Applied Thermal Engineering 110 (2017) 991–998

Contents lists available at ScienceDirect

Applied Thermal Engineering

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

Research Paper

# Estimation of synergetic effects of $CO_2$ in high ash coal-char steam gasification

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## HIGHLIGHTS

- Pyrolysis heating rate of coal affects the char structure.
- Steam and $CO_2$ gasification rate varied based on char production methods.
- Gasification rate determination for different conversion levels
- Synergetic phenomenon between steam and $CO_2$ in char gasification.
- Kinetic constants are differed based on particle size and pyrolysis rates.

## ARTICLE INFO

*Article history:*
Received 21 June 2016
Revised 2 September 2016
Accepted 4 September 2016
Available online 7 September 2016

*Keywords:*
High ash coal
Char gasification in steam and $CO_2$
Synergetic effect
Kinetic models

## ABSTRACT

Char particles of high ash Turkish coal with different sizes are produced in a thermo-gravimetric apparatus furnace using three heating rates. The effect of coal particle size on char production under various heating rates is evaluated. The gasification experiments of the produced char in steam and blended (steam + $CO_2$) ambiences were performed over the temperature range of 850–950 °C under ambient pressure conditions. It is observed that the changes in char structure porosity for various heating rates affect its gasification rates. Also, char gasification is affected by the parametric conditions such as reaction temperature, char production method, and particle size in addition to chemical composition and physical structure of char. The maximum reaction rate is shifted to higher conversion levels when the chars are produced from high heating rate pyrolysis conditions. In the argon, steam and $CO_2$ blended ambience, the substitution of $CO_2$ for argon improves the char gasification rate. There is no $CO_2$ inhibition effect observed in the char-steam gasification, whereas some synergetic effects are anticipated. Three kinetic models are used to describe the char gasification kinetics: volumetric model, grain model, and random pore model. The variation of activation energy during gasification is based on the char generation method, particle size and reactant concentrations. The activation energy for steam gasification is 156–173 kJ/mol, whereas in the steam blended with $CO_2$ gasification values are in between 162 and 196 kJ/mol for 3 mm particles. Besides, these values are considerably low for 800 μm particles. Similar trends are observed from Arrhenius constant values for both sized particles.



## 1. Introduction

Coal is considered as an important source of energy, not only for power generation, but also for the fuels (e.g., coal-to-syngas) and chemicals production; numerous studies are ongoing to improve its gasification efficiency. Coal has undergone a variety of physical and chemical changes towards for reaching the thermal decomposition temperature. Thermal decomposition and gasification of coal has been widely studied by many investigators [1–8]. Coal pyrolysis conditions can alter the resulting char structure, particle size, and density, thereby its reactivity. The thermogravimetric (TG) study of coal is a renowned method to understand the changes in the structural features of coal during thermal decomposition and its oxidation and gasification process [9–14].

Kristiansen [15] investigated for optimizing the design parameters during the coal gasification process under $CO_2$ and steam ambience. Several researchers [16–19] have reported the effect of coal rank on gasification using steam and $CO_2$ and its kinetics parameter estimation. Li et al. [20] examined the fast pyrolysis

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http://dx.doi.org/10.1016/j.applthermaleng.2016.09.011
1359-4311/

features of various originated coals. Van Heek and Muhlen [21] reported the properties effect of coal and char on the gasification phenomena. Chen et al. [22] examined the effect of fast pyrolysis char production using lignite and its gasification reactivity using steam and $CO_2$. Recently, Aranda et al. [23] have compared the high ash coal gasification rate and its kinetics in TG study and fluidized bed conditions under steam and $CO_2$ ambience. They have reported the gasification rate variations which are majorly instigated by coal particle shape and size, heating characteristics during thermal decomposition, reactant's inhibition and synergetic issues, and other fluid-dynamic effects. The mechanisms of carbon/char–$CO_2$ and carbon/char–$H_2O$ reactions have been extensively reported, by both experimental methods [11,13,24–26] and through computational chemistry process [27,28]. There is a debate on the interactions between $CO_2$ and $H_2O$ during the char gasification in this oxidant mixture.

Several researchers [11,29–31] have reported that char–$CO_2$ and char–$H_2O$ reactions occurred separately on discrete active sites on the char. Alternatively, Roberts and Harris [25] stated that the char–$CO_2$ and char–$H_2O$ gasification reactions are not independent and the possibility of enhancing effect. Supplement the carbon dioxide along with the steam slows down the char-gasification reaction [20], stating that $CO_2$ and $H_2O$ share same active sites on the char surface [25,32,33]. The present study aims to further elucidate the above phenomenon using high ash char particles.

