



Establishment of kinetic parameters of particle reaction from a well-stirred fluidized bed reactor



H.D. Haustein*, T. Kreitzberg, B. Gövert, A. Massmeyer, R. Kneer

Institute of Heat and Mass Transfer (WSA), RWTH Aachen University, Augustinerbach 6, 52056 Aachen, Germany

ARTICLE INFO

Article history:

Received 13 January 2015

Received in revised form 12 May 2015

Accepted 18 May 2015

Available online 28 May 2015

Keywords:

Kinetic parameters

Reaction rate

Fluidized bed

Char particles

Boudouard

FTIR

ABSTRACT

A novel method is presented for experimental study of gas-particle reactions, based on realizing a well-stirred reactor as a small scale fluidized bed. This reactor is evaluated against the drop tube reactor and the thermo-gravimetric analyser. It shows to enable high heat up rates ($\sim 10^4$ K/s), long timescale observation (up to several hours), operation with small fuel particles ($\sim 100 \mu\text{m}$) and accurate control of reaction conditions. Char reaction rates are established from real-time gas product analysis by FTIR spectroscopy, through a detailed data-analysis procedure. This procedure employs a particle surface-evolution model and accounts for sampling system signal attenuation. The validity of the well-stirred conditions is established, and the method is employed for char combustion and gasification. Highly consistent results for char gasification over a wide range of conditions ($T = 800\text{--}1100^\circ\text{C}$, $C_{\text{CO}_2} = 19\text{--}76\%$), are used to demonstrate the establishment of kinetic parameters for an n -th order approach. Activation energy and order of reaction are found and compare well with the literature.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

A well-stirred reactor provides spatially homogenous, controlled conditions for process and reaction analysis. Therefore, it might serve as a basis for model development and validation [1,2]. For example, it can be used to experimentally establish inherent reaction rates of char combustion, required for reliable reactive-flow CFD simulation [3]. However, practical realization of such an ideal system is difficult. The present study attempts to do this using a small-scale Fluidized Bed Reactor (FBR), with focus on the establishment of kinetic parameters of gas-particle reaction, under controlled conditions.

An FBR is a commonly used type of reactor, though generally operated on a larger scale and in continuous-feed mode, for processes such as gasification, bio-oil production or coal and char combustion (e.g., [4–6]). Here, this reactor type was chosen and adapted for kinetic studies, due to the possibility of conducting long timescale measurements up to reaction completion. Additionally, it is shown that the significant mixing of the reactor, as well as its operation with small fuel batches, promotes

homogenous and controlled conditions for more reliable kinetic measurements. This allows for the evaluation of the reaction over its entirety with well-defined conditions greatly simplifying the analysis and generality of results. Nevertheless, the FBR also has some short-comings, which are addressed a few paragraphs further down. Dedicating an FBR to chemical kinetic parameters study, places it among other well-known methods: thermo-gravimetric analyzer (TGA, [7]), drop tube reactor (DTR, [8]) or its variant – an entrained flow reactor (EFR, see Shaddix and co-workers [9,10]). By comparison, the present method has several advantages as it combines high heat up rates and high temperatures (characteristic to the DTR) with the strong signal and ability to observe long timescales (characteristic to the TGA). Furthermore, accurate control over gas composition and temperature allows reactions to be conducted at well-defined, uniform conditions. These inherent characteristics also enable examination of application-relevant conditions, e.g. high heat up rates, intermediate residence times and small fuel particles.

On the other hand, this method also has some limitations: First, it is not as suitable as the DTR for rapid reactions (time resolution of ms), and it does not allow direct measurement of the fuel conversion in contrast to the TGA (mass-loss with resolution of μg). Secondly, the mixing bed does not permit fuel-particle quenching and extraction, for examination of morphology and composition evolution, as possible in an EFR or DTR. Finally, the modeling of the transport processes in an FBR for conversion of results to a

* Corresponding author. Tel.: +972 (0)3 640 6515.

E-mail addresses: hermanh@post.tau.ac.il (H.D. Haustein), kreitzberg@wsa.rwth-aachen.de (T. Kreitzberg), govert@wsa.rwth-aachen.de (B. Gövert), massmeyer@wsa.rwth-aachen.de (A. Massmeyer), kneer@wsa.rwth-aachen.de (R. Kneer).

generalized/intrinsic form, is generally more complex than for other methods (Kunii and Levenspiel [11]). A concluding comparison of the FBR to these other methods will be conducted in Section 3.3.

The fluidized bed approach for performing char kinetic studies was first explored by Fennel et al. [6]. That study was instrumental for the methods and the approach employed in the present study. Indeed, many similarities to that study exist here (similar particle sizes, sampling rates and relative flow rates – 10 times the minimum fluidization), though in order to extend the knowledge obtained there key differences are introduced: (i) Bed diameter is 8 times smaller resulting in a total reactor volume about 200 times smaller which should increase reactor homogeneity. Larger fuel batch sizes are used for increased signal to noise ratio and lower sample size uncertainty; (ii) an extensive fluidization and homogeneity study is conducted here to validate the desired conditions; (iii) rather than the problematic, noise amplifying de-convolution (reverse) employed there, an iterative convolution (forward, noise reducing) and fitting process is used; (iv) by examining a slower, endothermic, gasification process errors related to sampling delay and sampling rate are reduced; (v) although changes in CO₂ levels could not be directly measured for carbon mass closure (whereas stoichiometry is assumed and only CO is measured here), due to the advantages listed above the present study has much higher repeatability and much lower uncertainty. Finally, the chars examined there are of the traditional kind (lignite, bituminous), while the present study examines an alternative emerging source – woodchar (biogenic fuel).

