Fuel 148 (2015) 160–167

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Kinetic study of coal steam and CO_2 gasification: A new method to reduce interparticle diffusion

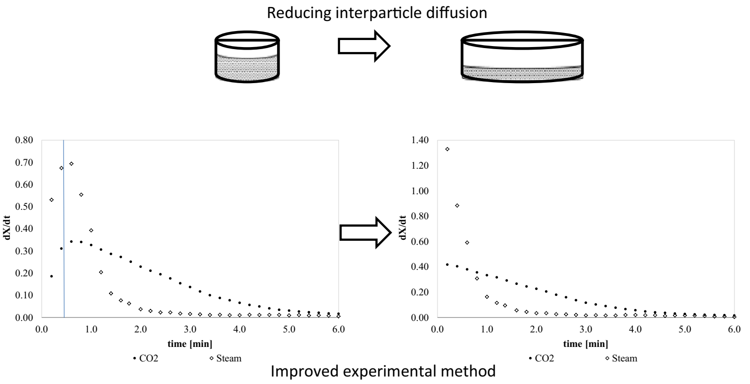
Arturo Gomez, Nader Mahinpey *

Department of Chemical and Petroleum Engineering, Schulich School of Engineering, The University of Calgary, Calgary, AB T2N 1N4, Canada

HIGHLIGHTS

- A new experimental method to perform either steam or CO_2 gasification was proposed.
- The time to replace the gases into the reactor will affect the kinetics analysis.
- The E_A of steam gasification reported in the literature is usually underestimated.
- Interparticle diffusion is affecting the gasification rate at low temperatures.
- Interparticle diffusion can be minimized by reducing the bed sample thickness.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 13 November 2014
Received in revised form 20 January 2015
Accepted 21 January 2015
Available online 7 February 2015

Keywords:
Steam gasification
Reaction rate
Mass transfer
Kinetic model
Random pore model
Activation energy

ABSTRACT

The effect of coal bed thickness was studied and compared between steam and CO_2 gasification. Despite using small amounts of coal sample, both gasifying agents' kinetics, i.e., steam and CO_2, proved to be affected by bulk and interparticle diffusion. Comparison between the gasifying agents indicates that mass transfer effects are minimized when the raw material layer and particle size are smaller than 0.14 mm and 90 μm, respectively.

In addition to mass transfer limitations, studies have confirmed that the reported maximum reaction rate is a consequence of the gas switching between inert and reaction gas during steam gasification; therefore, the time to replace the reaction medium cannot be considered as part of the kinetic analysis or taken into account in the kinetic model that represents the reaction mechanism. Nevertheless, it is not appropriate to use steam alone during pyrolysis and gasification in kinetic studies, since these two reactions overlap in the same temperature reaction range. An alternative method to overcoming these restrictions is proposed in this study.

The present study demonstrates a consistent method to perform gasification in the chemically controlled temperature range between 750 °C and 900 °C. In addition, the apparent activation energy is estimated independent of the kinetic model.

1. Introduction

Gasification is defined as the thermochemical conversion of a rich carbon feedstock into syngas, thus providing advantages in the undertaking of pre-combustion conditioning compared to

---

* Corresponding author at: Dept. of Chemical and Petroleum Engineering, Schulich School of Engineering, University of Calgary, 2500 University Drive NW, Calgary, AB T2N 1N4, Canada. Tel.: +1 (403) 210 6503; fax: +1 (403) 284 4852.
E-mail address: nader.mahinpey@ucalgary.ca (N. Mahinpey).

http://dx.doi.org/10.1016/j.fuel.2015.01.071
0016-2361/

conventional processes such as combustion. Steam gasification of coal and biomass increases the hydrogen to carbon monoxide ratio (H_2/CO) of the produced syngas [1]; therefore, it is suitable for power generation when carbon capture is an option [2–4] or as a source of reactants for further chemical transformation [5]. Steam gasification yields a much slower chemical reaction than combustion using the same feedstock and because steam is highly corrosive at the reaction conditions [6,7], it is not possible to perform steam gasification using the conventional setup used for CO_2 gasification. Different authors present particular setups, *i.e.* batch reactors with product gas product analysis [8–10], TGA [11,12] and flow reactors [1,13]; however, experimental procedures are not standardized and they are similar to those used for CO_2 gasification.

Kinetic modeling of steam gasification is usually reported using single-step reaction models [14,15] similar to those used for CO_2 gasification [16]. The most common kinetic model is the random pore model (RPM) proposed by Bhatia and Perlmutter [17]. This model can predict a maximum reaction rate; however, this is a consequence of the reaction medium change [18]. In the literature, intrinsic kinetic studies reveal that particle size and gas flow rate limit the overall reaction rate, considering 90 μm as a safe particle size to reduce intrapore diffusion [15,18]. There are studies in the literature that do not consider relationship of sample weight and existence of mass transfer effect, such as [11,14,15] whom authors have used less than 15 mg and [8–10,19] whom authors chose more than 100 mg as sample size. However, amount of sample, reactor configuration and crucible are significant in kinetic analysis, since the sample thickness affects the reaction rate due to interparticle diffusion [20].

