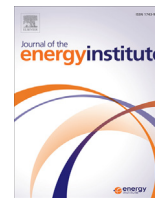




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Performance of active nickel loaded lignite char catalyst on conversion of coffee residue into rich-synthesis gas by gasification

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ABSTRACT

Performance of nickel-loaded lignite char catalyst on conversion of coffee residue into synthesis gas by catalytic steam gasification was carried out at low reaction temperatures ranging from 500 °C to 650 °C in the two-stage quartz fixed bed reactor. The effects of steam pressures (30, 36 and 50 kPa corresponding to S/B = 2.23, 2.92 5.16, respectively) and catalyst to biomass ratios (C/B ratio = 0, 1, 3) were considered. Nickel-loaded lignite char was prepared as a catalyst with a low nickel loading amount of 12.9 wt%. The gas yields in the catalytic steam gasification process strongly depended on the reaction temperature and C/B ratio. The total gas yields obtained in catalytic steam gasification was higher than that of catalytic pyrolysis, steam gasification and non-catalytic pyrolysis with steam absence by factors of 3.0, 3.8 and 7.7, respectively. To produce the high synthesis gas, it could be taken at 600 °C with total gas yields of 67.13 and 127.18 mmol/g biomass-d.a.f. for C/B ratios of 1.0 and 3.0, respectively. However, the maximum H₂/CO ratio was 3.57 at a reaction temperature of 600 °C, S/B of 2.23 and C/B of 1.0. Considering the conversion of coffee residue by catalytic steam gasification using the nickel-loaded lignite char catalyst, it is possible to convert the coffee residue volatiles into rich synthesis gas.

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1. Introduction

Currently, gasification is the most important strategy for changing to cleaner alternatives such as fossil fuel through renewable energy [1–16]. During years of gasification practices, various kinds of biomass have been more or less successfully gasified. The behavior of the biomass gasification mostly depends on the type of the biomass and the devolatilization conditions. In addition the low temperature biomass gasification during the catalyzed process is important, that can be as low as possible is desirable [3–9]. To produce the syngas from biomass using catalytic steam gasification or steam gasification in a fixed bed reactor, the various sources of biomass were reported in literature such as pig compost [7,10], municipal solid waste [11,12], sawdust [13], eucalyptus [14] and cashew nut [15]. In order to operate the gasification at a low temperature, tarry material is generated in producer gas. The tar in the producer gas is a significant impediment and reduces component performance in the catalytic water gas reaction. The formation of tar, a side product, from biomass gasification causes the problems in downstream process units since the condensation and deposition of tar result in plugging and fouling of turbines, pipelines and engines [16–21]. Among many processes, the catalytic steam gasification of biomass is one of the considerably attractive approaches for tar elimination during biomass gasification, moreover, the catalyst can improve the quantity of syngas. Garcia et al. [5] investigated the catalytic CO₂ gasification of pine sawdust at a low temperature of 700 °C using a Ni/Al catalyst prepared by coprecipitation and reported that a decrease in the catalyst/biomass flow rate ratio diminished the H₂ and CO yields. Li et al. [8] developed an efficient biomass gasification of Japanese cypress at low temperatures between 450 and 650 °C in a two-stage fixed bed reactor. Ni-loaded brown coal showed high activity for tar decomposition and their results illustrated that most of the tarry materials were converted to light gases such as H₂, CO₂, and CH₄. Wilson et al. [22] considered the coffee husk gasification using high temperature conditions, they reported that increased gasification temperature led to a linear increment of CO concentration in the syngas for all gasification conditions.

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With high coffee production projected in the upcoming years, there is an imperative need to balance this production with proper utilization [23–26]. As a consequence, the production of coffee residue has increased and their disposal has become a matter of increasing concern. Coffee residue is characterized chemically by a high content of carbon source [27], it is similar to various agricultural wastes used as good biomass fuels. There are few publications in the literature relating to coffee residue gained from the coffee production process [27–30]. According to the literature survey and the research on producing, the synthesis gas from catalytic steam gasification of coffee residue has not been fully investigated [13,15,16,22,31–33]. As there are a small number of publications in literature discussing the gasification of coffee residue in low gasification temperatures additional use of Ni on the special support as lignite is attentive [7,8,14,32–34]. Therefore, this present work has been focused on the performance of nickel-loaded lignite char catalyst on the conversion of coffee residue into synthesis gas by catalytic steam gasification in order to obtain beneficial gasification gas products. The gasification of derived volatiles was conducted in a two-stage fixed bed reactor. The effect of catalyst on distribution of gas products was considered. Also, the effects of catalytic temperature ranging from 500 °C to 650 °C, steam addition and catalyst/biomass ratio on product gas yields and gas compositions were discussed.

