

# The 9th International Energy Conference

## Gasification of sugarcane bagasse in supercritical water: effect of pressure and reaction time

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### Abstract

Energy and environment are expected to be the main challenges of the human life in the long term future. Biomass as a renewable source of energy has been of the great interest especially in the last decade. Hydrogen as a clean fuel can take a significant role in providing a better environment and sustainable development. Supercritical water gasification (SCWG) is a promising technology for hydrogen production from organic wastes. In this study, the effects of reaction time on gas yield, gas composition and carbon gasification efficiency (CGE) were investigated. Experiments were carried out in a batch stainless steel 316 reactor at the temperature of 400 °C and feed concentration of 9 wt%. Sugarcane bagasse was partially gasified in supercritical water (SCW) and a gas containing hydrogen, methane, carbon monoxide and carbon dioxide was produced. CGE of 18.7% was achieved after 105 minutes of reaction time. Increase in pressure up to 45 MPa could not improve the gasification efficiency. Higher gasification efficiency could be achieved by either catalyst or higher temperature.

**Keywords:** renewable hydrogen, agricultural wastes, supercritical water gasification,

### 1. Introduction

Energy shortage and environmental problems are two challenging problems the human have to deal with in the future. With the increase intake of energy sources, the supplies cannot be renewed because of its non-renewability nature [1]. The use of biomass energy has a potential to reduce greenhouse gas emissions [2]. Among the many options of the use of biomass, hydrogen as a green energy has been attracted extensive attention worldwide [1].

On the other hand, the increasing demand for H<sub>2</sub> for heavy oil upgrading, desulfurization and upgrading of conventional petroleum, and for production of ammonium, in addition to the projected demand for H<sub>2</sub> as a transportation fuel and for portable power sources, will require H<sub>2</sub> production on a massive scale [3]. Currently, 90% of the global hydrogen demand is derived from natural gas by steam reforming [4].

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Gasification of biomass in supercritical water (SCW) for hydrogen production from biomass is a promising technology [5]. Water at its critical conditions (temperature and pressure of more than 374 °C and 22.1 MPa respectively, Figure 1) has special properties so that biomass is degraded very quickly [6]. In such conditions weakness in hydrogen bonds of water molecules results in reduction of dielectric constant. “This change the water from a highly polar solvent at an ambient condition to a nonpolar solvent, like benzene, in a supercritical condition” [7] where organic compounds can be easily solved and react quickly [8-9].

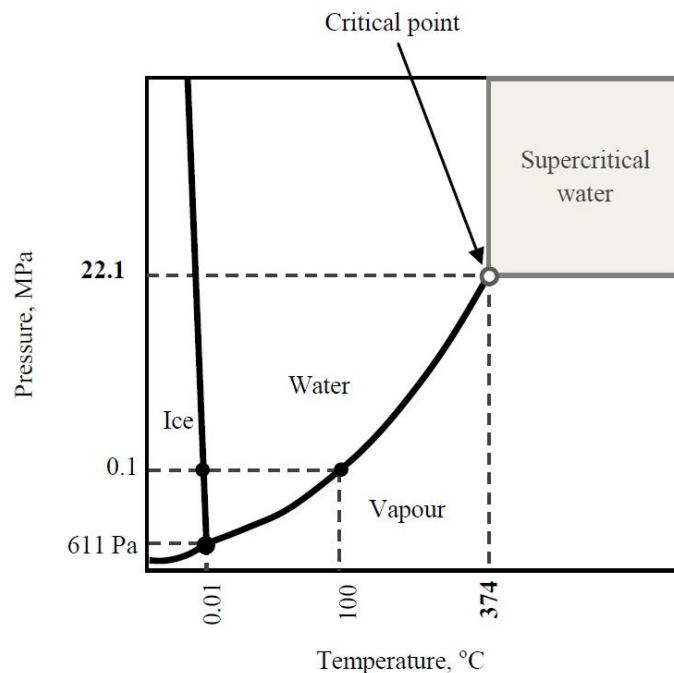


Figure 1: Schematic phase diagram of water [10]

Particular properties of SCW have attracted many scientists around the world in the last decade. So far, numerous reports on SCWG of model compounds such as glucose [5, 11-14], glycine and glycerol [15-17] have been published. Working on real biomass or agricultural wastes sounds to be more near to practical application of this technology. There are some major groups worldwide working in this area including; Karlsruhe institute of technology (KIT) in Germany, University of Twente in the Netherlands, Selcuk University in Turkey, Pacific Northwest National Laboratory and University of Hawaii in USA, National Institute for Resources and Environment as well as many universities in Japan, State Key Laboratory of Multiphase Flow in Power Engineering in China and Advanced Institute of Science and Technology in Korea are working in this field [10].

