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Original Article

Kinetic study and synergistic interactions on catalytic CO_2 gasification of Sudanese lower sulphur petroleum coke and sugar cane bagasse

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A B S T R A C T

In this study the effects of iron chloride ($FeCl_3$) on the CO_2 gasification kinetics of lower sulphur petroleum coke (PC) and sugar cane bagasse (SCB) via thermogravimetric analyser (TGA) were investigated. The $FeCl_3$ loading effects on the thermal behaviour and reactivity of CO_2 gasification of PC were studied. The possible synergistic interaction between the PC and SCB was also examined. Then the homogeneous model or first order chemical reaction (O_1) and shrinking core models (SCM) or phase boundary controlled reactions (R_2 and R_3) were employed through Coats–Redfern method in order to detect the optimum mechanisms for the catalytic CO_2 gasification, describe the best reaction behaviour and determine the kinetic parameters. The results showed that the thermal behaviour of PC is significantly affected by the $FeCl_3$ loading. Among various catalyst loadings, the addition of 7 wt% $FeCl_3$ to PC leads to improve the PC reactivity up to 39% and decrease the activation energy up to 22%. On the other hand, for char gasification stage of SCB and blend, the addition 5 wt% $FeCl_3$ improved their reactivities to 18.7% and 29.8% and decreased the activation energies to 10% and 17%, respectively. The synergistic interaction between the fuel blend was observed in both reaction stages of the blend and became more significant in the pyrolysis stage. For all samples model R_2 shows the lowest values of activation energy (E) and the highest reaction rates constant (k). Finally, model R_2 was the most suitable to describe the reactions of non-catalytic and catalytic CO_2 gasification.

1. Introduction

Developing countries suffer from the problem of over consumption of energy. Most likely, the solution to meet the energy needs in the future will emanate from the combination of energy resources such as petroleum coke (PC) and biomass. PC is a carbonaceous solid derived from oil refinery units consisting of polycyclic aromatic hydrocarbons with low hydrogen content [1,2]. The efficient use of PC for energy

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resource is strongly promoted [3]. Bayram et al. [4] reported that one tonne of crude oil produces approximately 31 kg of PC. PC is mainly used as fuel or for manufacturing dry cells and electrodes [2]. The most important feature that makes PC a very good fuel and attractive energy resource for power generation in gasification is related to its low price, high heating value (>32 MJ kg^{-1}), high carbon (>90 wt%) and low ash content [1,2,5,6]. Therefore, the low reactivity and high-sulphur content are its main disadvantages [6–8]. However, the main advantage of Sudanese PC is its lower sulphur. This is an important issue for clean energy generation [1,2].

Bagasse is a fibrous residue of the cane stalk after crushing and extracting the juice, which consists of approximately 26.6–54.3% cellulose, 22.3–29.7% hemicelluloses, 14.3–24.45% lignin and about 2–4% ash on a dry basis [1,2,9–12]. In comparison to other agricultural residues, bagasse is considered as a rich solar energy reservoir due to its very high yields. Moreover, bagasse is a cheap, plentiful and low emission fuel. In addition, harvesting chemical energy from bagasse is attractive. The combustion/gasification of sugarcane produces the same amount of CO_2 as it is consumed during its growth, so it is carbon neutral [1,9]. By implementing thermo-chemical upgrading of bagasse, the energy efficiency can be significantly increased, resulting in saving energy and surplus products [1,2,11,13].

Gasification is a clean, efficient, promising technology and an attractive option to provide high quality fuel gases [1–3]. In order to obtain high quality fuel gases, high reactivity and high conversion rate of char are essential. The char conversion directly depends on the reactivity of char with gasifying agents (H_2O, CO_2, etc.). However, low reactivity remains an important problem for utilising PC through gasification, due to compactness of carbon structure as well as its low volatile behaviour and ash content [3]. Several authors have reported that gasification reactivity can be significantly enhanced by different metal compound catalysts (K, Na, Ca, Mg, Ba, Fe, Ni, etc.) [3,14,15]. Catalytic gasification is one of the main techniques used to improve the gasification reactivity due to its efficiency, availability, and low cost [3,14,16]. The addition of catalysts, such as alkali (K), alkaline earth (Ca) and transition metal (Fe), can significantly improve the gasification reactivity of PC [3]. Considering these events, it should be an important evidence to study the effects of catalysts on CO_2 gasification of Sudanese PC.

