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## A non-equimolar mass transfer model for carbon dioxide gasification studies by thermogravimetric analysis



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#### A R T I C L E I N F O

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#### ABSTRACT

To determine the intrinsic gasification rate from experiments performed in a thermogravimetric analyzer, the influences of mass transfer limitations must be evaluated. In this study, a system of nonlinear equations was numerically solved to quantify the mass transfer limitations in three mass transfer steps: external, interparticle, and intra-particle. Unlike previous studies in this area, the reaction was not assumed to be first order and the volume was not assumed to be constant. In this model, the apparent rates of  $CO_2$  gasification of petroleum coke and activated carbon, obtained from thermogravimetric analysis, were used to determine the effectiveness factors in each mass transfer step. The model was verified with isothermal experiments at 1223 K and atmospheric pressure. The experimental results and the effectiveness factors calculated with the model showed that the initial mass and particle size were the main physical factors that influenced the gasification rate. The intrinsic reaction rate could only be obtained by thermogravimetric analysis if the effects of these factors on all mass transfer steps were determined. This model also demonstrated the importance of considering the volume change in the reaction of carbon with  $CO_2$  to evaluate the mass transfer steps.

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#### 1. Introduction

In general, the gasification process involves three steps: devolatilization of the solid fuel, oxidation, and gasification of the produced char. The latter step is the slowest step during the process and, thus, controls the rate of the overall process making this rate one of the key factors in the design of a gasifier. Thermogravimetric analysis (TGA) has been widely used to determine the kinetics of gasification [1–6]. There is, however, some debate about the direct applicability of the results obtained by this method to determine the intrinsic rate, i.e., the rate of chemical reaction free from heat and mass transfer limitations. In a typical TGA experiment, the reactant gas flows past, not directly through, the sample holder, which contains a few milligrams of sample, at a specific gas concentration and temperature. Due to this configuration, the mass and heat transfer limitations are important and may influence the results significantly such that the obtained rate may not be sufficiently accurate for scaling up the process.

Several studies have investigated the impact of mass transfer effects on gasification kinetics determined in TGA [2–6]. In these studies, the effect of mass transfer was investigated using effectiveness factors. This factor is a function of the Thiele modulus, which is the ratio of the surface reaction rate to the rate of diffusion. The direct application of the Thiele modulus requires knowledge of the intrinsic rate constant, and therefore, cannot be calculated by the rate constants measured in the presence of mass transfer limitations. The intrinsic rate can be measured in a separate apparatus and applied to the results obtained in a TGA apparatus to evaluate heat and mass transfer limitations with the TGA experiments [2–5].

A different approach [6–8] is the use of an iterative solution to obtain the intrinsic rate from mass transfer limited experiments in a TGA apparatus. In the iterative method, the effectiveness factor is evaluated by an arbitrary value of the rate constant. The values of the effectiveness factor and rate constant that predict the overall rate obtained in the TGA apparatus are adopted as the final solution. These studies were done with the oxidation of soot [6], petcoke [7], and carbon black [8] samples assuming that the reactions were first order and that there was no volume change due to the reaction. These assumptions cannot be applied to the reaction of carbon with CO<sub>2</sub>. Several studies have shown that the reaction order for carbon with CO<sub>2</sub> varies from zero to one [9–11]. In addition, the volume of the gas phase increases because of the increase in the number of moles on conversion of the reactants to products. Generally, the effect of the volume change on the rate of gas-solid reactions in porous solids is significant [12]. In such a reaction, in addition to the Thiele modulus, the effectiveness factor depends on the volume change modulus, which is a function of the stoichiometric coefficients and the mole fraction of the reaction gas exterior to the solid sample [13].

The objective of the present work is the development of a procedure to account for mass transfer limitations in the collection of kinetic data during the CO<sub>2</sub> gasification in a TGA apparatus. An iterative method was used to determine the effectiveness factors in external, intra-particle, and inter-particle mass transfer steps. In contrast to previous studies

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that used an iterative method [6–8], the reaction was not assumed to be first order or constant volume, which increased the complexity of the equations to be solved. The model developed in this work was verified with experiments performed in a TGA apparatus using petcoke and activated carbon. Specifically, isothermal CO<sub>2</sub> gasification was performed at 1223 K, and atmospheric pressure. The developed model can be applied to determine the intrinsic reaction rate and diffusion limitations for CO<sub>2</sub> gasification studies in instruments where all mass diffusion steps are significant.

