



## On the influence of different experimental systems on measured heterogeneous gasification kinetics



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### HIGHLIGHTS

- Investigation of the influence of experimental systems on observed reactivity.
- Comparison of the four most used experimental systems in literature.
- Identification of four fundamentally different reaction domains.
- All setups give valid results if operated in a specific range of process parameters.
- The relevant process conditions for each system are reported.

### ARTICLE INFO

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### ABSTRACT

The objective of this study was to gain further insight into the characteristic behavior of reaction systems for establishment of intrinsic and effective particle gasification kinetics. A wood-derived char was subjected to the carbon dioxide-containing atmospheres of four different reaction systems: a thermogravimetric analyzer (TGA), a fluidized-bed reactor (FBR), a fixed-bed reactor (FFB) and a drop-tube reactor (DTR). All systems contained the same CO<sub>2</sub> partial pressure of 800 mbar at atmospheric pressure. A temperature span from 700 to 1600 °C and residence times from 200 ms to over 8 h were investigated. Reactivities spanning five orders of magnitude were observed. The gasification experiments resulted in the identification of four fundamentally different reaction domains; two were classified as true particle behavior, while the observed reaction rates of the other two domains are mainly dominated by the characteristics of the reaction system applied. The domains were referred to as: chemical control, particle diffusion control, bed diffusion control, and system response control. Within the present work, the occurrence of these reaction domains is discussed in regard to the physical nature of the experiments, and implications towards the measurement of reliable particle kinetics are formulated.

### 1. Introduction

Utilization of low-grade biogenic and fossil fuels in enhanced gasification processes (e.g. high-pressure entrained-flow gasification, EFG) allows for the production of high-quality synthesis gas which can be converted into liquid fuels and chemicals or used for power and heat generation via Integrated Gasification Combined Cycle (IGCC) systems. In the future, EFG will play an increasingly important role in satisfying the demand for basic chemicals and power [1,2]. In entrained-flow gasification, the fuel is converted via thermal and thermochemical processes such as heat-up, drying and pyrolysis of the solid phase, and the subsequent heterogeneous gasification reactions of the resulting char in a CO<sub>2</sub>- and H<sub>2</sub>O-rich atmosphere [3]. For the achievement of

high cold gas efficiencies, complete char conversion is essential. In this context, the heterogeneous reactions are considered as the rate-limiting step for complete fuel conversion under technical gasification conditions. This motivates the determination of kinetic data for char gasification in diverse laboratory-scale experiments.

A tremendous amount of kinetic data for solid-fuel conversion is available in the literature; most of them established by thermogravimetric analyzers, fixed-bed-, drop-tube- or fluidized-bed reactors. Fig. 1 compares the number of papers reporting the use of different systems for measurements of kinetic data in terms of CO<sub>2</sub> gasification. The chart, summarizing experiments for coal and biomass gasification, is based on two review papers by Irfan et al. [4] and Di Blasi [5]. The majority of experiments which were considered in this study (100 in

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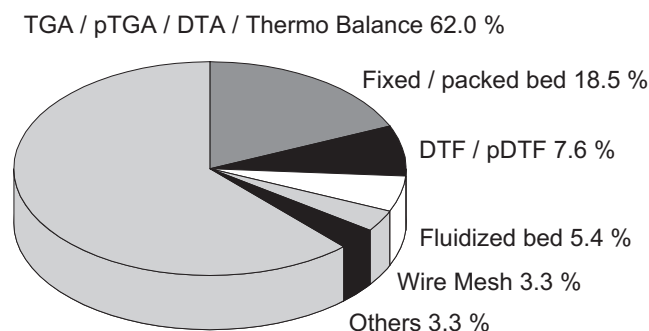


Fig. 1. Use of different reaction systems for determination of gasification kinetics with  $\text{CO}_2$  (based on [4,5]).

total), have been carried out in thermogravimetric systems (62.0%), followed by fixed-bed reactors (18.5%), and drop-tube furnaces (7.6%). Recent publications with contributions to the field of reaction kinetics of gasification reinforce this trend. Numerous research groups use thermogravimetric analyzers to determine reaction kinetic [6–12] while some favor fixed-bed reactors [13–15]. Furthermore, kinetic data is also determined with drop-tube furnaces [11,16] and fluidized-bed reactors [17]. However, the latter two reaction systems are still less frequent. Combined, these four systems claim well over 90 % of the results generated to date in terms of heterogeneous gasification kinetics.

The heterogeneous gasification kinetics derived in literature are commonly the reactions of solid carbon with  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , referred to as Boudouard- and heterogeneous water-gas reaction. Heterogeneous reactions are characterized by the occurrence of reactant fluxes through interface surfaces. In the case of the Boudouard reaction, the reaction takes place at the solid surface. The steps in heterogeneous conversion of porous solid carbon with  $\text{CO}_2$  are: (1) reactant film diffusion, (2) reactant pore diffusion, (3) reactant adsorption, (4) chemical reaction, (5) product desorption, (6) product pore diffusion, (7) product film diffusion. Since most of these steps depend on partial pressures and temperature, applying considerably different reaction conditions can result in different reaction behaviors. The observed reaction rate of a porous carbon particle can be depicted in an Arrhenius plot (Fig. 2). It describes the temperature dependency of the reaction rate and was divided into three regimes where the reaction is governed by different mechanisms by Rossberg and Wicke [18].