Iron compounds are potential gasification catalysts due to their abundance, low cost, and environmentally friendliness. Several iron compounds have been tested to catalyse coal gasification and their effects on coal pyrolysis and char gasification as well as tar formation during the whole coal gasification process have been studied [14,17]. Li et al. [3] studied the catalytic effects of $FeCl_3$, $CaCl_2$, KCl, K_2CO_3, K_2SO_4, KAC (CH_3 COOK) and KNO_3 during steam gasification of PC. They have found that the gasification of PC was inefficient at temperature <1000 °C. However, with the addition of catalysts the efficiency greatly improved. In particular, with the addition of K_2CO_3, gasification was quickly completed in 10 min and the final temperature was about 900 °C. Zhou et al. [18] investigated the catalytic effect of iron species ($FeCl_3$, $Fe(NO_3)_3$, $FeSO_4$) on CO_2 gasification of PC using TGA. They found that the catalytic activity of iron species followed the order of $FeCl_3 > Fe(NO_3)_3 > FeSO_4$. Lahijani et al. [19] studied the catalytic effect of iron species ($Fe(NO_3)_3$, $FeCl_3$ and $Fe_2(SO_4)_3$) on CO_2 gasification reactivity of oil palm shell char. They reported the catalytic effect of iron species on promoting reactivity of char was considerable in the order of $Fe(NO_3)_3 > FeCl_3 > Fe_2(SO_4)_3$.

The catalytic mechanism of the gasification reaction could be explained by the reaction of some active intermediate sites in the gasification process such as C(O) (active intermediates of carbon matrix) and M–C–O (active intermediates of carbon matrix with catalyst) with the gasification agent CO_2. When catalyst-PC or SCB or blend mixture was heated, the metal cations were combined with the edge C atom of char surface to form the intermediate M–O–C (where M is a metal) in the CO_2 atmosphere. Meanwhile, the distribution of the electron cloud in C atom of char surface was changed with the structure of M–O–C. Consequently, the intensity of C–C was weakened. As a result, the concentration of the intermediate (C(O)) and (M–C–O) increased rapidly, leading to a rapid increase in the gasification reactivity [3]. The gasification of char in carbon dioxide is popularly known as the Boudouard reaction (Eq. (1)).

$$C + CO_2 \leftrightarrow 2CO \tag{1}$$

Di Blasi et al. [20] describes the Boudouard reaction through the following steps:

In the first step, CO_2 dissociates at a carbon-free active site (C_{fas}), releasing carbon monoxide and forming a carbon–oxygen surface complex, C(O). This reaction can move in the opposite direction as well, forming a carbon active site and CO_2 in the second step. In the third step, the carbon–oxygen complex produces a molecule of CO.

$$\text{Step 1} \quad C_{fas} + CO_2 \xrightarrow{k_1} C(O) + CO \tag{2}$$

$$\text{Step 2} \quad C(O) + CO \xrightarrow{k_2} C_{fas} + CO_2 \tag{3}$$

$$\text{Step 3} \quad C(O) \xrightarrow{k_3} + CO \tag{4}$$

where k_i is the rate of the reaction.

The formation of active intermediates from char sample and gasifying agent was essential for gasification to occur. Therefore, the contact area between char and CO_2 was critical for gasification reactivity [3].

The previous studies revealed that a synergetic interaction could be expected in the co-processes of biomass and coal or PC because of the high thermochemical reactivity and high volatile matter content of biomass [2]. The synergistic interaction during non-catalytic gasification of the combining fuels such as coal or PC with biomass has been investigated by several authors [1,2,6,21,22]. However, the synergistic interaction between the Sudanese low sulphur PC and SCB during CO_2 catalytic gasification has not been reported yet. In spite of significant on-going research of the thermal conversion technologies such as pyrolysis and gasification for production of energy and fuels, there is no information about catalytic activity of iron species in the Sudanese low sulphur PC. This remains a relatively unexplored area of research. Based on these points, the aims of this study are:

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