



Impact of K_2CO_3 catalyst loading on the CO_2 -gasification of Genesee raw coal and low-ash product



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ABSTRACT

In this study, the effects of K_2CO_3 addition to Genesee sub-bituminous coal, before and after ash reduction, on conversion and gasification rate were investigated for CO_2 gasification at 700–800 °C. For the uncatalyzed samples, no significant changes in gasification rate and char conversion were observed for the low-ash product (12 wt% ash) compared to the raw coal (33 wt% ash). However, with the addition of 10 wt% potassium catalyst, the low-ash product exhibited a higher gasification rate than the raw coal. An increase of the catalyst loading up to 50 wt% resulted in a decline of the gasification rate for both coal samples. The activation energy increased with conversion and at higher K_2CO_3 loadings. Kinetic modeling showed that the extended-random pore model fits the experimental data well for both coal samples and supported the speculation that excess catalyst blocks pores, resulting a reduction in gasification rate.

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1. Introduction

Coal is an abundant resource that can be gasified to produce valuable gas mixtures for further processing such as gas turbines and fuel synthesis. Coals vary in composition depending on the deposit – high-rank coals have higher heating values, lower moisture contents and lower ash contents than low-rank coals. Most gasifiers work well with high-rank coals. Although there is interest in the development of gasifiers that can utilize low-rank coals, the higher ash contents are problematic as they can increase costs of flue gas treatment, increase particulate matter in the exhaust gas and decrease furnace efficiency [1]. The ash is composed of a variety of minerals, and dealing with the ash increases the complexity of the gasification operation. For example, the minerals can cause erosion and corrosion of turbine blades, and fouling when used in integrated gas combined cycle (IGCC) processes [2].

To improve the situation, the ash content of the coal can be reduced prior to gasification through either wet or dry beneficiation processes [3–5]. Although the removal of the ash reduces problems in the operation of the gasifier, the removal of the mineral species also significantly reduces the reactivity of the coal [6]. More specifically, at 750 °C, the gasification rate of ash-free coal was 20 times lower than that of the raw coal [7]. Thus, catalysts, typically alkali and alkali earth metals [8],

must be added to the beneficiated coal to restore the activity. Potassium is the most commonly used alkali metal catalyst for gasification because of its high activity, and is typically added to the feed in the form of potassium carbonate (K_2CO_3) [8].

The components in the ash react with, and deactivate, catalytically active species. For example, alumina and silica species in the ash will react with potassium catalysts to form potassium aluminosilicates that are not catalytically active [9]. It is energy intensive to remove all the ashes in the coal. Thus, the removal of ash is a balance between the energy input and the removal required to minimize catalyst deactivation. With one of the dry beneficiation processes – air dense medium fluidized bed – a product that contains significantly less ash than the raw coal can be obtained with a lower energy requirement since this process does not require the use of fresh water and as such, no energy is expended in drying the coal – a step required in the wet beneficiation process [1].

In this study, we have compared the gasification behavior of a raw coal and its low-ash product, with different catalyst (K_2CO_3) loadings to determine the impact of removing only a fraction of the ash from the coal. Gasification studies were conducted in a thermogravimetric analyzer at temperatures between 700 °C and 800 °C in a CO_2 atmosphere, and the experimental data were fit to various kinetic models. The coal samples were characterized using proximate and elemental analysis to determine composition, and X-ray diffraction to detect crystalline phases. The results suggest that partial removal of the ash does not significantly change the behavior of the coal but does influence how much catalyst must be added.

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2. Material and methods

2.1. Experimental

A low rank coal from the Genesse coalmine in Alberta, Canada (sub-bituminous coal) was used in this study. The as-received sample or raw coal will be referred to as GEN-raw and contains ~33 wt% ash on a dry basis. The second sample is partially reduced in ash (12 wt% ash) and referred to as GEN-LAP (low-ash product). Ash reduction has been carried out in an air dense medium fluidized bed process. The details of this dry physical coal beneficiation method are described elsewhere [1,10].

In the present work the potassium catalyst (i.e., K_2CO_3 powder, Fisher Scientific >99.0%, particle diameters less than 90 μm) has been added to the coal by means of dry mixing using a mortar and pestle at room temperature. Samples with target catalyst weight loadings of 5, 10, 25, and 50 wt% were prepared, where the weight percent is with respect to the total mass (K_2CO_3 plus coal). Both the GEN-raw and GEN-LAP samples (with and without catalyst) were ground using a mortar and a pestle and sieved to a particle size less than 90 μm .

