

Effect of Reaction Temperature and Type of Catalyst on Hydrogen Production in Supercritical Water Gasification of Biomass

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Abstract: The aim of this study was to investigate the feasibility of hydrogen production from sugarcane bagasse by supercritical water gasification (SCWG) at low temperature and in presence of alkali catalyst. Experiments were carried out in a batch autoclave reactor at 400 °C and 9% solid content. Effect of reaction time and alkali catalyst on gas yield, gas composition, carbon gasification efficiency (CGE) and hydrogen gasification efficiency (HGE) were investigated. Influence of reaction time on gas yield and composition as well as on CGE was found to be insignificant. Extending the reaction time even up to 4 h could not cause an attractive conversion of bagasse. In the presence of catalysts (K_2CO_3 , $KHCO_3$, $NaHCO_3$ and $NaOH$), sugarcane bagasse was partially gasified in SCW and hydrogen-rich gas containing CO_2 as the main carbon compound was produced. Among the implemented catalysts, K_2CO_3 was identified to be the most effective for improvement of HGE. Use of the catalyst under our experimental conditions, the maximum HGE of 19% was achieved; however the highest CGE occurred with $KHCO_3$. Results showed that feed to catalyst ratio of 2 was high enough to reach the greatest possible gasification of hydrogen at 400 °C and 45 min. More CGE and HGE would be possible only by increasing the temperature, pressure and/or reaction time.

Key words: Supercritical water gasification % Sugarcane bagasse % Alkali catalyst % Hydrogen gasification efficiency

INTRODUCTION

It seems that fossil fuels will continue to be the main resource of energy for coming decades particularly in oil producer countries, though these fuels release huge amount of greenhouse gases and other pollutants each year. This together with the reality of finiteness of the crude oil reserves caused policy makers and researchers to have an especial interest on the renewable energy possibilities especially from agricultural residues.

The use of biomass energy has a potential to reduce greenhouse gas emissions [1]. Biomass is a substance made of organic compounds originally produced by fixing

carbon dioxide in the atmosphere during the process of plant photosynthesis. Since the concentration of carbon dioxide in the atmosphere theoretically remains constant in this cycle, biomass is expected to become one of the key sources of renewable energy in the future sustainable society [2].

Among all forms of deriving fuels from biomass, hydrogen has the highest specific energy content [1]. On the other hand, the increasing demand for H_2 for heavy oil upgrading, desulfurization and upgrading of conventional petroleum and for production of ammonium, in addition to the projected demand for H_2 as a transportation fuel and for portable power sources, will require H_2 production on

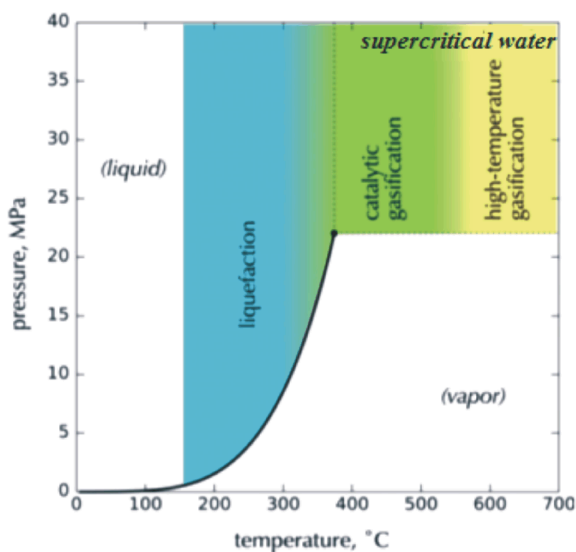


Fig. 1: Position of supercritical water in phase diagram of water [38]

a massive scale [3]. Gasification of biomass in supercritical water (SCW) is a promising technology [4] which is relatively new and has not yet been commercialized. Water at its critical conditions (the critical temperature and pressure are 374 °C and 22.1 Mpa, respectively; Fig. 1) has special properties in which biomass is degraded very quickly [5]. It is actually the highest temperature and pressure at which liquid and gas phases of water can exist [5]. In such conditions weakness in hydrogen bonds of water molecules results in reduction of dielectric constant which converts the water to a nonpolar solvent [6] where organic compounds can be easily solved and react quickly [7-8].

Particular properties of SCW have attracted many scientists around the world in the last decade. Since biomass is a very heterogeneous feedstock and represents a complex mixture of various, also inorganic constituents, understanding of chemical processes during the conversion of real biomass is difficult [8]. Therefore, many of the reported literatures deal with model compounds such as glucose [4, 9-12], glycine and glycerol [13-15].

