



A new model to estimate CO₂ coal gasification kinetics based only on parent coal characterization properties



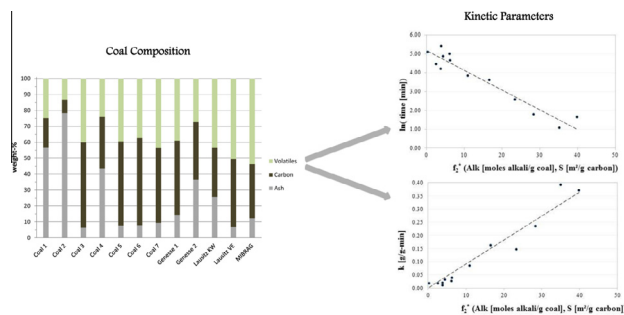
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HIGHLIGHTS

- A mathematical model to predict gasification rate and residence time was proposed.
- Gasification rate is affected mainly by micropore surface area and alkaline content.
- Residence time for coal gasification can be predicted without a kinetic model.
- Surface area based on carbon content is an important parameter in kinetic analysis.
- The model can predict the kinetic of coal blends in any ash composition range.

GRAPHICAL ABSTRACT



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ABSTRACT

A new mathematical model is proposed for the estimation of CO₂ gasification kinetics of different rank coals and ash contents. There are no previous reports on the determination of the conversion rate or even residence time of CO₂ or steam gasification based on coal characterization and for a wide range of ash content. This new approach can be used to infer the residence time and other parameters required for reactor design and operation optimization of newly mined coals or coal mixtures used as feedstock.

The coal micropore surface area and the alkaline content determined by the ash composition were proved to be the most significant variables influencing the gasification rate. These variables were correlated to formulate a semi-empirical expression based on the Arrhenius equation. An equation to infer residence time, independent of the kinetic model, is also presented.

The new equation is important in understanding the catalytic effect of the alkaline content in the temperature range where the chemical reaction is the controlling step. It can also be used as the corresponding term of the chemical reaction in a gas–solid kinetic model when working at higher temperatures. This new approach is valid, if there is not loss of alkali and alkaline earth metals due to sublimation or melting, which results in a glassy slag structure. The proposed model has direct industrial application in simulation of gasifiers' performance with the knowledge of only coal characterization properties.

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1. Introduction

Gasification is the thermochemical conversion of carbonaceous feedstock into carbon monoxide (CO), carbon dioxide (CO₂) and

hydrogen (H₂). Other by-products are generated from the rest of the raw material's components reacting at a high temperature with gasification products. The non-reactive components are termed ash; however, they are not totally inert, since they can change their morphology due to solid-phase changes, partial oxidation or reduction, or even metal and oxide sublimation [1,2].

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Nomenclature

a_k	regression constant to obtain k_M from f_2^* ($\text{min}^{-1} \text{m}^{-2} \text{g}$)	m_o	initial mass of char (g)
a_t	first regression parameter to obtain t from f_2^* ($\text{min}^{-1} \text{m}^{-2} \text{g}$)	m_t	mass of char at the particular time 't' (g)
Alk	specific molar alkaline content (mol g^{-1})	r	conversion rate (min^{-1})
b	correlation parameter in Arrhenius' exponential factor ($\text{mol g}^{-1} \text{K}^{-1}$)	R	ideal gas law constant ($\text{Pa m}^3 \text{mol}^{-1} \text{K}^{-1}$)
c_t	second regression constant to obtain residence time from f_2^* (g m^{-2})	S	specific surface area ($\text{m}^2 \text{g}^{-1}$)
Ea	activation energy (kJ mol^{-1})	t	time (min^{-1})
$f_1(1 - X)$	function of the conversion, instead of surface for gas–solid reaction ($\text{m}^2 \text{g}^{-1}$)	T	temperature (K)
$f_2(\text{Alkali}, T)$	function of the alkali (mol g^{-1}) content and temperature (K), (dimensionless)	X	conversion (dimensionless)
f_2^*	product of f_1 and f_2 , ($\text{m}^2 \text{g}^{-1}$)	<i>Greek letters</i>	
k	rate constant for a first order reaction (min^{-1})	α	change on activation energy due an alkali decrease (kJ/g)
k_o	frequency factor (min^{-1})	Δ	gradient of a determined variable
k_M	rate constant for the particular kinetic model 'M' (min^{-1})	<i>Abbreviations</i>	
m_a	mass of ash (g)	IM	integrated model or power-law model
		TGA	thermogravimetric analysis
		RPM	random pore model
		VM	volumetric model

