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Lab-scale investigations on catalyst recovery of gasified residue collected from the potassium-catalyzed steam gasification process

XiangZhou Yuan *, Liang Zhao, Hueon Namkung, Tae-Jin Kang, Hyung-Taek Kim *

Department of Energy Systems Research, Ajou University, Woncheon-Dong, Youngtong-Gu, Suwon 443-749, Republic of Korea

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ABSTRACT

The catalyst recovery process was investigated utilizing different washing methods and operating conditions after potassium-catalyzed steam gasification. During potassium-catalyzed steam gasification, the H_2 yield and carbon conversion (X_C) could reach 101.18 g/kg-coal and 73.39%, respectively, when utilizing Lanna clean coal as a sample; the potassium compounds mainly existed in three forms: $KAlSiO_4$, $KHCO_3$, and K_2SO_4. In the catalyst recovery process, the highest recovery efficiency of potassium (η_K) on Lanna raw coal and clean coal gasified residue reached 92.14% after six limewater washings and 93.37% after three limewater washings, respectively. When utilizing the combined washing method for the Lanna clean coal gasified residue, the recovered catalyst showed a longer catalyst reuse lifetime even though the recovery efficiency of potassium (η_K) only reached 89.42%, which was 4% lower than that obtained after three limewater washings.

1. Introduction

The application of catalysts to coal gasification has a long history. Through utilizing active catalysts, carbon conversion at a given temperature can be significantly increased and the gasifier can be operated at substantially lower temperatures than required for non-catalytic gasification; this leads to lower required investment on the gasifier and its related facilities [1,2]. Despite the attractive features listed above, very few industrial-scale catalytic gasification processes are in operation; this suggests that some key technical and economic challenges in the field of catalytic gasification remain for further investigation: One of these challenges is the catalyst recovery process that mainly influences the economic evaluation of the entire catalytic gasification process and leads to soil/water pollution caused by water-soluble alkali metal compounds that exist in ash that does not undergo catalyst recovery treatment.

Many catalysts are known to be effective at increasing the gasification rate of coal char or carbon in steam and CO_2, especially Ni-based catalysts, alkali and alkaline earth metallic (AAEM) species [3–5]. Nickel catalyst is the most widely used in industry but relatively expensive which increase the investment costs of the process [6]. Among the alkali salt catalysts, the reaction rate has been found to increase with the cation atomic weight, i.e., uncatalyzed $<$ Li $<$ Na $<$ K $<$ Rb $<$ Cs [7,8]. Since Rb and Cs are prohibitively expensive, K_2CO_3 is the catalyst of choice among alkali salts, and it was chosen for this study since it is cheap, effective, and widely used. Alkaline earth metal salts [9,10] and transition metal oxides [11] have also long been known to be effective gasification catalysts. And the AAEM species catalyst, potassium and calcium salts are the most interesting and have been widely used in laboratory-scale research where catalyst loading is frequently achieved by ion-exchange or impregnation [12–15]. In addition, it is generally expected that low rank coal will play a significant role as an energy source, mainly due to the fact that it is the most abundant and cheapest fossil fuel available and contains highly dispersed lots of AAEM species [4,16]. Hydrogen is the main product of catalytic coal gasification and is an attractive fuel with no greenhouse gas emissions; it is also likely to become a routine energy fuel carrier with widespread application in advanced fuel cell techniques for transportation and stationary power generation in the foreseeable future. Potassium-catalyzed steam gasification is a more attractive way of producing H_2-rich syngas than conventional steam gasification [12,17–19]. Unfortunately, few efforts toward the recovery and reuse of the catalyst have been made [20]. These deficiencies may be an obstacle to the development of catalytic industrial-scale gasification processes. Therefore, as catalytic gasification technology rapidly expands, catalyst recovery technology should be concurrently developed and will play a significant role in the near future.

The objective of this study is trying to determine and optimize operating parameters of catalyst recovery process, in order to improve the catalyst recovery efficiency. This research can be divided into the two sections displayed in Fig. 1: one section focuses on the potassium-

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* Corresponding author. Tel.: +82 31 219 2321; fax: +82 31 219 2969.
E-mail addresses: yuanxiangzhou@hotmail.com (X. Yuan), htkim@ajou.ac.kr (H.-T. Kim).