There are also some valuable studies on SCWG of agricultural residues and wastes. Williams and Onwudili examined the influence of temperature on subcritical and supercritical regimes of water for Cassava waste [16]. Yanik and coworkers in KIT¹ studied SCWG of eight different types of biomass including tobacco stalk, corn stalk, cotton stalk, sunflower stalk, corncob and oreganum

stalk [17]. They have reported that the highest percentage of hydrogen (39.47% or 4.68 mol H₂/kg) was obtained from tobacco stalk at 500 °C.

Elliott and his co-workers in NPNL² examined wet gasification of dairy manure and produced a gas primarily containing methane and carbon dioxide and effluent with COD content of less than 1000 mg/l [18]. In another study at NPNL, complete gasification of manure in a continuous reactor at the pressure of 21 MPa and temperature of 350°C was reported [18]. In this experiment the aqueous products had very low COD (less than 100 ppm).

Youssef and his co-workers at the University of Western Ontario in Canada investigated the catalytic and non-catalytic hydrogen production from hog manure using supercritical water partial oxidation, gasification and sequential gasification partial oxidation in a batch autoclave reactor under the pressure of 28 MPa and the temperature of 500 °C using several metallic catalysts. They found Pd/AC to be the best catalyst in favor of hydrogen [19].

There are also some interesting review articles on SCWG of biomass such as the case for catalysis in sub- and supercritical water [20-21], status of SCWG of biomass [22] and general characteristic of SCWG of biomass [6].

The authors could not find any report on catalytic effect of alkali salts on SCWG of sugarcane bagasse. Effect of reaction time on supercritical water gasification of bagasse is also unknown. Therefore the main objective of this work was to assess the feasibility of hydrogen production from sugarcane bagasse by gasification at low temperature but still supercritical water in the presence of alkali catalyst. Hence the focus of the study was on the gas phase. In this regard the effect of reaction time and some alkali catalysts on gas yield, gas composition, carbon gasification efficiency (CGE) and hydrogen gasification efficiency (HGE) were investigated.

MATERIAL AND METHODS

Raw Material Preparation: Sugarcane bagasse was obtained from sugar mill of Dehkhoda Agricultural and Industrial Company in Khuzestan province of Iran. Analytical and component analysis of the raw material was accomplished according to DIN 51721. All experimental works were done in the laboratories of IKFT³ at KIT, Germany. The bagasse was milled and sieved to make the particle size of less than 180 µm.

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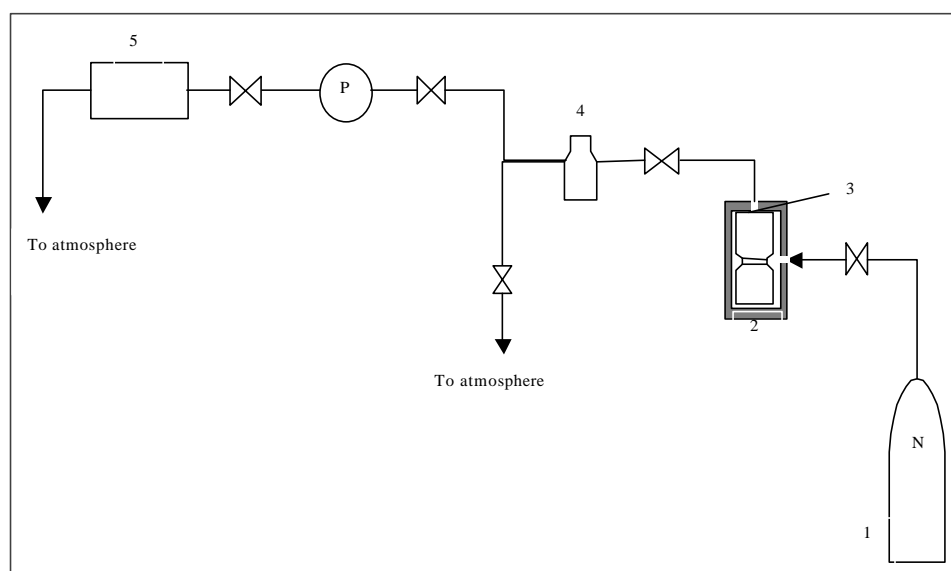


Fig. 2: Schematic diagram of gas sampling and reactor closing/opening system

1- Nitrogen tank, 2- Reactor closing chamber, 3- autoclave reactor, 4- Gas mouse, 5- volumetric measurement system

K_2CO_3 , $KHCO_3$ and $NaHCO_3$ were purchased from Merck Company (Darmstadt, Germany) and NaOH from VWR International Ltd. (UK). In each experiment, 46 mg of catalyst was used to make the ratio of 2:1 for feed to catalyst (FC) (equal to 5% of the total mixture).