In regime I, the reaction rate is solely affected by the before-mentioned reaction steps 3–5 because of constant reactant gas concentrations throughout the particle. This regime is often referred to as chemically controlled or quasi-homogeneous regime. Here, increasing the temperature leads to higher reaction rates with a slope proportional to

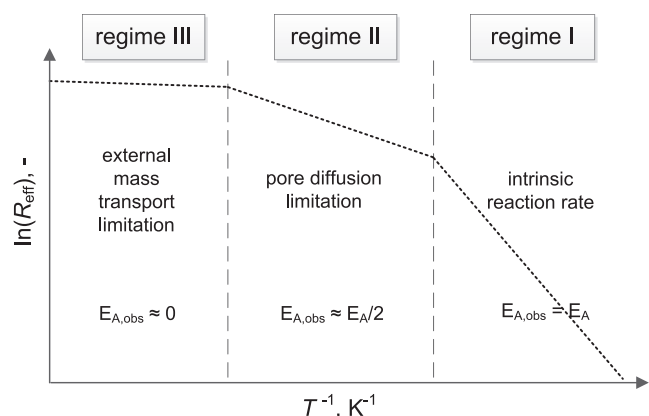


Fig. 2. The three reaction regimes representing the change in reaction rate of porous carbon with temperature according to Rossberg and Wicke [18].

the intrinsic activation energy  $E_A$ . At a certain temperature, due to the exponential nature of the reaction rate, mass transport becomes noticeable. In the resulting regime II, the dominant factor limiting the reaction rate is diffusion of the reactant gas through the porous particle. Here, the observed activation energy is approximately  $E_A/2$  [18]. At even higher temperatures (regime III), the resistance of the external mass transport (film diffusion) is the predominant process affecting the reaction rate. Due to the weak temperature dependency of the diffusive mass transport in contrast to the chemical reaction, the observed reaction rate increases only slightly with temperature [19].

A transition to lower observed activation energies at high temperature is reported by authors applying all different kinds of reactors [6,13,14,20–24]. In most cases, there are explanations or suggestions given by the authors. While some authors conclude that in their case, this is caused by a transition to another regime according to Rossberg and Wicke [18], others suspect fuel-specific effects, such as ash transformation, thermal annealing and structural effects, causing the observed reactivity to deviate from the intrinsic trend at high temperature.

Since the majority of experiments reported in the literature use either different reaction systems or different fuels and are hence not directly comparable, our goal was to conduct a systematic investigation of the influence of the four most used reaction systems on observed reactivity. Special care had to be taken to guarantee, that the fuel did not undergo changes in composition, structure or reactivity on its way from feeding to the gasification segments of the different reaction systems. In a previous study [25], it was shown that a differing change of fuel properties in different systems prior to the gasification segment can be largely suppressed by an appropriate thermal pre-treatment of the fuel. If the resulting chars contain low amounts of volatiles, their physical and chemical properties will most likely not be changed significantly during in-situ pyrolysis in the reaction system used for kinetic studies and therefore should result in similar reactivity values. Consequently, at first a wood char was produced at high temperature and low residence time. This char was then conditioned and characterized. Subsequently, the Boudouard reactivity was determined in four different reaction systems: a thermogravimetric analyzer (TGA), representing a non-flow through fixed-bed, a fluidized-bed reactor (FBR), representing a stirred-tank, a free-fall fixed bed reactor (FFB), representing a flow-through fixed-bed, and a drop-tube reactor (DTR), representing an entrained-flow reactor. All systems used the same  $\text{CO}_2$  partial pressure at atmospheric conditions (80%  $\text{CO}_2$ , 1 bar). A total temperature span of 700–1600 °C and residence times from 200 ms to over 8 h were investigated. Reactivities spanning five orders of magnitude were observed. Detailed results and conclusions concerning the importance of interpreting results from the reaction systems applied are discussed in the course of this work.

## 2. Materials and methods

A systematic investigation was performed using the same high-temperature wood char, four different reaction systems, and the equal  $\text{CO}_2$  partial pressure of 800 mbar in  $\text{N}_2/\text{Ar}$  at atmospheric pressure. Following the generation of char, the setup of the reaction systems as well as the corresponding data analysis are explained.

### 2.1. Fuel characterization

The char used in this study was derived from a bark-less soft wood. Wood chips were chopped to sizes of approximately 1 mm and fed to a screw-pyrolysis reactor, described in the literature [26,27]. A temperature of 500 °C was chosen. The solids had a residence time of 5 min and were cooled in an inert, tar-free atmosphere. The produced char was further milled and sieved to particle sizes between 50 and 150  $\mu\text{m}$ . To produce a high-temperature char with low volatile content as the one inside the hot flame zone of an entrained-flow gasifier, the char was

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