Yanik and his co-workers from KIT studied the gasification of 8 varieties of biomass (tobacco stalk, corn stalk, cotton stalk, sunflower stalk, corncob, oreganum stalk, chromium-tanned waste, and vegetable-tanned waste) in a batch autoclave at 500 °C. They obtained the hydrogen yields ranging between 4.05 and 4.65 mol H<sub>2</sub>/kg biomass [18].

Kyoung and co-workers from Pacific Northwest National Laboratory conducted some extensive investigation on feasibility of wet gasification for treatment/energy conversion of both animal and municipal wastes. They reported that Wet wastes

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such as swine manure and raw sewage sludge could be processed directly via current wet gasification technology [19].

Onwudili and Williams studied the influence of sodium hydroxide, water density and reaction temperature on the SCWG of refuse derived fuel (RDF). According to their report, a hydrogen rich gas containing CO, CO<sub>2</sub>, and small amounts of C<sub>1</sub>–C<sub>4</sub> hydrocarbons is achievable from RDF in the presence of NaOH as catalyst.

Osada and his co-workers studied the Gasification of sugarcane bagasse on activated-carbon- and titania-supported ruthenium catalysts in SCW. Sugarcane bagasse is the solid residue remaining after the process of juice extraction from sugarcane for sugar or ethanol production. They reported that Sugarcane bagasse was completely gasified to methane, carbon dioxide, and hydrogen over Ru/C and Ru/TiO<sub>2</sub> catalysts at 673 K. They also found that the gas yield of sugarcane bagasse increased with an increase in the water density [20].

The effect of catalyst (K<sub>2</sub>CO, KHCO, NaHCO and NaOH), on gas yield and composition of SCWG of sugarcane bagasse was reported by the present authors. We also examined the influence of reaction time at high pressure of 45 MPa [21]. From practical point of view, high pressure corresponds to more energy consumption and needs more resistant material [7, 22]. In this paper, the effect of reaction time in the constant pressure of 25 MPa on gas yield, gas composition, and carbon gasification efficiency (CGE) were investigated. Effect of pressure on CGE of bagasse was also studied.

## 2. Material and methods

### 2.1 Raw material preparation

Sugarcane bagasse was obtained from sugar mill of Debal Khazae Agricultural and Industrial Company in Khouzestan province of Iran. The composition of the sugarcane bagasse used in this experiment was 25.7% lignin, 46.6% cellulose, and 27.9% hemicelluloses, and its elementary analysis was 46.4% C, 5.69% H, <1% N, and 0.09% S. All experimental works were carried out in the laboratories of IKFT<sup>1</sup> at KIT, Germany. The bagasse was milled and sieved to make the particle size of less than 180 μm.

### 2.2 Analytical equipment

The experiments were done in a batch type 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. Feed concentration of 9wt% sugarcane bagasse and pressure of 25 MPa was considered for all experiments. This pressure was achieved by introducing the density of 167 kg/m<sup>3</sup> according to the steam table [23].

