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Sugarcane bagasse supercritical water gasification in presence of potassium promoted copper nano-catalysts supported on γ -Al₂O₃

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ABSTRACT

Supercritical water gasification (SCWG) of sugarcane bagasse was performed to produce hydrogen. The process was manipulated with nano-catalysts to make it highly selective for hydrogen production. Copper based catalysts impregnated on γ -Al₂O₃ were tested to find the best Cu percentage. The catalyst was promoted with different percentages of potassium. Catalysts were characterized using different techniques. They were used in SCWG to find effect of potassium on hydrogen selectivity. Results showed remarkable role for K on improvement of hydrogen selectivity. Addition of 2.5 wt.% of potassium increased H₂ selectivity from 0.76 to 1.17 with no significant decrease in total hydrogen production. The catalysts were characterized using ICP, XRD, TPR, BET and TEM techniques. Bagasse feedstock elemental structure was analyzed using CHNS technique.

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Introduction

Fossil fuel consumption has made great environmental problems in last decades. Air pollution as a result of environment carbon balance disarrangement through releasing petroleum carbon content is the main problem of fossil fuel consumption. Using new energy resources can reduce consumption of petroleum [1,2]. Sun, wind and waves are renewable energy resources and can be used as electrical type of energy [3,4]. Biomass is also another renewable energy resource. Direct burning of biomass for making heat has a history as old as mankind's. Recently, many biomass treatments have been developed to achieve value added products such as hydrogen, transportation fuels, syngas and even

chemicals [5–7]. Hydrogen can be produced via different methods especially from water precursor and used as fuel cells feed as a completely clean fuel [8,9]. Hydrogen rich gas production through different thermal and hydrothermal processes has been investigated. Studies have revealed promising methods to obtain hydrogen rich gas from woody biomass. Pyrolysis, steam reforming, near and supercritical water gasification are most interesting methods in this field of research [10–13]. Supercritical water gasification (SCWG) of biomass is hydrothermal treatment of biomass in a water medium with temperatures over 370 °C and pressures over 180 bar [14]. The chemical structure of biomass is a rich source of carbon and hydrogen atoms. The structure cannot break and dissolve easily in regular solvent media while producing

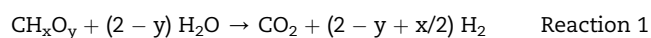
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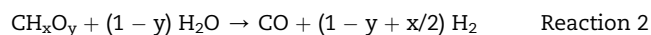
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hydrogen and syngas intensively depends on quality of dissolving and breaking [15–17]. The higher amount of breaking gives higher amounts of hydrogen and syngas. Water in supercritical condition is an ideal medium for dissolving and consequently breaking biomass structure and this is a key point in biomass gasification processes [18]. Water also has a main role of reactant in producing hydrogen through this process. Biomass SCWG is a complex process, but the overall chemical conversion can be represented by the simplified net reaction (Reaction 1) [19].



where x and y are the elemental molar ratios of H/C and O/C in biomass, respectively. Product is syngas and the process performance depends on x and y . Reaction (1) is endothermic and it is obvious that water plays as a reactant in addition to the solvent. The reaction also shows that hydrogen atoms in H_2O are released through gasification as H_2 molecules. Reaction (1) summarizes two competing intermediate reactions which occur in the process (Reactions 2 and 3). Reactions 2 and 3 are known as steam reforming and water-gas shift, respectively.



Simultaneously, an important reaction that is known as methanation (Reaction 4) occurs in SCWG of biomass. It consumes produced hydrogen and reduces process yield and selectivity. So, it is important for a selective SCWG of biomass to decelerate this reaction with manipulating process [20].