#### 2. Experimental

The samples used for the gasification studies were petroleum coke (petcoke, Suncor Energy), and commercial activated carbon (Darco, Sigma Aldrich). These two samples were chosen because of their different reactivities and, thus different mass transfer limitations in the system. A thermogravimetric analyzer (TGA, Cahn Thermax 500) was used to measure the mass loss of each sample during gasification. The experiments were done isothermally at atmospheric pressure with undiluted CO<sub>2</sub>, in a quartz closed-bottom crucible (inner diameter of 19 mm). In order to validate the model results, some experiments were also conducted in a platinum flow-through crucible (hole size of 149 µm). A schematic of the crucibles and TGA set-up is shown in Fig. 1. The reaction gas  $(CO_2)$  was introduced at the bottom of the TGA and flowed upward inside the reactor tube in which the crucible was located. The sample was heated up to the desired temperature in N<sub>2</sub> at a constant heating rate (25 K/min) and flow rate (350 mL<sub>N</sub>/min, all flows were controlled by mass flow controllers). The gas was switched from N<sub>2</sub> to CO<sub>2</sub> once the desired temperature was reached and the mass signal had stabilized. The experiments were performed with different initial masses (25 mg, 50 mg, 100 mg, and 150 mg) of petcoke (crushed,  $<90 \,\mu\text{m}$ ) and activated carbon (as received, 841–1680  $\mu\text{m}$ ), as well as different particle sizes (<90 µm, 90–180 µm, 180–300 µm,  $300-600 \,\mu\text{m}$ ) of samples with ~25 mg of initial mass, to study the effect of these factors on the rates. The results shown in this paper are the average results obtained over two or three experiments.

The petcoke was characterized for volatile matter, ash, and fixed carbon in the TGA using standard ASTM D5142. The surface characteristics of activated carbon and petcoke were analyzed by physisorption, performed on an adsorption instrument (Tristar, Micromeritics). The pore volume and mean pore diameter of petcoke and activated carbon were obtained by N<sub>2</sub> adsorption at 77 K and calculated by the Barrett–Joyner–Halenda (BJH) method. The surface area of petcoke was measured by N<sub>2</sub> physisorption at 77 K and CO<sub>2</sub> physisorption at 273 K using the Brunauer–Emmett–Teller (BET) and Dubinin–Asthakov (DA) methods, respectively. CO<sub>2</sub> physisorption was used to determine the micropore surface area.

#### 3. Methodology

#### 3.1. Main assumptions

The kinetic steps involved in a TGA experiment are [2]: (1) external mass transfer from the bulk gas stream to the outer surface of the bed in the crucible through a stagnant gas layer; (2) inter-particle diffusion of the reactants through the bed; (3) intra-particle diffusion of the reactants into the interior of the sample particles through the pores; (4) heterogeneous reaction including adsorption, surface reaction, and desorption; and (5) counter-diffusion (intra-particle, inter-particle, external) of the product gas. Only the fourth step is associated with the chemical reaction while the remaining steps are mass transfer steps. Since the reaction gas flows upward in the TGA reactor tube, the reaction gas diffuses in the z direction. Based on computational fluid dynamics calculations, it was determined that the influence of turbulence on the mass transfer inside the crucible was negligible compared to the molecular diffusion (see Fig. 2, velocity profile of the gas inside the reactor and crucible was simulated by COMSOL). In addition, CO<sub>2</sub> did not diffuse through the walls of the crucible and the height of the bed was small (3 mm for 150 mg petcoke) compared to its diameter (19 mm). Therefore, it was assumed that the system was one-dimensional. Steady-state conditions for the gas-solid system [14], the ideal gas law, and constant total gas pressure throughout the system were also assumed. The overall reaction occurring in the CO<sub>2</sub> gasification of petcoke and activated carbon was assumed to be the basic reaction of carbon with CO<sub>2</sub> as follows:

$$CO_2 + C \rightarrow 2CO.$$
 (1)

Intrinsic reactivity was expressed in the form of a global power law, *n*th order irreversible rate expression. The kinetics of the gasification of carbon with carbon dioxide was described by a Langmuir–Hinshelwood type rate expression [15]. However, several studies successfully applied



Fig. 1. Schematic of (a) the TGA set up and (b) crucibles used for experiments.

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