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Gasification of sugarcane bagasse in supercritical water; evaluation of alkali catalysts for maximum hydrogen production

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ABSTRACT

Sugarcane bagasse is one of the major resources of agricultural wastes in the Khuzestan Province of Iran. With the aim of maximum hydrogen production, supercritical water gasification of lignocellulosic feedstock was studied in a batch reactor at the constant pressure of 25 MPa. The effect of catalyst (five different alkali salts, Raney nickel, and activated carbon) and reaction temperature (400–800 °C) on gas yield and composition, gas heating value, carbon gasification efficiency (CGE), and hydrogen gasification efficiency (HGE) was investigated. An increase in reaction temperature led to significant improvement in hydrogen yield. The highest amount of hydrogen (75.6 mol kg^{-1}) was achieved at 800 °C with the presence of KOH as catalyst where the complete gasification of bagasse took place. The annual potential of hydrogen production in the Khuzestan Province of Iran was roughly estimated to be 470 millions of Nm^3 and this calculation showed that this figure is capable of substituting the need of 6550 ha of sugarcane farms to chemical fertilizer.

1. Introduction

Energy and environment protection are expected to remain two of the main challenges of the human life for the long-term future. Agricultural wastes have a great potential for energy production because of their non-food nature and renewability [1]. Sugarcane bagasse is an abundant source of lignocellulose [2]. Bagasse is the solid residue remaining after the process of juice extraction from sugarcane for sugar or ethanol production. Crushing of every 3 kg of sugarcane in sugar mills produces 1 kg of bagasse [3]. Currently, it is mainly used for combustion to produce heat and power required for the related sugar and ethanol factories [3] whilst it is known that with the technological improvements it is possible to supply the energy requirements of the plants with only half of the produced bagasse [4]. In Iran however, from the total annual production of 0.84 million tons of bagasse, only a small portion is being used for paper and medium-density fiberboard (MDF) production and the rest is usually disposed and causes environmental problems such as spontaneously ignition [5].

Conversion of biomass to fuel gases can reduce environmental issues [6] and progress its utilization [7]. Compared with conventional thermal gasification, supercritical water gasification (SCWG) is characterized by its high reaction efficiency and H_2 selectivity [8]. This technology benefits from the specific properties of water at supercritical conditions. With the operating temperature and pressure greater than its critical point (374 °C and 22.1 MPa for water) a fluid is termed as a supercritical fluid [9]. The density of water, above the critical point (0.2–0.7 g cm^{-3}), is much lower than that at normal conditions and hydrogen bonds of water molecules are considerably weakened. The lower density leads to a decrease of the dielectric constant from 78 at normal conditions to the range of 2–20. This changes the water from a

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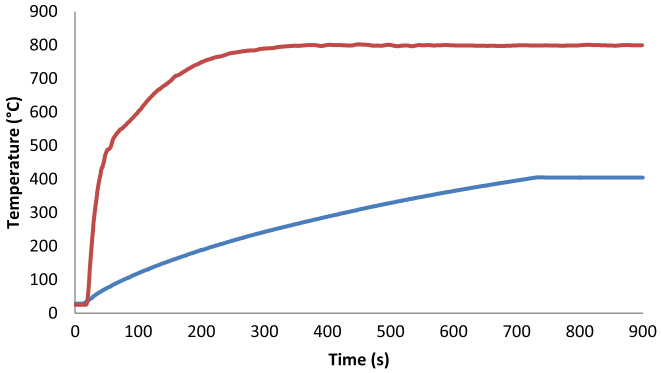

Fig. 1. A typical variation of the reactor temperature with time; red curve: GC oven, blue curve: electrical oven. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

highly polar solvent at an ambient condition to a non-polar solvent, like benzene, in a supercritical condition [10]. Such conditions enhance the solubility of organic substances and depress unwanted polymerization processes [11–14]. In addition, heat transfer is fast and the water molecule is still reactive which both supports fast reaction of the solved molecules [7]. Compared to conventional gasification, SWG is relatively efficient with no additional energy requirement for biomass drying. Lignocellulose biomass components can break down into simple molecules during SCWG to produce synthesis gas [9]. A verity of biomasses including lignocellulosic biomass from different sources such as manure [15–17], sewage sludge [18–20], food wastes [21], algae [22–24], and biorefinery residue [24] have been successfully gasified in SCW.

