

Ndibe et al. [20] used a DTR with five heating elements for studying the combustion of biomass/coal mixtures. No information was provided about the temperature profile in the equipment, but it is mentioned that the temperature plays an important role in the determination of the gas residence time. The carbon conversion was calculated using the mineral matter content in the combustion residues.

Reichel et al. [21] used a PDTR for studying pyrolysis of brown coal (temperature range 873–1073 K, pressure range 25–60 bar). Particle and gas residence time were varied by controlling the gas flow. The progress of the reaction was measured by analysis of the product gas using a gas chromatography coupled with mass spectrometry. The pyrolysis products distribution as function of the process parameters was determined. The particle velocity was estimated using the gas velocity and the particle sinking velocity based on the Haider-Levenspiel correlation.

Roberts et al. [22], studied the reactivity of chars from three Australian bituminous coals with mixtures of CO_2 and steam using a PTGA at a temperature range between 1123 and 1173 K and pressure up to 50 bar. The CO_2 and steam partial pressure were varied between 5 and 10 bar. The results point to an apparent competition between the steam and the CO_2 for the active points of the char. They used equations of the Langmuir-Hinshelwood type to explain their results and proposed an expression to estimate the reaction rate of char with CO_2 – steam mixtures based on the individual reaction rates. Specific surface areas for the initial char samples and for selected partially converted samples (X_C = 10%) was presented. In later works [23,24], the authors points that the inhibition effects of CO_2 on the char-steam reaction are determined by two factors: the char specific surface area and the partial pressure of the reactants. The bigger the reactants partial pressures are, the inhibition effects are more important. Simultaneously, the bigger the char specific surface area is, the less inhibition is observed.

Tremel et al. [7,25] studied the pyrolysis of lignite using a PDTR at temperatures between 1473 and 1873 K and a total pressure up 25 bar. The particle velocity was estimated with the gas velocity (corrected using the radial velocity distribution in the tube and the change in the gas flow due to devolatilization reactions) and the particle sinking velocity. Data on the specific surface area for different estimated residence times was presented.

Zellagui et al. [26] studied the pyrolysis of coal and biomass in the temperature range between 873 and 1673 K using a DTR with five heating elements. The gas temperature was measured axially and radially for different set wall temperatures. This information was used to model the reactor behavior and to estimate the particle velocity in the equipment. The carbon conversion was calculated using the analysis of the remaining mineral matter in the residue.

2. Experimental

2.1. Description of the equipment

KIVAN facility (German: KInetische VersuchsANlage – facility for the investigation of reaction kinetics) was built by the HTM Reetz GmbH in cooperation with the Institute of Energy Process Engineering and Chemical Engineering of the Technical University Bergakademie Freiberg. KIVAN is a pressurized drop tube reactor for investigating of kinetics of heterogeneous gasification reactions.

The reactor operates up to a maximum pressure of 100 bar gauge and a maximum reaction temperature of 1420 K. Fig. 1 gives an overview of the main components of the facility.

The facility has a height of about 8 m (feeding system included). The outer diameter of the water-cooled pressure vessel is about 0.6 m.

The reactor consists of five parts, which are connected by flanges:

a gas pre-heater on the reactor top, including one reaction tube heating zone,
three parts containing a reaction tube heater each and
a water quench at the bottom of the reactor.

The feeding system based on a screw feeder and a vibrating conveyer, is placed separately at the top of the reactor in a separate pressure vessel. The feedstock is injected through a water cooled feeding lance (1) directly above the first heating zone of the reaction tube. An integrated balance in the feeding vessel allows controlling the feeding rate. Separated small fuel chambers in a revolver arrangement ensure a continuous and stable feeding rate.

The gasification agents are preheated to the operating temperature in 4 separated heaters (2) before entering the reactor. This avoids possible gas phase reactions before the proper reaction zone and ensures a very high particle heating rate.

The facility height is minimized as the gases reach the operating temperature before entering the reaction tube and the horizontally mounted preheaters.

There are four independent reactor heating zones along the reaction tube. Each zone has a 12 kW Kanthal®-wire heating element (4). The heated length of the reaction tube is about 2.7 m. After exiting the reaction zone, product gases and solid residues are quenched with water