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Hydrogen production from high temperature steam catalytic gasification of bio-char



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ABSTRACT

Hydrogen production from the catalytic steam gasification of bio-char derived from the pyrolysis of sugar cane bagasse has been investigated in relation to gasification temperature up to 1050 °C, steam flow rate from 6 to 25 ml h⁻¹ and type of Nickel catalyst. The catalysts used were Ni-dolomite, Ni–MgO and Ni–Al₂O₃, all with 10% nickel loading. The hydrogen yield in the absence of a catalyst at a gasification temperature of 950 °C was 100.97 mmol g⁻¹ of bagasse char. However, the presence of the Ni–MgO and Ni–Al₂O₃ catalysts produced significantly improved hydrogen yields of 178.75 and 187.25 mmol g⁻¹ of bagasse char respectively at 950 °C. The hydrogen yield from the char with the Ni-dolomite only showed a modest increase in hydrogen yield. The influence of gasification temperature showed that the optimum temperature to obtain the highest hydrogen yield from 45.30 to 187.25 mmol g⁻¹ of bagasse char at 950 °C, but was followed by a decrease in yield at 1050 °C. The influence of steam flow rate showed that with the increase in steam flow rate from 6 to 15 ml h⁻¹ hydrogen yield was increased from 187.25 to 208.41 mmol g⁻¹ of bagasse char. Further increase in steam flow rate resulted in a decrease in hydrogen yield.

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1. Introduction

Energy recovery from different types of waste biomass such as agricultural waste, food manufacture waste and forestry residues is gaining interest due to concerns about the limited supply of fossil fuels and the environmental impact from fossil fuel use. Sugar cane (*saccharum officinarum*) bagasse is a fibrous material which occurs as a by-product of sugar manufacture and it is estimated that 180 million tonnes of sugar cane bagasse is generated each year [1]. Such large tonnages of waste biomass have the potential to be used for a range of energy conversion processes with the added benefit of mitigating against climate change problems.

Pyrolysis is amongst the thermochemical processes commonly used to recover energy from biomass. In the case of pyrolysis of biomass, a bio-oil product is generated with by-product bio-char also formed in addition to pyrolysis gases. The relative proportion of bio-char, bio-oil and gases depends on the process conditions such as temperature and heating rate. There is growing interest in the production of hydrogen from biomass since it is regarded as a clean, low carbon future source of energy [2,3]. Steam gasification of bio-char produces a syngas with a high hydrogen content and higher calorific value [4]. It has been reported that the steam gasification of bio-char is 2–3 times faster as compared to coal gasification [5].

Several researchers have investigated different aspects of bio-char gasification [4–14]. Many studies have focused on oxidation of biochar using thermogravimetric analysis (TGA). For example Luo et al. [6] and Maiti et al. [8] studied the kinetics of bio-char using TGA. Some authors have investigated the mechanism of char gasification. For example, Moilanen et al. [7] reported that the gasification of solid char particles starts by the diffusion of the gasifying agent to the particle surface and then to the inside of the particle resulting in adsorption onto the surface followed by the chemical reaction. Haykiri-Acma et al. [9] suggested that the high temperature steam gasification of char is recommended for the production of hydrogen as the mechanism of gasification varies with the temperature and hydrogen production is favoured at high temperature.

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In this paper, hydrogen production from the steam catalytic gasification of bio-char in a high temperature fixed bed reactor has been investigated. The influence of process operating parameters such as catalyst, gasification temperature and steam flow rate were researched. The influence of three different catalysts; 10 wt.% Ni-dolomite, 10 wt.% Ni–Al₂O₃ and 10 wt.% Ni–MgO on H₂ production at a temperature of 950 °C was investigated. The influence of gasification temperature (750–1050 °C) and steam flow rate (6–25 ml h⁻¹) on H₂ yield was also investigated.