CO_2 gasification studies were performed in a thermogravimetric analyzer (TGA, Thermo Scientific, TGA Thermax 500). The detailed setup and experimental procedure have been described elsewhere [6]. Briefly, approximately 15 mg of sample was placed in the TGA crucible and heated to the desired temperature (i.e., 700–800 °C) under a N_2 (300 mL min^{-1} , Praxair, 99.999%) atmosphere, while the mass change was recorded. The heating rate to the desired temperature was varied between 5 °C min^{-1} and 15 °C min^{-1} , but no significant change in the gasification rate was observed (Fig. S1), and hence, the faster rate (15 °C min^{-1}) was used for all subsequent TGA runs. Prior to adding the gasification agent (CO_2 , 300 mL min^{-1} , Praxair, 99.99%), the sample was held for 150 min in N_2 at the reaction temperature to release volatile matter and to reduce K_2CO_3 to its catalytically active form. A previous study indicated that a longer holding time (150 min vs. none) in N_2 improved the extent of K_2CO_3 reduction to more active surface intermediates such as $-COK$ and/or $-CK$ [6]. These surface intermediates allow faster oxygen exchange reactions during CO_2 dissociation, oxygen transfer to a free carbon surface and subsequent gasification to CO. Direct introduction of CO_2 during the heating of the coal samples to 700 °C suppresses the K_2CO_3 reduction to the active intermediates and reduces the oxygen exchange reaction [6].

CO_2 gasification was carried out at 700 °C, 750 °C and 800 °C. Each experiment was performed twice and the results were consistent between runs. The experimental data (mass and time) were smoothed using the locally weighted scatterplot smoothing (LOWESS) function in the graphing software (Sigmaplot), which decreased the number of data points and reduced the noise from the experimental data. The smoothed data (1000 points) were used to calculate the char conversion defined as:

$$X = \frac{m_0 - m_t}{m_0 - m_{end}} \quad (1)$$

where m_0 is the initial char mass of the samples with or without catalyst, m_t is the mass of the samples with or without catalyst at time t , and m_{end} is the mass of the samples with or without catalyst after complete conversion. The exit stream from the TGA was directed through a condenser and to a non-dispersive infrared gas analyzer (Uras 26 AO2020 ABB) to determine the concentration of CO produced during the gasification of the coal samples.

2.2. Sample characterization

Proximate analysis was performed with the TGA instrument to quantify the amount of the volatile matter (VM), fixed carbon (FC) and ash based on the ASTM D3172 method. The samples were used directly (no initial drying step) and heated to 950 °C under flowing N_2

(300 mL min^{-1}) before switching to flowing air (300 mL min^{-1}), while monitoring the mass.

Elemental analysis was performed using an elemental analyzer (Perkin Elmer 2400 Series II) to quantify the amounts of carbon, hydrogen, nitrogen and sulfur in the GEN-raw and GEN-LAP samples. The ash composition was obtained using an Orbis EDAX energy-dispersive X-ray fluorescence (XRF) microprobe system from AMETEK. X-ray diffraction (XRD) powder patterns of the samples were obtained on a Rigaku Multiflex diffractometer using Cu $K\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$).

2.3. Kinetic modeling

The TGA experiments allow differential conditions to be achieved. That is, the measured mass change in a given time interval is very small compared to the total mass (i.e., 0.001–0.05 mg min^{-1} versus an initial mass of 15 mg). The reaction gas, CO_2 , was fed in excess (300 mL min^{-1}) and the produced CO was on the order of a few parts per million by volume, so that the CO_2 partial pressure did not change significantly during the gasification experiment. Thus, the CO inhibition effect could be neglected. Only the random pore (Eq. (2)) and extended random pore (Eq. (3)) models were considered to model the gasification behavior.

$$\frac{dX}{dt} = k_{RPM} \cdot (1-X) \cdot \sqrt{1-\Psi \cdot \ln(1-X)} \quad (2)$$

$$\frac{dX}{dt} = k_{eRPM} \cdot (1-X) \cdot \sqrt{1-\Psi \cdot \ln(1-X)} \cdot (1 + c(1-X)^p) \quad (3)$$

where K is the reaction rate constant, Ψ is the structural factor, and c and p are semi-empirical parameters. The last three parameters were assumed to be independent of the temperature. Other models including the volumetric, shrinking core and integrated models did not capture the CO_2 gasification behavior of Genesee coal in a previous study [7].

Regardless of the model used, the temperature dependency of the reaction rate constant was determined by a modified Arrhenius equation (Eq. (4)), with a reference temperature, T_{ref} , of 750 °C (1023 K), as follows:

$$k_j = k_{Tref} \cdot \exp\left\{\frac{E_A}{R \cdot T_{ref}} \cdot \left(1 - \frac{T_{ref}}{T}\right)\right\} \quad (4)$$

where E_A is activation energy and R is the gas constant.

Athena Visual Studio v14.2 software was used for kinetic parameter estimation and model discrimination by means of a non-linear least-squares method and Akaike information criterion, respectively. The Akaike information criterion (AIC) is defined as:

$$AIC = m \cdot \frac{2}{n} + \ln\left\{\frac{1}{n} \cdot RSS\right\} \quad (5)$$

where m is the number of estimated parameters, n is the number of observations, and RSS is residual sum of squares. The model with the lowest AIC value was considered to be the preferred model. For comparison, the Akaike probability share (π_{AIC} , Eq. (6)), relative likelihood (L_k , Eq. (7)), residual sum of squares (RSS) and the R^2 -values were also calculated and presented.

$$\pi_{AIC} = \frac{L_k}{\sum_{i=1}^k L_k} \quad (6)$$

$$L_k = \exp\left\{\frac{AIC_{\min} - AIC_k}{2}\right\} \quad (7)$$

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