Activation energy of steam gasification ($E_{A\ steam}$) is reported as significantly smaller than the activation energy of the CO_2 gasification ($E_{A\ CO2}$) in the same temperature range [21,22], but the experimental procedure affects E_A results, and its calculation depends on the kinetic model since the rate constant is obtained from a linear regression when a single-step chemical reaction model is considered. This leads to some unexpected results such as similar E_A values for steam and CO_2 gasification [23]. An alternative E_A can be calculated without assuming a kinetic model [24,25]; therefore, providing a more accurate value of the estimated E_A.

A new method to perform steam and CO_2 gasification with negligible bulk and interparticle diffusion effects is presented in this work. Different setup configurations are compared to determine if coal bed thickness is the most important variable associated with interparticle diffusion, instead of the sample amount which depends on the setup configuration. The activation energy of steam gasification calculated with an independent kinetic model approach with the proposed experimental method is consistently smaller than the activation energy of CO_2 gasification. This study helps to explain the difference between laboratory studies and pilot results using reactors with better fuel distribution. It also demonstrates that activation energy of steam gasification may be underestimated in the literature [20,21] as a consequence of the mass transfer limitations with small thicknesses of the coal bed layer.

2. Experimental methods

2.1. Experimental setup

A TGA TherMax 500 coupled with a home-built quartz reactor was used to perform atmospheric gasification in steam and CO_2 atmosphere. The schematic of the experimental setup is presented in Fig. 1a. The time interval to replace 98% of the inert gas with the reaction gas into the quartz reactor with 10 mg coal sample was 0.8 min, which was preliminary determined by estimation of the gases residence-time distribution with a step tracer experiment [18]. The volumetric flow rate of the gases was 1.8 times the reactor volume per minute to avoid bulk diffusion as presented elsewhere [15,18]. A quartz crucible with a 12 mm internal diameter and external conical shape allows support of a layer of coal smaller than 1 mm with a stable weight reading. A graphical comparison between this crucible and the conventional alumina crucible is illustrated in Fig. 1b. In contrast, the time interval to replace all gases using a NETZSCH TG 209 Libra F1 analyzer (TGA) was 1.8 min, with the same ratio of gas flow rate to reactor volume [18].

2.2. Coal characterization

Two Central-Western Canadian coals, Genesee coal (mined in Alberta) and Boundary Dam coal (mined in Saskatchewan), were analyzed in this study. Coal samples with particle size smaller than 90 μm were prepared as presented elsewhere [15,18] to insure intrapore diffusion does not control the coal gasification rate. The coal sample was composed of 70% of particles between 75 and 90 μm, and 30% smaller than 75 μm. The elemental composition was determined using a Perkin Elmer CHNS/O 2400 elemental analyzer (ultimate analysis). The proximate analysis was performed at atmospheric pressure using a NETZSCH TG 209 Libra F1 analyzer (TGA) according to the ASTM D5142 standard for coal and coke. The coal micro-pore surface area was determined using a Micrometrics model ASAP 2020 analyzer by CO_2 adsorption at 273 K (Dubinin–Radushkevich method).

2.3. Steam gasification

Silbermann et al. [15] suggested that direct gasification using CO_2 is the best method to carry out their experiments, since it shows a higher reaction rate [18]. Unfortunately, direct gasification (using same reaction gas during pyrolysis and gasification) cannot be applied when steam is the gasifying agent, since gasification overlaps with pyrolysis in the same temperature range due to the steam gasification rate being much higher than CO_2 [19,21,22] and the overall reaction is not thermodynamically limited by the Boudouard reaction below 700 °C [26]. Other methods that separate pyrolysis and gasification reduce char reactivity due to the reduction of the initial char mesopore area during the isothermal pyrolysis [18].

Another method consists of changing an inert gas by the gasifying agent; which is the most common experimental procedure presented by other authors to study steam gasification [8–12,19]. The beginning of the gasification is often considered when the reaction system reaches the reaction temperature if there is no isothermal pyrolysis step, the exact time at which the gases are simultaneously changed. The main disadvantage of this method is that a maximum gasification rate is observed at the same time after switching the inert gas for the gasifying agent [8,18,19,21]. Thus, the starting point of the gasification should be reconsidered to avoid misinterpretations about the reaction mechanism [18]. As a consequence, this work presents an alternative method to overcome the main limitations of most common gasification experimental procedures.

Using the new experimental setup, the proposed method to perform gasification either with steam or CO_2 as gasifying agents consisted of: (1) keeping the sample at an ambient temperature in a N_2 atmosphere until its weight became stable; (2) heating up the sample at 100 °C/min (limitation of the new experimental setup); (3) decreasing the heating rate from 100 °C/min to 20 °C/min, when the temperature reaches 10 °C below the reaction temperature, to avoid overheating; and (4) replacing N_2 with steam or CO_2 at the reaction temperature. The gasification was considered to start