Apparatus: The experiments were carried out in a batch autoclave reactor made of SS316 with the volume of 5 ml. Before each experiment, the reactor was washed three times by acetone to remove any residuals from the previous experiment. The next step was to feed the reactor with a mixture of sugarcane bagasse, distilled water and catalyst (where needed) with the total solid content of 9%. All experiments were conducted at 400 °C. Pressure was adjusted to 45 and 25 MPa by introducing the density of 540 and 167 kg/m³ according to steam table [23].

For each closing or opening of the reactor, nitrogen was used to purge the gas through the entire system (Fig. 2) for 5 min. Neutral gas purging, reactor closing and subsequently gas sampling were made in a unit system which its schematic is shown in Fig. 2. After the feed loading, the reactor was closed and put in a HP-5890 GC oven which was set to the desired temperature of 400 °C.

After the reaction time of 45 min (the time needed for heating up the reactor is not included), reactor was rapidly cooled down by putting into ice-water bath. The reactor was then opened and the gas quantified volumetrically and sampled on two gas chromatographs (GC) by a 100 µl syringe for 3 times and the average was reported.

Analytical Procedure: Two gas chromatographs (GC) were used to analyze the gas samples for separate detection of hydrogen and other gases.

The first GC for H₂ detection was a GC- Oven 5890 series equipped with thermal conductivity detector and Shin Carbon ST 80/100 packed column with dimensions of 2 m length × 2 mm internal diameter. The GC output can be obtained as vol%, mol%. Nitrogen was used as carrier gas. In GC analysis, the initial temperature was 100 °C for 6.5 min followed by the final temperature of 200 °C with the rate of 30°C/min where it was kept constant for 3 min.

The second GC which was used for other gases was a HP 7890A equipped with a 30 m Porapak Q Molsieve column, a front flame ionization detector (FID) and a TCD back detector which was controlled by a HP-Chem laboratory data system. The heating program was as follow; the initial temperature of 50 °C was maintained for 22.2 min after which the temperature was raised with the rate of 20 °C/min up to 150°C. After 15 min stay at this temperature, it was further raised at a rate of 50 °C/min up to 220 °C. This temperature was held constant for 5 min. The whole run had a duration of 48.6 min. The temperature of the injection port and the FID was maintained throughout the run at 250 °C and 300 °C, respectively. The pressure was kept constantly at 255 kPa. For each sample three injections were made by a 100 µL syringe and the average value was reported.

Table 1: Component and analytical analysis of sugarcane bagasse

Component analysis			Ultimate analysis				
Lignin	Cellulose	Hemicelluloses	C	H	N	S	HHV (kJ/kg)
25.7	46.6	27.9	46.4	5.69	<1	0.09	18.44

Table 2: Experimental conditions and results from first series of experiments

General conditions	Reaction time (min)	Gas yield (mol/kg of biomass)						CGE (%)
		H ₂	CH ₄	C ₂ H ₆	C ₃ H ₈	CO ₂	CO	
T = 400 °C	15	0.52	0.30	0.02	0.00	4.55	0.00	12.69
P=45 Mpa	45	0.73	0.56	0.12	0.05	4.61	0.00	13.98
Water density	75	0.56	0.41	0.10	0.04	5.85	0.00	16.72
= 540 kg/m ³	4 (h)	0.46	0.58	0.14	0.04	6.06	0.00	17.94

CGE and HGE were defined as the following formulas:

$$\text{CGE (\%)} = (\text{Carbon in gas phase} / \text{Carbon in feedstock}) \times 100 \quad (1)$$

$$\text{HGE (\%)} = (\text{Hydrogen in gas phase} / \text{Hydrogen in feedstock}) \times 100 \quad (2)$$

The amount of carbon and hydrogen in the feedstock was calculated based on the ultimate analysis (Table 1).

RESULTS AND DISCUSSIONS

Effect of Reaction Time on Gas Yield and Carbon Gasification Efficiency:

So far, there has not been any report on the effect of reaction time on gasification behavior of sugarcane bagasse. Therefore in the first series of experiments, the effect of reaction time on gasification at the temperature of 400 °C and pressure of 45 MPa was investigated. Table 2 summarizes the experimental conditions and corresponding results. As it can be found in the table, sugarcane bagasse was partially gasified to a CO₂ reach gas. Carbon monoxide was not formed in all cases.

