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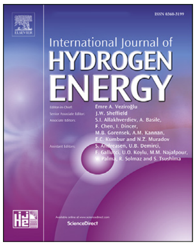

Experimental study of dual fixed bed biochar-catalytic gasification with simultaneous feed of O_2-steam-CO_2 for synthesis gas or hydrogen production

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ABSTRACT

The catalytic gasification of biochar was investigated in the presence of a Ni/SiO_2 catalyst in a fixed bed reactor with an O_2-steam-CO_2 gas feed. The effects of operating temperature, catalyst nickel loading and composition of O_2-steam-CO_2 feed gas on biochar carbon conversion and gas products were investigated. The results indicate that the highest biochar carbon conversion could be obtained at approximately 800 °C, whilst the 10% Ni/SiO_2 catalyst was shown to produce the greatest syngas yields. The presence of O_2 in the feed gas can result in slightly more CO in the gas product, whilst a higher steam content leads to more H_2 in the gas product. The CO_2 offered a benefit as an adjusting agent for achieving a desired H_2/CO ratio. No evidence of coke deposition on the catalyst was found under any of the tested conditions.

Introduction

The world energy consumption is currently and continually growing. Fossil fuels supply approximately 80% of the current Global energy demands, but due to declining low cost reserves, various renewable energy sources are becoming increasingly important. Biomass resources are renewable energy resources, which like fossil fuels, are carbonaceous feedstocks and compatible with current fossil fuel energy power generation technologies, which in turn provides significant cost benefits and removes a number of implementation barriers [1–4].

Gasification of biomass produces syngas, a fuel gas used in numerous applications such as gas turbine power plants [5–7], Fischer-Tropsch synthesis [8,9], fuel cells [10–12] and other downstream processes [13–15]. Air is commonly used as a gasifying agent in biomass gasification due to its availability

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and low cost; however, the presence of N_2 in the syngas is problematic, as a result of the lower energy density and propensity for NO_x production [16]. These issues can be avoided with the use of O_2 gas as a gasifying agent, leading to a higher heating value, elimination of NO_x production and greater conversion of carbon into CO_2 [17]. However, the use of an O_2 gasifying agent requires the separation of O_2 from N_2, an expensive and energy intensive process. Steam can also be used as an oxidant, the H_2 content in syngas product increases with increasing steam utilization; however, the steam production is associated with large energy demands [3]. Carbon dioxide has been reported for use as a gasifying agent, offering several advantages such as increasing the efficiency of the syngas product, the ability to control the H_2/CO ratio and reducing the CO_2 emission [18–20].

Gasification experiments recently conducted by Gile-Lalaguna et al. [21], involved the use of sewage sludge as a fuel with an air-steam gasifying agent in a fluidized bed gasifier. It was found that the most influential operating parameter was temperature, with increases in temperature not only improving the product gas yield and fuel conversion rate, but also reducing the tar and solids yield. Further, high steam to oxygen ratios favored higher H_2/CO ratios and higher heating values. Many researchers have investigated the use of various catalysts in gasification experiments. A study on gasification by Huang et al. [22] revealed Fe/CaO catalyst to provide a significant improvement in performance when compared to other catalysts. This is attributed to the use of a metal precursor to improve the stability of the support and can enhance the catalytic char-tar gasification.

Miccio et al. [23] studied biomass gasification with different catalyst materials in fluidized bed reactors. Compared to dolomite, olivine and inert quartzite catalysts, Ni-alumina provided the highest H_2 yields, lowest tar production and least catalyst deactivation. The use of novel catalysts possessing Rh, Pt, Pd or Ru supported on CeO_2/SiO_2 have been reported by Tomishige et al. [24]. The results showed that a $Ni/CeO_2/SiO_2$ catalyst performed similarly to the novel catalysts at high operating temperatures, in addition, biomass with a higher volatile content led to a high tar yield.

