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Experimental and kinetic study of catalytic steam gasification of low rank coal with an environmentally friendly, inexpensive composite K_2CO_3–eggshell derived CaO catalyst

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HIGHLIGHTS

- The composite catalyst improved the yields of H_2-rich syngas.
- RPM was the best model to fit the experimental data.
- The composite catalyst performed higher catalysis ability at 800 and 900 °C.
- The composite catalyst reduced the activation energy about 51 kJ/mol.

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ABSTRACT

The objective of this research was to study effects of composite catalysts (K_2CO_3 and eggshell derived CaO) on gasification of Indonesian sub-bituminous KPU coal, which was conducted in a fixed bed reactor at atmospheric pressure. The effects of composite catalysts were evaluated from two sections: syngas compositions and reactivity. At 800 °C, the H_2 yield of 1.34 mol/mol-C was obtained and the H_2 fraction was 62 vol% when using the composite catalyst (15%K + 5%ES). Compared with only utilization of pure K_2CO_3 and no catalyst, the composite catalyst (15%K + 5%ES) could increase the yields of H_2 by 6% and 123%. In addition, a CO yield of 0.32 mol/mol-C was obtained by utilizing composite catalyst (15%K + 5%ES), and the CO yield increased by 19% compared with utilization of K_2CO_3 and increased by 100% compared with no catalyst utilization. Through regression, kinetic parameters were determined from the random pore model (RPM), which provided a basis for design and operation of a realistic system. The RPM could adequately describe the conversion rate. Compared with results of non-catalytic steam gasification, the composite catalyst (15%K + 5%ES) was active in increasing the carbon conversion rate constant by more than three times within 700–900 °C due to its ability to reduce the activation energy of gasification by about 38%. It can be concluded that the composite catalyst not only enhances the catalytic effect, but also is environmentally friendly and inexpensive.

1. Introduction

Coal gasification has been considered as one of the most promising clean coal technologies that can convert a "dirty" solid fuel into a "clean" gaseous fuel [1]. It is the core of the integrated gasification combined cycle (IGCC) technology that can achieve high efficiencies and near-zero emissions of greenhouse gases and other pollutants. To produce hydrogen, the most recommended gasifying agent is pure steam [2]. Steam gasification proves to be a promising, and arguably the cheapest route, for hydrogen production. It has long been an important source of hydrogen for many industrial sectors, for example, ammonia synthesis, which is the base of the modern fertilizer industry and thus the core of modern agriculture [3]. Catalytic gasification is always an attractive topic having advantages of low operating temperature, high energy conversion efficiency, low capital cost, and a variety of reaction pathways towards the production of desired gases. Catalytic steam gasification includes a series of reactions in the reactor. The main reactions of this process are written in Eqs. (1)–(5).

$$\text{Steam char gasification}: C + H_2O \rightarrow CO + H_2 \quad \Delta H_{298} = 132\ \text{kJ/mol} \tag{1}$$

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$$\text{Water gas shift reaction(WGS)}: CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H_{298} = -41 \text{ kJ/mol} \tag{2}$$

$$\text{Boudouard reaction}: C + CO_2 \leftrightarrow 2CO \quad \Delta H_{298} = 172 \text{ kJ/mol} \tag{3}$$

$$\text{Methanation (I)}: C + 2H_2 \rightarrow CH_4 \quad \Delta H_{298} = -75 \text{ kJ/mol} \tag{4}$$

$$\text{Methanation (II)}: CO + 3H_2 \rightarrow CH_4 + H_2O \quad \Delta H_{298} = -206 \text{ kJ/mol} \tag{5}$$

Catalytic coal gasification with alkali and alkaline earth metals (AAEM) has been extensively used because of their superior catalytic activity and low cost. It is generally expected that low rank coal, containing large quantities of AAEM species [4–8], will play a significant role in the supply of major energy sources, mainly due to the fact that it represents the most abundant and cheapest fossil fuel available. Therefore, catalytic steam gasification of low rank coal should be intensively studied and successfully commercialized in the next several years [9].

The effects of AAEMs as catalysts to enhance steam gasification have been widely discussed [10,11], with the order of effectiveness as follows: K > Na > Ca > Fe > Mg [12]. A reduction in methane formation was found when potassium carbonate (K_2CO_3) was added to the feedstock [13]. Li et al. studied the role of AAEM species during the pyrolysis of low rank coal and found that their roles are related to how they transform during pyrolysis, and between AAEM species and the char matrix, there might have been a repeated bond-forming and bond-breaking process [14]. Kopyscinski et al. studied the catalytic effect of K_2CO_3 with ash-free coal and found that adding potassium to ash-free coal increased the steam gasification rate more than 10-fold, and decreased the activation energy by 100 kJ mol^{-1} [15]. Wang et al. showed that CaO acted as a CO_2 absorbent and enhanced hydrogen production [16]. Jiang et al. studied the K_2CO_3-catalyzed gasification with initial addition of three calcium species, $Ca(OH)_2$, $Ca(CH_3COO)_2$, and $CaCO_3$. It was found that each calcium additive was effective for suppressing the potassium–mineral interaction thus promoting catalytic gasification, and this promotion depended on coal and calcium materials [17].