2. Materials and methods

2.1. Materials

Coffee residue sample used in this study was collected from the coffee production process of soluble coffee industry in Japan. The biomass feedstock were milled and sieved to 0.5–1.0 mm [10,34–38] with the aim of attaining fractions of uniform particle size for use. Loy Yang lignite coal (LY) used for this research was sourced from Australia and applied as a catalyst support. The particle size of LY was 0.25–0.5 mm [32,33]. The coffee residue and LY characteristics were analyzed according to Japanese Industrial Standards and ASTM methods provided proximate analysis and ultimate analysis (conducted with a Leco CHN-2000 Elemental Determinator). Those analysis results are illustrated in our previous work [39] and their empirical and molar formulas by calculation are explained in Table 1.

2.2. Preparation of catalyst

The nickel addition to the coal matrix was achieved by ion-exchange [7,8,14,34] with a solution of basic hexa ammine nickel carbonate. The LY coal was mixed with distilled water and $(\text{NH}_3)_6\text{NiCO}_3$ aqueous solution and then stirred with the mixture for 24 h. After that, the sample was recovered by filtration and the recovered solid was washed by using distilled water and dried in N_2 flow at 107 °C for 24 h. Ni loading in LY called LY-Ni coal was the low amount at 12.9 wt% (by ash analysis) which was considered from our previous researches [33,34,40]. To activate LY-Ni coal into LY-Ni char, the LY-Ni coal was heated up to 650 °C with a continuous flow of Ar for 1 h, and then was reduced at the desired temperature. The experimental setup was described previously [39].

2.3. Experimental setup

To convert the coffee residue into rich-synthesis gas by catalytic steam gasification using nickel-loaded lignite char catalyst, the gasification experiments were carried out in the two-stage laboratory quartz fixed bed as seen in Fig. 1. The reactor used was set up in two electrically heated ovens (biomass and catalyst beds). The inert gas Ar was sourced from gas cylinders in a panel of precision mass flow controllers. Steam was generated in the upper furnace and the flow rates of steam that were dependent on the operating steam partial pressures were controlled by the micro feeder. The procedure of experimental setup was followed our previous research [14,33,39]. In this research, the enhancement of investigation was considered on the effect of catalyst on distribution of gas products, reaction temperature effect, steam pressure effect and catalyst/biomass ratio effect on the conversion of coffee residue volatiles to gas yields and gas compositions by gasification.

The steam was fed under the experimental conditions from 30 kPa to 50 kPa while the steam gasification took place. The total gas flow rate in all the experiments was approximately 120 ml/min consisted of Ar + steam. When the gasification was complete, oxygen gas was provided to burn out of the deposited carbon in the reactor and to calculate the carbon balance. The effect of catalyst to biomass ratio (C/B ratio) was considered at the selected operating conditions as well. The product gases formed, CH_4 , C_2H_6 , CO, CO_2 and H_2 , from volatile decomposition were analyzed by using FID and TCD gas chromatographs (SHIMADZU GC-14B). The characterization of LY-Ni char catalyst was analyzed using X-ray diffraction (XRD; Mac Science M03XHF, 40 kV, 30 mA) to obtain XRD patterns at a scanning rate of 2°/min and scanning electron microscopy (SEM; JSM-6700F, JEOL Datum Ltd.) was also performed. The specific surface of the biomass char (coffee residue char) and LY-Ni char was investigated using BET (BELSORP-max, BEL Japan, Co., Ltd.). X-ray fluorescence (XRF; Shimadzu EDX-7000) was applied to analyze ashes including coffee residue, LY, LY-Ni coal and LY-Ni char ashes. The ashes were prepared in furnace (KDF S-90) with oxygen flow rate of 100 ml/min for 1 h.

3. Results and discussion

In the present study the coffee residue was first paralyzed to tar, char and gas and then the tar and gas products passed through the catalytic reactor, in which tar was converted to gas. In this case the important reactions may be described as following reactions as shown in Eqs. (1)–(6) [10,14,31,36].

Table 1
Empirical and molar formulas of coffee residue and LY.

	Coffee residue	LY coal
Empirical formula (Calculation)	$\text{C}_{1.490}\text{H}_{0.385}\text{O}_{0.132}\text{N}_{0.011}$	$\text{C}_{0.841}\text{H}_{0.283}\text{O}_{0.133}\text{N}_{0.003}$
Molar formula (Calculation)	$\text{C}_{0.344}\text{H}_{0.512}\text{O}_{0.132}\text{N}_{0.011}$	$\text{C}_{0.469}\text{H}_{0.394}\text{O}_{0.133}\text{N}_{0.003}$

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