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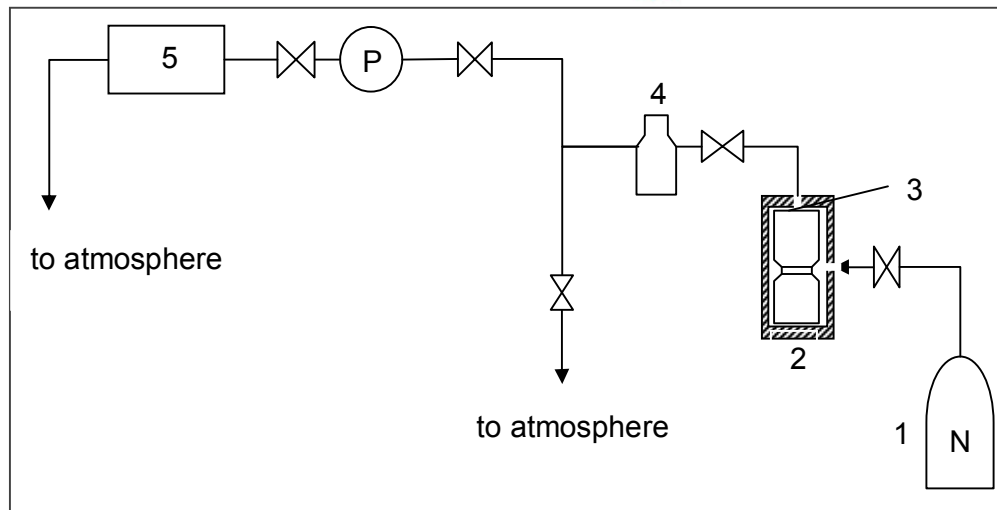


Figure 2: Schematic of gas sampling and reactor closing/opening system [21]  
1- Nitrogen tank, 2- Reactor closing chamber, 3- autoclave reactor, 4- Gas mause, 5- volumetric measurement system

Nitrogen was used to purge the air through the entire system for 5 minutes. Neutral gas purging, reactor closing and subsequently gas sampling were made in a unit system which its schematic is shown in figure 2. After the feed loading, the reactor was closed and put in a HP-5890 GC oven which was set to 400 °C.

After the certain reaction time, 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 for 3 times and the average was reported. Two separate gas chromatographs (GC) were used to analyze the gas samples for separate detection of hydrogen and other gases. The details for gas chromatographs can be found elsewhere [21].

For each sample three injections were made by a 100 µL syringe and the average was reported.

CGE was defined as the following formula;

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

The amount of carbon in the feedstock was calculated based on the ultimate analysis.

### 3. Results and discussion

#### 3.1 Effect of reaction time on gas yield and carbon gasification efficiency

Table 1 summarizes the experiments condition and corresponding results. As could be seen from the table, the gas is composed mainly from CO<sub>2</sub> in every reaction time. Increase in reaction time led to increase in hydrogen, methane, and carbon dioxide but decrease in carbon monoxide fraction.

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Table 1: gas yield and composition from differation reaction times

Reaction time (min)	Gas yield (mol/kg)				Gas yeild (%)			
	H <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>	CO	H <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>	CO
15	0.04	0.20	4.48	0.61	0.71	3.76	84.02	11.52
45	0.20	0.47	5.45	0.66	2.96	6.99	80.26	9.77
75	0.36	0.60	5.78	0.47	4.95	8.23	79.49	6.50
105	0.81	0.53	5.89	0.00	11.2	7.32	81.03	0.00

In all cases, the change in the amount of hydrogen and methane is not significant. Such trend was also observed by [24] 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 [25] but Williams and Onwudili reported that the total gas yield in supercritical water gasification of glucose was not significantly affected by reaction time [14]. Carbon monoxide tends to be vanished as the reaction time goes higher than 95 min.

Figure 3 shows CGE as a function of reaction time. As it could be seen from this chart, though the trend is additive however, the amount is very low. CGE increased from 13.7% in 15 minutes to 18.7% in 105 minutes. On the other hand, from table 1 it could be concluded that this conversion is almost in the favor of CO<sub>2</sub> not of useful hydrocarbons or hydrogen. During the experiments, char contain of the liquid phase was visible. It shows that gasification was not complete even through the long reaction time of 105 minutes. Clearly longer reaction time would increase the input energy of a system which reduces the overall energy efficiency of conversion. Higher gasification efficiency could be achieved by either catalyst or higher temperature.