The char gasification rate can be computed using several models such as the volumetric model, the grain model and the random pore model [25,31,34–38]. A detailed understanding and comprehensive study of char reactivity in steam and $CO_2$ and the corresponding gasification kinetics is considered as vital parameter for the mathematical and process modeling of practical gasifier systems. Besides, coal properties also usually varied based on its origination, kinetic parameter estimation for char gasification characteristics is usually coal-specific. In our on-going research, we are investigating pyrolysis, combustion and gasification reactions of Turkish and Indian high ash coals [4,11,13,14].

The main objective of the present study is to investigate the gasification kinetics of chars produced from Turkish high ash coals using thermogravimetric (TG) analysis at different heating rates. The effect of parent coal size variation and the appropriate kinetic models to determine the char reactivity variation under steam and blended mixture gasification and its potential synergetic effects during gasification reactions are investigated. The kinetic parameters (e.g., activation energy and the Arrhenius constant) are estimated using the specified three kinetic models.

## 2. Experimental details

High ash Turkish coal from Saray region in the Western Turkey (Thrace bassinà with average particle sizes of 800 μm and 3 mm) are used for this study. A NETZSCH STA 429 thermo gravimetry analyser (TGA) with platinum furnace is used to prepare the char particles through pyrolysis. Three heating rates, namely 100 K/min, 500 K/min and 800 K/min are employed to produce char particles in an argon ambience. The experimental setup used for the gasification studies was specified in detail elsewhere [9,11,13,14] and also shown in Fig. 1. A water vapour (steam) generation system is connected with the TG apparatus. The steam generator and the transfer lines are maintained at the temperature of 180 °C and 150 °C respectively. The generated char particles has undergone the dynamic heating of 40 K/min in an argon ambience to the preset temperature and further gasified in steam and blended (steam + $CO_2$) ambience under isothermal regime for a specified time. The TG system tracks the record of sample mass loss using a highly sensitive analytical balance with a resolution of $10^{-3}$ mg. The experimental error limits are estimated, obtaining an accuracy for all studied samples of ±0.5% in weight loss measurements and ±2 °C in temperature measurements. The ultimate and proximate analyses of the Turkish coal are tabulated (Table 1).

## 3. Kinetic models

The TG experimental results, obtained as mass loss versus time data, are expressed as conversion level (X) versus time profiles (on ash-free basis), defined as

$$X = \frac{m_o - m}{m_o - m_{ash}} \tag{1}$$

m denotes the instantaneous mass of the sample, $m_0$, initial mass; and $m_{ash}$ is the remaining mass, which corresponds to the ash content. The reaction rate is calculated as a differential of the conversion degree versus time, denoted as $\frac{dX}{dt}$.

The apparent reaction rate is calculated from the following relation,

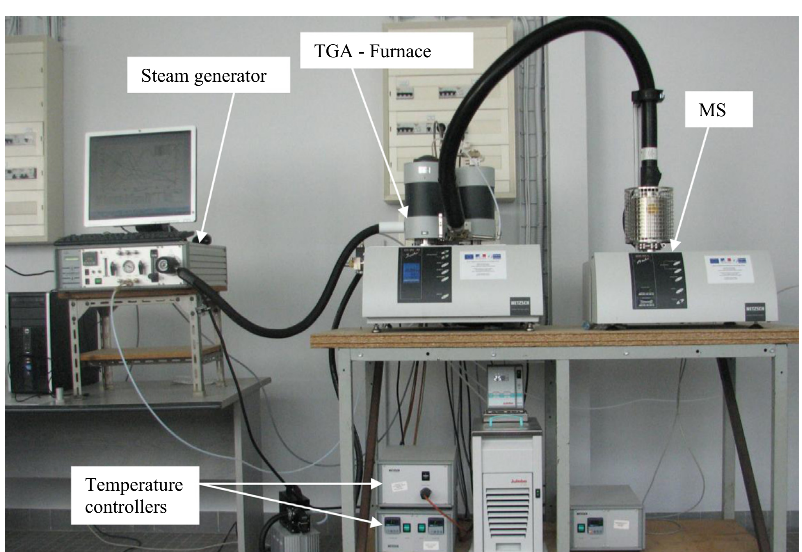


**Fig. 1.** Experimental set-up (steam generator-TGA-MS).