Annually, more than six hundred thousand tons of sugarcane bagasse is burned in Haft Tappe Industries Company in Iran, which creates serious environmental problems and wastes huge amounts of energy. So, it is necessary to find methods for converting bagasse to value added products and for extracting its energy content as other energy carriers that can be easily stored, moved and used [21]. Catalytic and non-catalytic SCWG processes for real and model biomasses have been investigated. It has been demonstrated that using catalysts that can accelerate water–gas shift reaction and/or decelerate methanation reaction are very useful for increasing hydrogen selectively [22].

Copper is one of the metals that showed accelerating effect on water–gas shift reaction and subsequently on hydrogen production. It has been used as base metal as well as promoter in supercritical water gasification of biomass [23]. Furthermore, simultaneous production of hydrogen, syngas and liquid fuels has been performed in presence of catalysts based on Cu [24–26]. To produce a hydrogen rich gas from SCWG, it is necessary to formulate a catalyst which is more selective for hydrogen production. Decelerating reactions that consume

hydrogen especially methanation reaction can highly help to manipulate process to be a hydrogen selective one [22].

Potassium has been introduced as a metal that reduces hydrocarbon production from syngas. The fact made it a good candidate to use as promoter in higher alcohols production. It has been demonstrated that potassium can made the process more selective for alcohol production with reducing hydrocarbon production [27,28]. Since methane as the main hydrocarbon in SCWG also produces from CO and H_2 , this is an idea that it can decelerate hydrocarbon production and subsequently increase hydrogen selectivity in SCWG.

In our previous work, we tried to use Ru as base metal on $\gamma\text{-Al}_2\text{O}_3$ for producing hydrogen rich gas from Iranian bagasse via supercritical water gasification. Ru showed a high performance in gasification of bagasse. However, it accelerated producing hydrocarbons especially methane. Therefore, we promoted it with zinc nanoparticles. Zn could improve hydrogen selectivity with reducing hydrogen consumption in hydrocarbon production reactions. However, Ru and Zn are expensive metals and supercritical water gasification of biomass needs to be progressed to a large scale industrial process in our country. So, using cheaper metals with no significant negative effect on hydrogen production rather than expensive ones can be an important key point in this way [13]. In this work, Iranian sugarcane bagasse was used as a real biomass feedstock. Supercritical water gasification of bagasse was performed to produce a hydrogen rich gas. $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$ with different amounts of copper was used as catalyst to investigate the effects of copper loadings on hydrogen production yield. Catalyst with the best performance was selected for manipulating with K as promoter with different percentages to find its effect on hydrogen selectivity of process.

Materials and methods

Materials and reagents

Sugarcane bagasse was supplied from Haft-Tappe Industries, Iran. After washing, drying, grinding and sieving, bagasse was used as feed with particle sizes up to 1 mm. Gama alumina with $212.4 \text{ m}^2 \text{ g}^{-1}$ specific surface area and impurities of $\text{Na}_2\text{O} < 0.05 \text{ ppm}$, $\text{SiO}_2 < 0.9 \text{ ppm}$, sulfates $< 1.5 \text{ ppm}$ was thermally treated before use. The materials used for catalysts preparation including $\text{Cu}(\text{CH}_3\text{COO})_2$, KNO_3 and K_2CO_3 were all purchased from Sigma–Aldrich company.

Methods

Catalyst preparation

$\gamma\text{-Al}_2\text{O}_3$ was calcined in air at $400 \text{ }^\circ\text{C}$ for 4 h to remove water content and probable combustible impurities. Aqueous solutions of $\text{Cu}(\text{CH}_3\text{COO})_2$ and KNO_3 were prepared to impregnate support via co-impregnation method. After that it is dried at $120 \text{ }^\circ\text{C}$ for 2 h and calcined at $400 \text{ }^\circ\text{C}$ for 4 h. Catalysts were prepared with 2.5, 5, 10, 15 and 20 weight percentages of Cu and after finding the catalyst with 20 wt.% Cu as the most effective one in hydrogen rich gas production, potassium was added as promoter with 1, 2.5, 5, 7.5 and 10 wt.% to the catalyst. Prepared catalysts were nominated and presented in Table 1.

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