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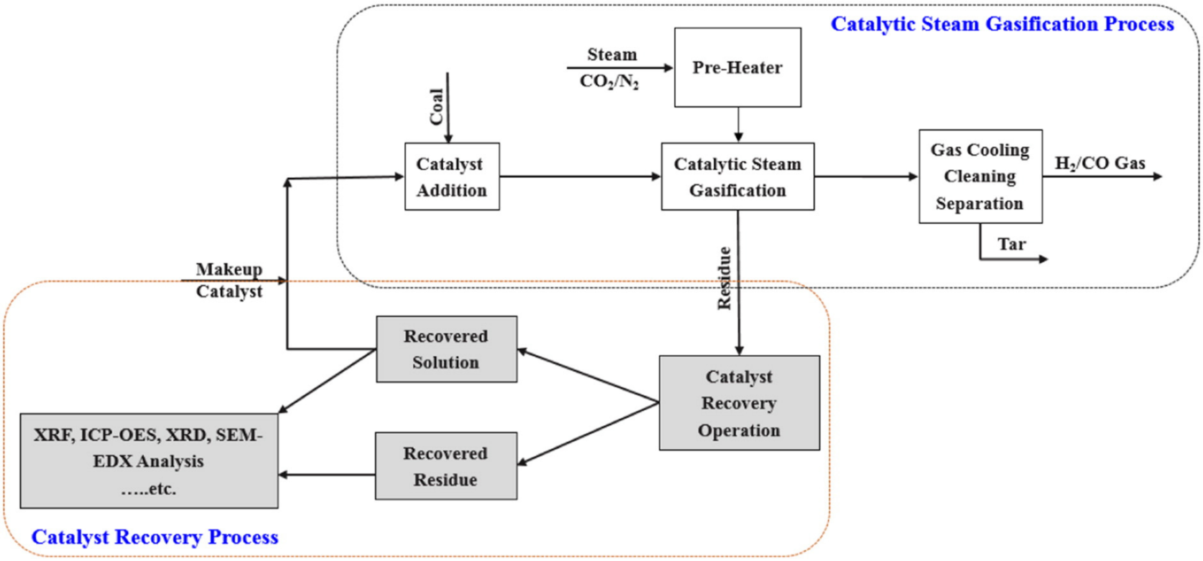

Fig. 1. Schematic of potassium-catalyzed steam gasification and catalyst recovery processes.

catalyzed steam gasification process and the other section mainly focuses on the catalyst recovery process. Catalytic steam gasification is a better known process for producing H_2-rich fuel. Through conducted potassium-catalyzed steam gasification process, the gasified residue could be collected and then utilized as sample for investigating the catalyst recovery process. Three different washing methods were used for the catalyst recovery process. Several parameters, such as reaction time, temperature, solution-to-residue (wt.%) ratio, and number of washings, were taken into consideration in order to optimize the entire process of catalyst recovery.

2. Experimental

2.1. Coal sample preparation

Lanna raw coal (LRC), which is a kind of Indonesia low-rank coal, was utilized in this study. The LRC was first placed in a drying furnace for 24 h at 110 °C to remove the maximum amount of moisture present in the coal sample and then was crushed and pulverized to obtaining a fraction with 150–300 μm particles. In addition, clean coal was made and used in this study. The production of clean coal mainly involves two steps: the LRC was consecutively washed with a sodium hydroxide solution and hydrofluoric acid [21,22]. Proximate and ultimate analyses and determination of the higher heating values were also performed, as shown in Table 1. In addition, LRC and LCC were analyzed via XRF; the results are shown in Fig. 2. No sodium was detected in LRC. For above-mentioned reasons [7,8], Na also has catalytic property in coal gasification process, thus it is not needed to wash sodium compounds out of Lanna coal during the demineralization treatment process, increasing weight percentage of Na in LCC.

2.2. Experimental apparatus and procedures

For the potassium-catalyzed steam gasification process shown in Fig. 3, the purpose of these experiments was to compare the gasification effects of 1) utilizing LRC mixed with fresh catalyst and recovered catalyst and 2) utilizing LCC mixed with fresh catalyst and recovered catalyst under conditions of 800 °C and 10 wt.% K_2CO_3. After 1 h of the potassium-catalyzed steam gasification process, the gasified residue was collected and utilized as a sample for investigating the catalyst recovery process.

For the catalyst recovery (Fig. 4), the pressurized batch reactor was adopted in this research, the effective volume of reactor was about 500 mL with internal diameter of 43.3 mm. This batch reactor mainly consistsed of heating and cooling systems, in order to control reaction time and temperature availably. There were three methods utilized in this research: 1) water washing method, 2) limewater washing method, and 3) combined water washing and limewater washing method. The effects of the major process variables, such as reaction time and temperature, solution-to-residue weight ratio, and number of washings, on the catalyst recovery efficiencies were evaluated. As shown in Fig. 5, the life-side part was showing the water washing process and the right-side part was showing the limewater washing process, the experimental procedures mainly comprised the following three steps: 1) reaction at different temperatures, time periods, solution-to-residue weight ratios and number of washings, 2) solid–liquid separation under a blanket

Table 1
Proximate/ultimate analyses and higher heating values of Lanna raw coal, its clean coal, and Illinois #6 coal.

Name	Samples	Proximate analysis (wt.%, db)				Ultimate analysis (wt.%, daf)					HHV
		M	VM	FC	ASH	C	H	O[a]	N	S	(MJ/kg)
Lanna	LRC[1]	–	45.74	50.05	4.21	69.7	5.11	22.34	1.5	1.35	28.90
	LCC[2]	–	45.71	51.59	2.70	71.63	4.92	21.21	1.44	0.8	30.18
Illinois #6[3]		–	42.21	50.05	9.58	77.24	5.60	10.48	2.04	4.64	29.79

Dry basis (db); Dry-ash free basis (daf).
[a] Calculated by difference.
[1] Raw Lanna Coal.
[2] Clean Lanna Coal.
[3] Sourced from Exxon large pilot plant alternatives for scale-up of the catalytic coal gasification process. Final report in 1979.

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