Interestingly, eggshell is available as a waste material from the alimentary and bakery industries and has been used as a rich source of calcium oxide (CaO). As a waste resource, eggshell can also act as a catalyst for coal gasification, which could be meaningful, since its efficient and mass utilization might be one of the ways to promote the development of the economy. Taufiq-Yap et al. studied the biomass gasification of *Azadirachta excelsa* wood promoted by waste eggshell catalyst, and found that the addition of waste eggshell enhanced the catalytic activity, and increased the hydrogen yield compared to the reaction without catalyst [18]. In this research, eggshell was used to give rise to an obvious increase in the reactivity of catalytic gasification between low rank coal and K_2CO_3. In addition, K_2CO_3 and eggshell were mixed together to make composite catalysts to enhance hydrogen production. As a kind of waste material, eggshell can be large-scale collected from the bakery, biscuit factory, restaurant and so on. The use of eggshell can reduce the usage of potassium, and produce more H_2 and CO, from this point of view, the composite catalysts are inexpensive and quite economical. On the other hand, the random pore model (RPM) was adopted in order to investigate the gasification reactivity which is greatly dependent on the characteristics of coal. Catalytic coal gasification is far different from traditional coal gasification, leading to difficulties in the realistic design and operation of a utility [19]. Hence, it is necessary to conduct more in-depth research on coal gasification with composites of K_2CO_3 and eggshell as catalysts. In addition, determination of reaction kinetic parameters is very important to acquire a complete knowledge of gasification [20].

In this research, steam gasification of Indonesian sub-bituminous KPU coal with the use of innovative composite catalysts of K_2CO_3 blended with eggshell in a fixed bed reactor was investigated. All of the gasification products were well-recovered and subjected to detailed quantitative analyses. Furthermore, their gasification behavior under a steam atmosphere was simulated using RPM. The kinetic parameters inherent in the gasification of KPU coal using catalysts were determined, and the RPM was used in this research to simulate catalytic gasification of selected coals.

2. Experimental methods

2.1. Coal and catalyst preparation

Indonesian KPU sub-bituminous coal (KPU) was utilized in this study. Properties of KPU are shown in Table 1. Proximate analysis was performed using an STA-MS (NETZSCH), and ultimate analysis was conducted on a CHN-2000, S-144DR (LECO Corp.). KPU was ground and sieved to select a particle size range between 300 μm and 425 μm. Selected KPU particles were dried at 70 °C for 2 days to remove free water, and then kept in a sealed glass bottle in a desiccator prior to gasification measurements.

Chicken eggshells were collected from residential wastes. The membrane that sticks on eggshells was washed with hot water followed by scraping then rinsing with tap water several times. Washed eggshells were dried in an oven at 70 °C overnight to remove adhering water, then ground to a fine power using a mortar and pestle and sieved to 210 μm. The powdered shell was calcined at 800 °C for 2 h. Upon completion of the calcination, a chalky-white fine power was generated that was active calcium oxide [21], in addition, this product was analyzed via XRF, the results are shown in Table 2, the main mineral element is Ca, which accounts for 99%, it is denoted as ES-Ca.

Pure K_2CO_3 (99.5 wt%, DAEJUNG chemicals and metals Inc.), ES-Ca, and the mixture of K_2CO_3 with ES-Ca were loaded with KPU by an impregnation method for catalytic gasification. The catalyst and KPU mixtures were prepared by adding the appropriate

Table 1
Proximate and ultimate analyses of KPU coal.

Sample	Proximate analysis (as received basis, wt%)				Ultimate analysis (dry, ash free basis, wt%)				
	Moisture	Ash	Volatile matter	Fixed carbon	C	H	N	S	O
KPU	16.7	3.0	39.1	41.2	75.9	5.3	1.3	0.3	17.2

Table 2
Mineral elements that exist in calcined eggshell at 800 °C (2 h).

Component	Na	Mg	Si	P	S	K	Ca	Sr	Nb
Wight percentage (wt%)	0.032	0.253	0.004	0.119	0.055	0.061	99.4	0.104	0.01