2. Materials and methods

2.1. Bio-char samples

Pyrolysis char recovered from the pyrolysis of sugar cane bagasse was used in this study [15]. The properties of the feed stock sugar cane bagasse used for pyrolysis are shown in Table 1. The sugar cane bagasse was sourced from Pakistan and obtained from fields near Samundri (30 48 N 71 52 E). These fields supply sugar cane to Gojra Samundri Sugar Mills Limited. Pakistan is the fifth largest sugar cane producer in the world with an estimated 49 million tonnes of sugar cane produced annually resulting in 16 million tonnes of bagasse in the form of residue from the sugar industry. The sugar cane baggasse biomass sample was pyrolysed in a fixed bed reactor in an inert atmosphere of nitrogen and was heated from ambient temperature to a temperature of 950 °C at a constant heating rate of 20 °C min⁻¹ with a dwell time of 40 min at 950 °C. The char samples were ground and sieved to obtain a particle size in the range of 0.2-0.5 mm.

2.2. Catalyst

Three different catalysts; 10 wt.% Ni-dolomite, 10 wt.% Ni–Al₂O₃ and 10 wt.% Ni–MgO were used in this study. These catalysts were synthesised in the laboratory using a wet impregnation method [16]; a known quantity of Ni(NO₃)₂·6H₂O was dissolved in 25 ml of deionized water; 10 g of support material (dolomite, Al₂O₃ or MgO) was then mixed in the solution and heated up to 105 °C with constant stirring. Each catalyst was dried overnight at 105 °C and then calcined at 900 °C for 3 h in an air atmosphere. These catalysts were later ground and sieved to achieve a final particle size between 0.050 and 0.212 mm.

2.3. Material characterization

A Thermoquest CE Flash EA 2000 series instrument was employed for C, H, N and S analysis of the bio-char (Table 2). Proximate analysis was carried out on a Shimadzu TGA-50H thermogravimetric analyser. In addition, ashing of the bio-char sample was carried out and the residual ash was analysed using an Olympus Innovex X-5000 X-ray Fluorescence (XRF) equipped with a Rh source to determine the bulk metal composition.

The freshly prepared catalysts were characterised using a range of techniques. The surface area (BET (Brunauer, Emmett and Teller)), pore volume, and pore size distribution of the fresh catalysts was determined using a Nova-2200e surface area and pore size analyser from Quantachrome instruments USA.

The surface morphology of the catalyst was determined using scanning electron microscopy. The system used was a Field Emission Gun Scanning Electron Microscope (FEGSEM) LEO 1530 equipped with 80 mm X-Max SDD detector.

2.4. Experimental reactor

Steam gasification of the bio-char recovered from the pyrolysis of sugar cane bagasse was carried out in a high temperature fixed bed reactor system, 60 cm in length with 2.5 cm inner diameter and constructed of Inconel (Fig. 1). Nitrogen was used as the purge gas. During this study, the bio-char sample was gasified (with and without catalyst) in the presence of steam at high temperature of 950 °C, this high temperature was chosen, since literature data suggests that higher temperatures of char gasification produce higher yields of H₂ [9,15]. In addition, the influence of gasification temperature on the catalytic steam gasification of the bio-char was also investigated at temperatures of, 750, 850, 950, and 1050 °C. During the catalytic steam gasification of the sugar cane bagasse bio-char samples, the Ni-dolomite, Ni–Al₂O₃ and Ni–MgO catalysts were used. The catalyst was mixed with the bio-char sample (catalyst to sample ratio of 1:1) and then placed on a perforated mesh inside the reactor. The reactor was then heated from room temperature to a temperature of 950 °C at a constant heating rate of 20 °C min⁻¹, with a continuous purge of nitrogen. Once the reactor reached the required temperature, steam was introduced into the reactor via water injected from a syringe pump which was immediately converted into steam at high temperature and swept through the reactor by the nitrogen carrier gas. For all experiments, the steam flow rate was constant at 6 ml h⁻¹ except when the influence of steam flow rates from 6 to 25 ml h⁻¹ were used. Product volatiles and excess steam were condensed in a series

Table 1

Proximate and ultimate analysis of sugar cane bagasse.

Feed stock	Volatile matter (wt.%)	Fixed carbon (wt.%)	Moisture (wt.%)	Ash (wt.%)
Proximate analysis (a	as received)			
Bagasse	81.55	10.91	5.92	1.62
Feed stock	C (wt.%)	H (wt.%)	N (wt.%)	O ^a (wt.%)
Ultimate analysis (as	h-free basis)			
Bagasse	46.25	5.72	0.81	47.21

^a Calculated by difference.

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