Different models are used to represent the chemical reaction kinetics of CO_2 gasification as a particular case of gas–solid reactions. The simplest models are the volumetric model (VM), the shrinking core model (SCM), and the integrated core model (ICM), which are equivalent to a first, two third, and a general unknown reaction order on the solid phase, respectively [3–5]. The most widely used model is the random pore model (RPM), which was proposed by Bhatia and Perlmutter [6] to explain the existence of a maximum conversion rate usually observed experimentally. Other models with additional parameters can generate similar results than the RPM [7,8]. It was proved that this maximum is a consequence of the experimental procedure when the inert gas is replaced by the reaction gas instead of associated changes on the char surface area [9]. The ICM and the VM fit better to the experimental results than other models, if the experimental procedure is adjusted in order to avoid the gas switching [5,9].

The heterogeneity among different feedstock is a challenge to implement gasification as an alternative process for coal and biomass utilization. Therefore, accurate and reliable gasification rate estimation is necessary to infer the performance of different reactors when the feedstock is changed. Information obtained from coal characterization, such as proximate and elemental analyses, has been widely studied, but there have been no results for the estimation of the kinetic behavior of coals, even with similar ash contents. Previous works in gasification have not mentioned the calculation of kinetic parameters based on parent coal properties, since consistent correlations had not been obtained; however, the effects of the most important variables, i.e., coal rank, temperature, pressure, ash composition and gasifying agents, have been reported [10]. A first attempt to estimate the reactivity of coals based on the physical and chemical properties of the coal was proposed by Adschiri et al. [11], who correlated porosity and micropore surface area with the initial carbon content of the parent coal. Other works have shown improvement in the gasification rate with an increase in ash content [12] and a general correlation for different rank coals using experimental kinetic parameters, such as the frequency factor and activation energy, without considering measurable properties of the raw material [13].

As coal reactivity is significantly affected by their ash content, alternative methodologies have been proposed to compare their gasification rates. For example, Ochoa et al. [14] presented master

curves for different coals, which show the ratio between the conversion rate at a particular conversion and the conversion rate at 50% conversion. Reported results show that low-rank coals exhibited higher reactivity than high-rank coals. This reactivity was associated with the alkaline content [15]. There have also been differences in the literature related to the activation energy even for the same rank coals [16,17].

The most common chemical reaction kinetic models do not consider the effect of the ash composition [3,4]; however, its catalytic nature has been mentioned as a variable affecting the activation energy [5]. The effects of alkali and alkaline earth metals as catalysts to enhance CO_2 gasification [18–20] have been widely discussed, with the order of effectiveness as potassium (K) > sodium (Na) > calcium (Ca) > iron (Fe) > magnesium (Mg) content [21]. Similar results have been presented for steam gasification [22,23], plus a reduction in methane (CH_4) formation when potassium carbonate (K_2CO_3) was added to the feedstock [24]. Hatting et al. [25] showed that micropore surface area and mineral composition (determined by the ash analysis) were the most significant variables during CO_2 gasification, but did not present a model to estimate kinetic parameters.

Thermogravimetric analysis (TGA) studies have been conducted at low temperatures, where the chemical reaction was the controlling step and it was assumed that there were no slagging conditions but operating temperature for entrained flow reactors is higher than 1400 K [26]. For gas–solid reactions; adsorption, desorption, and surface reaction should be considered assuming a particular reaction mechanism [24], such as the Langmuir-Hinshelwood kinetic model [27]. However, many authors use a single step reaction model, when the chemical reaction is the controlling step [3–7,9–11,14,17]. In addition, other attributes like pore diffusion and partial pressure resulted from the competition of gasifying agents to reach active surface sites must be taken into account [27]. Recent models assume that gasification rate of coal mixtures behaves as a linear combination of the pure coal gasification rates [28]; however, this is not necessarily true for low rank-coals, because the effect of the catalyst amount on the activation energy should be considered in the Arrhenius equation [5,23], which is a non-linear expression. It is a common practice in the laboratory set-up to have an isothermal stage prior to gasification to separate the pyrolysis from the gasification [3,19]. This

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