Change in the amount of hydrogen and methane by extending the reaction time was not significant. Such trend was also reported by [19] in the case of hog manure at 500 °C and 31 MPa. Lu showed that longer reaction time is favorable for gasification of wood sawdust [24] but Williams and Onwudili reported that the total gas yield in SCWG of glucose was not significantly affected by reaction time [12]. All in all, effect of reaction time on gas yield is very dependent on biomass nature and experimental conditions.

From Table 2 it can be seen that longer reaction time led to increase in CGE however, the amount is not satisfying. Extending the reaction time up to 4 h resulted in still low CGE of 18%. After each experiment in this series one could easily see char particles in the liquid phase. Since such a long reaction time could not act in favor of hydrogen formation, applying suitable catalysts sound to be crucial.

Effect of Catalyst on Gas Yield and Carbon Gasification Efficiency:

From the first series of experiments, it was found that higher CGE could not be achieved by longer reaction time, therefore in the second series we tried to improve gasification efficiency through applying various catalysts.

In general, alkali catalysts are expected to progress gasification in favor of hydrogen [25-29] however, depends on the condition and the nature of biomass, the reaction pathway and the yield would change [30].

In the second series of experiment, effect of catalyst at the temperature of 400 °C and the pressure of 25 MPa was investigated. In these series, the experiments were done in the presence of four alkali catalysts including KHCO₃, K₂CO₃, NaHCO₃ and NaOH.

Fig. 3 shows the effect of catalyst on the gas yield and composition. The first column in this chart is as a base for better understanding the catalyst effect and relates to an experiment at higher temperature (500 °C) and without catalyst. As it is shown in the figure, all the alkali catalysts directed the reactions to hydrogen formation. Interestingly, the amount of hydrogen is even more than the experiment with higher temperature of 500 °C. This fact confirms that by use of alkali catalyst, one can obtain more gas with lower input energy. For this reason, the overall energy efficiency of a system would increase.

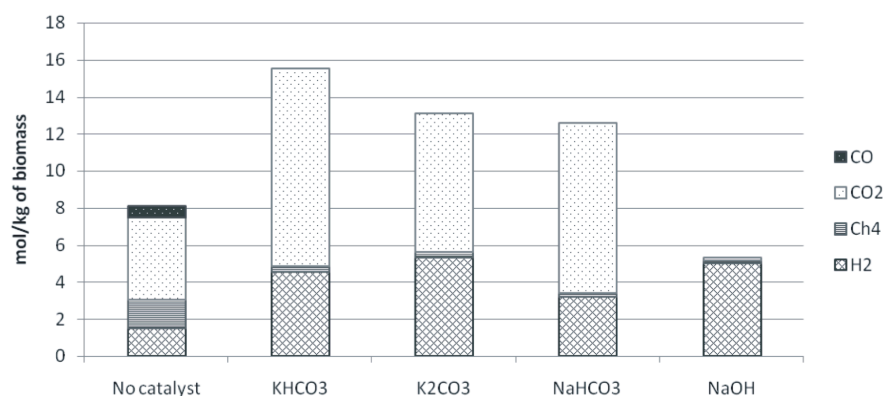


Fig. 3: Effect of catalyst type on gas composition (T=400 °C, P=25 MPa, SC=9%, FC=2, RT=45 min)

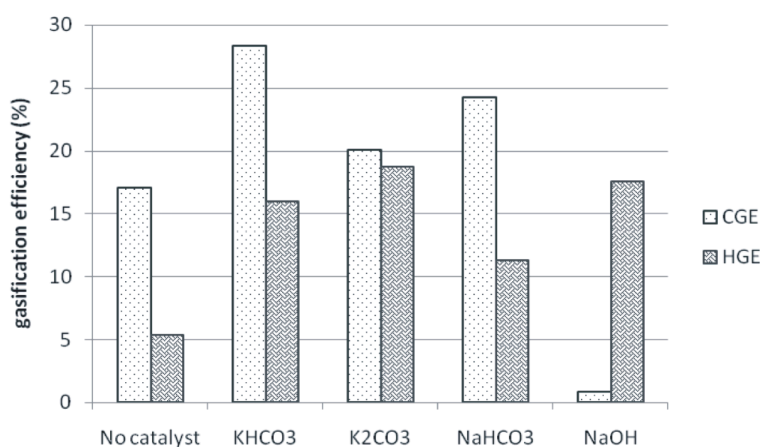


Fig. 4: Effect of catalyst type on CGE and HGE

The highest amount of hydrogen (5.33 mol/kilogram) achieved by K₂CO₃. This represents 40.75% of the total produced gas while without catalyst only 18% (1.5 mol/kg) of hydrogen was formed. These findings are in accordance with [17] in the gasification of corn stalk.