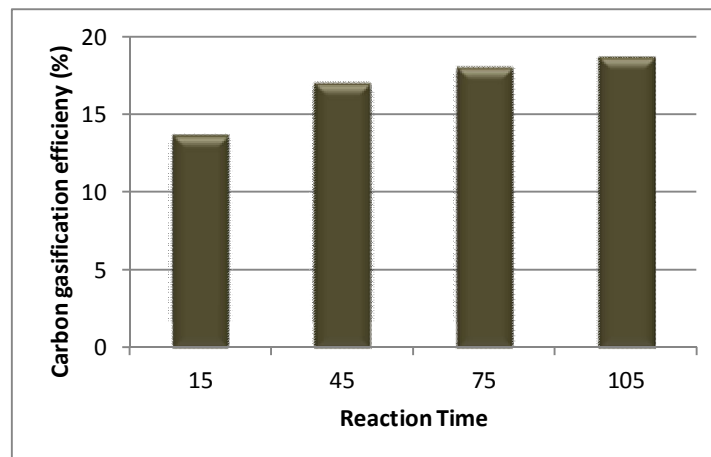


Figure 3: Change in carbon gasification efficiency as a function of reaction time (T=400 °C, P=25 MPa, 9%wt solid)

### 3.2 Effect of pressure on CGE in different reaction time

Figure 4 shows the effect of pressure on CGE in different reaction time. This chart has been obtained based on the results from the current study and the previous publication [21]. One should consider that increase in pressure obtained through increase in water density. Slow rising in CGE is almost the same for both pressures,

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however from this chart it is clear that CGE did not affected by increase in pressure. This fact is very important in practical large scale plants. While increase in pressure requires more resistant tubing and etc, it does not promote gasification efficiency. Pacheco De Resende suggested that increase in pressure inhibits gas formation and leads to lower carbon conversion [6].

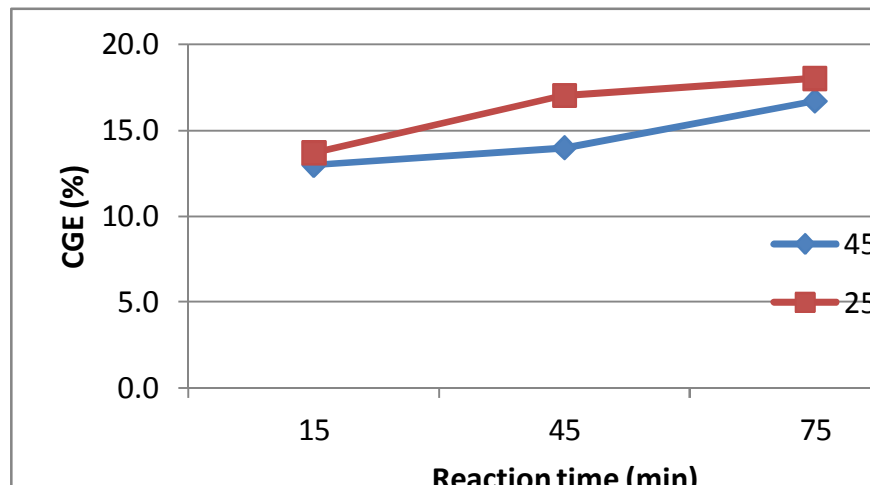


Figure 4: effect of pressure on CGE in different reaction time

### 4. Conclusion

Supercritical water gasification of sugarcane bagasse was studied in a batch reactor at the temperature of 400 °C and feed concentration of 9 wt%. A gas containing hydrogen, methane, carbon monoxide and carbon dioxide was produced. CGE of 18.7% was achieved after 105 minutes of reaction time. Increase in pressure up to 45 MPa could not improve the gasification efficiency. Higher gasification efficiency could be achieved by either catalyst or higher temperature.

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### References

- [1] Y Guo, SZ Wang, DH Xu, YM Gong, HH Ma, XY Tang. Review of catalytic supercritical water gasification for hydrogen production from biomass. *Renewable and Sustainable Energy Reviews* (2010);14:334-43.
- [2] A Campen, K Mondal, T Wiltowski. Separation of hydrogen from syngas using a regenerative system. *Int J Hydrogen Energy* (2008);33:332-9.
- [3] DB Levin, R Chahine. Challenges for renewable hydrogen production from biomass. *Int J Hydrogen Energy* (2010);35:4962-9.
- [4] J Hetland, G Mulder. In search of a sustainable hydrogen economy: How a large-scale transition to hydrogen may affect the primary energy demand and greenhouse gas emissions. *Int J Hydrogen Energy* (2007);32:736-47.
- [5] Y Lu, S Li, L Guo, X Zhang. Hydrogen production by biomass gasification in supercritical water over Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ni/CeO<sub>2</sub>- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts. *Int J Hydrogen Energy* (2010);35:7161-8.