The gasifier effluents consist of syngas, unreacted and remaining hydrocarbons, hence the product gas yield can be upgraded using a catalytic reforming process [25–27]. Steam is often used as an oxidant in reforming processes, and a study by Karim and Metwally [28] investigated the kinetics of natural gas steam reforming. They found that the non-catalytic reforming reaction is favored by high temperatures, more than 1500 °C, hence a catalyst must be introduced to avoid this constraint. A study on Ni-based catalytic steam reforming of bio-oil carried out by Azad et al. [29] showed that in the presence of a Ni/Al_2O_3 catalyst the operating temperature can be reduced to 850 °C whilst achieving H_2 yields over 80%. Furthermore, less coke deposition was observed on the Ni/Al_2O_3 catalyst than on the Ni/ZrO_2 catalyst, with optimum Ni loadings being within the range of 5–15%. Recently, investigations into the use of a $Ni/CeO_2–SiO_2$ catalyst in the CO_2 dry reforming of methane into syngas have been reported by Taufiq-Yap et al. [30]. The results indicate CH_4 and CO_2 conversions as high as 90% can be achieved at temperatures as low as 750 °C, even without CeO_2 in the catalyst. The presence of 9 wt.% CeO_2 in the $Ni/CeO_2–SiO_2$ catalyst helps to reduce coke deposition and hence improve the catalyst stability. Moreover, increasing steam feed ratios can also reduce coke deposition on catalyst as reported by Vicente et al. [31]. Combined CO_2 and steam reforming of ethanol in the presence of a Ni-based catalyst was investigated by Bednarczuk et al. [32]. They found that using a CO_2/steam feed ratio of 1:1 not only increased the ethanol conversion over Ni/La_2O_3 and Ni/Y_2O_3 but also reduced the carbon deposition on the catalyst via CO formation.

With regards to combined gasification and reforming processes, most research has focused on various types of catalyst and biomass [33–41]. Polypropylene fixed bed catalytic steam gasification in the presence of a Ni catalyst, was investigated by Wu and Williams [33]. Several nickel-based catalysts were used, however, out of those catalysts tested, Ni/Al_2O_3 was shown to provide the highest H_2 production yields. Wu et al. [34] studied the use of a two stage reactor for the gasification of biomass in the presence of a nickel-based catalyst. Several types of biomass were tested including cellulose, hemicellulose and lignin. Lignin, which has a low VOC content and a high fixed carbon content, provided the highest H_2 yields with negligible coke deposition on the catalyst. Gao et al. [35] investigated biomass gasification in porous ceramic reformers (SiO_2, Al_2O_3 and MgO). They found that by increasing the O_2 concentration in the feed gas the CO_2 production increased but the H_2 production decreased. Moreover, increasing the steam concentration in the feed gas not only increased the H_2 production but also reduced the CO_2 content in the gas product. Furthermore, the porous ceramic promoted the formation of water-soluble tar that in turn led to a higher H_2 yield and concentration in the gas product.

In this work, combined fixed bed gasifier and catalytic reformer experiments were studied using an O_2-steam-CO_2 gas feed stream, over a fixed bed of biochar and catalyst for the production of syngas. The influence of the operating temperatures, the O_2-steam-CO_2 feed ratio and percentage of Ni loading on the Ni/SiO_2 catalyst on the process performance were studied. The performance of the process was evaluated in terms of the product gas composition, cold gas efficiency (*CGE*), syngas ratio (*H_2/CO*) and efficiency factor (*EF*) as a CO_2 emission parameter.

Methodology

Materials

Mangrove tree charcoal was used as biochar due to its availability in Thailand. Samples were ground and sieved using a 16–20 mesh size, and then characterized using ultimate and proximate analysis to know the physical and elemental properties.

Catalysts preparation and characterization

Nickel(II) nitrate hexahydrate (Sigma–Aldrich) and commercially available silica sand (SiO_2) (Sigma–Aldrich) were used for preparation of the Ni/SiO_2 catalyst with nickel loadings of