Although the fraction of hydrogen in the presence of NaOH is very high (94%), but the fact is that this figure is due to dilution of CO₂ in the liquid not because of high hydrogen gasification efficiency. Gue and co-workers showed that sodium hydroxide captures CO₂ to form sodium carbonate and water [31].

Generally, it is believed that after gas formation alkali catalysts improve H₂ and CO₂ yield by catalyzing water-gas shift reaction [5, 27, 30, 32-34]. These reactions have been known to be as:



In the case of K₂CO₃, Onsager believes that it catalyzes the water-gas shift reaction by formation of HCOO⁻K⁺ which reacts with water to produce hydrogen

and KHCO₃. Potassium bicarbonate then reacts with water to form water, carbon dioxide and potassium carbonate [35].

According to Eq. (3), CO amount decreases where an alkali catalyst exists [14]. Accordingly, in our experiment without catalyst but at higher temperature of 500 °C there was a trace of carbon monoxide (Fig. 3).

Fig. 4 shows the effect of the type of catalyst on CGE and HGE. As it is clear from this figure, CGE in the presence of KHCO₃ is higher than that of other catalysts while HGE is better in the case of K₂CO₃.

Effect of K₂CO₃ Loading on Gas Yield and Composition:

From the first series of experiments, K₂CO₃ was recognized to be the most effective catalyst for hydrogen production and results in better HGE (Fig. 4). Therefore, this catalyst was chosen for further experiments to study the effect of catalyst loading on gas yield. Feed to catalyst (FC) ratio of 6, 2 and 1.5 (equal to 1.7, 5 and 7% of the total mixture, respectively) were applied at the same temperature and pressure of 400 °C and 25 MPa.

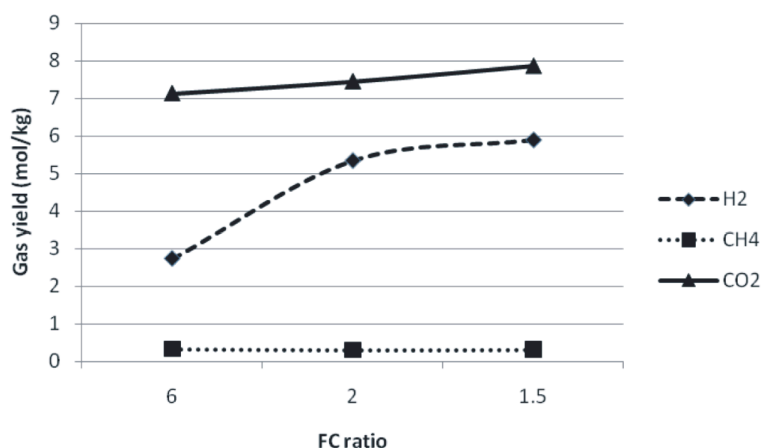


Fig. 5: Effect of FC ratio on gas yield and composition

The results are shown in Fig. 5. As it is clear from the figure, hydrogen yield increased sharply from 2.73 mol/kg at FC=6 to 5.33 mol/kg at FC=2 following with almost steady state till 5.88 mol/kg at FC=1.5. Change in methane yield was not significant in all cases. It could be due to the fact that alkali catalysts promote water-gas shift reaction which resulted in more hydrogen yield [15, 25, 28, 35]. They are actually neutral for CH₄ formation. Therefore while the temperature and the reaction time were constant, there was no reason for increase in CH₄.

From this experiment it could be concluded that FC ratio of 2 (5% of the total mixture) was sufficient to reach the highest possible gasification of hydrogen at 400 °C and 45 min. Therefore, more HGE could be achieved by increase in either temperature or reaction time [8, 24, 36-37]. Increase in pressure has been confirmed not to be very effective in SCWG of biomass [8].

CONCLUSION

Sugarcane bagasse was partially gasified in SCWG with and without the presence of alkali salts. Experiments were carried out in a batch type autoclave reactor at the temperature of 400 °C and solid content of 9%. Effect of reaction time on gas yield and composition as well as CGE was found not to be significant. Extending the reaction time even up to 4 h could not cause an attractive conversion of bagasse.

Various alkali catalysts were examined in the reaction time of 45 min among which K₂CO₃ was found to be the most effective one for improvement of HGE. By this catalyst maximum HGE of 19% under our experimental condition was possible. However the highest CGE occurred with KHCO₃.

Results showed that FC ratio of 2 was high enough to reach the maximum possible gasification of hydrogen at 400 °C and 45 min. Therefore, more CGE and HGE would be possible by increasing the temperature and/or the reaction time.

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