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- [6] FL Pacheco De Resende. Supercritical Water Gasification of Biomass: The University of Michigan; 2009.
- [7] P Basu. Hydrothermal Gasification of Biomass. Biomass Gasification Design Handbook. Boston: Academic Press; 2010.
- [8] K Cantrell, K Ro, D Mahajan, M Anjom, PG Hunt. Role of Thermochemical Conversion in Livestock Waste-to-Energy Treatments: Obstacles and Opportunities. *Ind Eng Chem Res* (2007);46:8918-27.
- [9] A Kruse. Hydrothermal biomass gasification. *J Supercrit Fluids* (2009);47:391-9.
- [10] P Basu, V Mettanant. Biomass Gasification in Supercritical Water -- A Review. *International Journal of Chemical Reactor Engineering* (2009);7.
- [11] J Chen, Y Lu, L Guo, X Zhang, P Xiao. Hydrogen production by biomass gasification in supercritical water using concentrated solar energy: System development and proof of concept. *Int J Hydrogen Energy* (2010);35:7134-41.
- [12] P Azadi, AA Khodadadi, Y Mortazavi, R Farnood. Hydrothermal gasification of glucose using Raney nickel and homogeneous organometallic catalysts. *Fuel Process Technol* (2009);90:145-51.
- [13] L In-Gu. Effect of metal addition to Ni/activated charcoal catalyst on gasification of glucose in supercritical water. *Int J Hydrogen Energy* (2011);36:8869-77.
- [14] PT Williams, J Onwudili. Composition of Products from the Supercritical Water Gasification of Glucose: A Model Biomass Compound. *Ind Eng Chem Res* (2005);44:8739-49.
- [15] A Kruse, E Dinjus. Hot compressed water as reaction medium and reactant: 2. Degradation reactions. *J Supercrit Fluids* (2007);41:361-79.
- [16] H Schmieder, J Abeln, N Boukis, E Dinjus, A Kruse, M Kluth, et al. Hydrothermal gasification of biomass and organic wastes. *J Supercrit Fluids* (2000);17:145-53.
- [17] S Guo, L Guo, C Cao, J Yin, Y Lu, X Zhang. Hydrogen production from glycerol by supercritical water gasification in a continuous flow tubular reactor. *Int J Hydrogen Energy* (2012);37:5559-68.
- [18] J Yanik, S Ebale, A Kruse, M Saglam, M Yüksel. Biomass gasification in supercritical water: Part 1. Effect of the nature of biomass. *Fuel* (2007);86:2410-5.
- [19] KS Ro, K Cantrell, D Elliott, PG Hunt. Catalytic Wet Gasification of Municipal and Animal Wastes. *Ind Eng Chem Res* (2007);46:8839-45.
- [20] M Osada, A Yamaguchi, N Hiyoshi, O Sato, M Shirai. Gasification of Sugarcane Bagasse over Supported Ruthenium Catalysts in Supercritical Water. *Energy Fuels* (2012).
- [21] M Ebrahimi-Nik. Effect of Reaction Temperature and Type of Catalyst on Hydrogen Production in Supercritical Water Gasification of Biomass. *Iranica Journal of Energy and Environment* (2012);3:202-9.
- [22] N Boukis, V Diem, U Galla, E Dinjus. Methanol reforming in supercritical water for hydrogen production. *Combust Sci Technol* (2006);178:467-85.
- [23] C.A. Meyer, R.B. McClintock, G.J. Silvestri, R.C. Spencer. *SteamTables—Thermodynamic and Transport Properties of Steam*: American Society of Mechanical Engineers; 1992.
- [24] EA Youssef, E Elbeshbishy, H Hafez, G Nakhla, P Charpentier. Sequential supercritical water gasification and partial oxidation of hog manure. *Int J Hydrogen Energy* (2010);35:11756-67.
- [25] YJ Lu, LJ Guo, CM Ji, XM Zhang, XH Hao, QH Yan. Hydrogen production by biomass gasification in supercritical water: A parametric study. *Int J Hydrogen Energy* (2006);31:822-31.