High moisture content of sugarcane bagasse makes it suitable for conversion in SCW [1] however, only a few reports on the treatment of sugarcane bagasse are available. Osada and his co-workers studied the effect of ruthenium catalyst on the gasification of bagasse at 400 °C and compared the results with those of cellulose and lignin [25]. They reported that without a catalyst, only 11.9% of bagasse converted to the gas. Barati and co-workers investigated the use of un-promoted and zinc promoted Ru/γ-Al_2O_3 nanocatalysts on hydrogen yield from bagasse. They reported that the maximum hydrogen yield in their experiments was 15.6 mol kg^{-1} [26].

Generally, there is a lack of knowledge about the role of alkali catalyst on gas yield from sugarcane bagasse. Moreover, the potential of hydrogen production from sugarcane bagasse in supercritical is unknown. We previously reported the effect of reaction time (RT) and pressure on gas yield and composition of sugarcane bagasse [27]. We also studied the SCWG of sugarcane bagasse in the present of some alkali catalysts (K_2CO_3, $KHCO_3$, $NaHCO_3$ and NaOH) in the reaction time of 45 min and pressure of 25 MPa at 400 °C [28].

In the present project, we designed a simple 3 stage framework in order to explore the highest possible hydrogen yield from supercritical water gasification of sugarcane bagasse. In this framework different alkali catalysts (KOH, NaOH, K_2CO_3, $KHCO_3$, $NaHCO_3$), Raney Nickel and activated carbon were applied. The effect of temperature on gas yield and composition was also investigated.

2. Experimental

2.1. Raw material

Sugarcane bagasse was obtained from a sugar mill of Debal Khazae Agricultural and Industrial Company in the Khuzestan Province of Iran. All experimental studies were performed in the laboratories of IKFT[1] at Karlsruhe Institute of Technology (KIT), Germany. The bagasse was milled and sieved to make the particle size of less than 180 μm. The K_2CO_3, $KHCO_3$, Na_2CO_3, KOH and Raney Nickel were purchased from Merck Company (Darmstadt, Germany). The NaOH and activated carbon were purchased from VWR International Ltd. (UK) and applied in the amount of feed to catalyst (F/C) of 2. This amount of catalyst was chosen based upon literature [29–32].

2.2. Experimental procedure

The experiments were done in two batch autoclave reactors made of SS316 (for 400 °C) and Inconel alloy 625 (for the temperatures more than 500 °C) with the inner diameter of 11.5 mm and outer diameter of 13 mm and a volume of 5 ml. Before each experiment, the reactor was cleaned thoroughly with acetone to remove any residuals from the prior experiments [15]. The next step was to feed the reactor a mixture of sugarcane bagasse, water, and catalyst. Feedstock was prepared by bagasse powder loading of 9 wt%. In the experiments where a catalyst was applied, the mass ratio of 2:1 of F/C was taken into account. An exception was the case of a co-loading of Raney Nickel and K_2CO_3 where the amount of each catalyst was only half. For the experiments at the temperature of more than 400 °C, the feeding weight was decreased proportionally to keep the pressure constant at 25 MPa according to the steam table [33]. The heating source for the later experiments was an electrical oven while a gas chromatograph (GC) oven was used for the experiments at 400 °C. The typical temperature kinetics of the inside of the reactor in either of the ovens is shown in Fig. 1. The given reaction time does not include the heating up period.

After the certain reaction time, the reactor was cooled down rapidly by putting it into an ice-water bath. The reactor was then opened and the gas was quantified volumetrically. The gas was sampled by a 100 μl syringe and injected into the GC. This was replicated for 3 times and the average was reported. Further details on experimental set up could be found elsewhere [28].

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