The reaction process examined here is related to coal combustion and gasification. The complexity of this process can be reduced by splitting it in two: pyrolysis and char reaction, corresponding to shorter and longer timescales (see [12,13]). In the present study, only the slower process of char reaction is examined experimentally, which is characterized by three different regimes [14]: **Regime (I)** For smaller particles/low temperatures the reaction is limited only by the inherent chemical reaction rate (“kinetically controlled”) and takes place throughout the accessible particle surface; **Regime (II)** At increased temperatures (or particle size) it is controlled by both kinetics and intra-particle pore diffusion and takes place closer to the outer surface of the particle; **Regime (III)** At high temperatures, pressures and particle sizes the reaction is limited by the transport of reactant-gas to it (“diffusion controlled”) and reaction takes place only on its outer surface.

In the current study, char reaction rates were established experimentally through real-time FTIR gas sampling and comprehensive data analysis, under Regime I conditions. Since the presented method is quite novel, the analysis method is described in detail. Furthermore, the first part of the results focuses on the validation of the desired operating conditions (well stirred). This is followed by a parametric study of char gasification reaction rates under various conditions. The method and its validation are conducted for both gasification and combustion, although the full parametric study and finding of kinetic parameters is done for gasification alone in this work. In the light of these results, the method’s advantages and limitations are re-evaluated and discussed.

2. Experimental method

The experimental setup consists of a small-scale bed of inert particles, which is fluidized by a rate and composition controlled gas-mixture. Into this, small batches of well-characterized fuel are introduced, while the products are continuously analyzed from the exhaust gas. The analysis procedure accounts for the evolution of the char particle surface during the reaction and the dispersion

caused by the sampling system, to calculate a characteristic reaction rate from measurement data.

2.1. Experimental setup

The experimental system employed here is the same that has previously been used by the authors and is only briefly described at this point [15,16]. The FBR is located inside a controlled electric oven, allowing temperatures up to 1280 °C to be imposed with high stability (e.g.: 1000 ± 2 °C). The desired composition of the gas mixture can be set from a base gas (air, CO₂, N₂ or Ar), which can be enriched with a reactant (O₂ or CO₂) by independent temperature-corrected mass flow controllers (MFC), in order to set flow rate *at reactor conditions*. This gas mixture heats up as it flows down the annular gap to the gas distributor (sintered silica glass, pore diameter range 40–100 μm) which uniformly distributes the flow to fluidize an inert bed of round sand-like alumina (Al₂O₃ diameter $d_p = 112 \pm 30 \mu\text{m}$ and sphericity $\phi_s = 0.80 \pm 0.18$, established by laser diffraction analysis and microscopy). A small portion of this gas mixture is used to purge and mildly pressurize the char injection (fuel feed) system. For each run a small batch (<25 mg) of pulverized fuel is dropped onto the bed, where it heats up and reacts with the fluidizing gas. The heating rate has been approximated analytically taking radiative and convective heat transfer into account. The emissivity of the bed has been calculated adapting the model of Palconok [17]. The approximation gives values on the order of 10⁴ K/s similar to the values found by Yu et al. [18]. After complete reaction of the char, the remaining ash becomes an inert part of the bed material which is periodically exchanged. The pressure loss over the distributor and fluidized bed is measured by differential pressure gauge, while the bed temperature is measured with an immersed ceramic-shielded type S thermocouple. The bed has a diameter of $D = 34 \text{ mm}$, with a non-fluidized bed height of $H_d = 30 \text{ mm}$, and a typical fluidized height fluctuating around $H_f = 70 \text{ mm}$. The gaseous reaction products are captured just above the fluidized bed. Driven by a slight reactor overpressure (typically 10 mbar) the exhaust gas is fed into the gas analyzer through a sampling line and a filter; afterwards it exits out to a safety venting system. The entire sampling system is heated to 180 °C to prevent unwanted tar condensation. A Gaset DX-2000 FTIR spectrometer, measuring in the mid-IR range (wave numbers of 600–4200 cm⁻¹) was employed for real-time gas analysis, sampling at 0.5 Hz with an accuracy of 2% of the measurement range after initial calibration.

For additional validation experiments (Section 3.1), some of the tubes in the FBR were exchanged to measure the temperature and gas composition at various heights within the bed (details in Fig. 1). An identically scaled, transparent *cold* fluidized bed was used for observation of bed fluid-dynamics. Therein the pressure drop across the distributor and bed height was measured as a function of flow rate, under standard air conditions. This system demonstrated that the char particles are thoroughly mixed into the bed in less than 2 s.

2.2. Data analysis

The char reactions examined here can be well-described by the carbon conversion curve, or “burnout” (the mass fraction of solid carbon that has reacted). While obtaining the curve from analysis of exhaust gas-analysis is straightforward, establishing a *characteristic* reaction rate for the entire conversion requires a more complex analysis procedure: In general, an appropriate char surface evolution model is used to generate a predicted curve and the reaction rate (control parameter) is found by iterative comparison to the experimental one.

As the particle is consumed its surface is constantly changing, and eventually decreases towards complete burnout. By using a

Download English Version:

<https://daneshyari.com/en/article/6634944>

Download Persian Version:

<https://daneshyari.com/article/6634944>

[Daneshyari.com](https://daneshyari.com)