

# The Gasification of Fructose in Supercritical Water

Shyh-Ming Chern, H. Y. Cheng

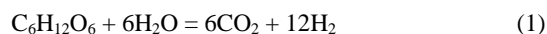
**Abstract**—Biomass is renewable and sustainable. As an energy source, it will not release extra carbon dioxide into the atmosphere. Hence, tremendous efforts have been made to develop technologies capable of transforming biomass into suitable forms of bio-fuel. One of the viable technologies is gasifying biomass in supercritical water (SCW), a green medium for reactions. While previous studies overwhelmingly selected glucose as a model compound for biomass, the present study adopted fructose for the sake of comparison. The gasification of fructose in SCW was investigated experimentally to evaluate the applicability of supercritical water processes to biomass gasification. Experiments were conducted with an autoclave reactor. Gaseous product mainly consists of H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>. The effect of two major operating parameters, the reaction temperature (673-873 K) and the dosage of oxidizing agent (0-0.5 stoichiometric oxygen), on the product gas composition, yield and heating value was also examined, with the reaction pressure fixed at 25 MPa.

**Keywords**—Biomass, Fructose, Gasification, Supercritical water.

## I. INTRODUCTION

**B**IO MASS energy is renewable and hence sustainable. One of the practical ways of utilizing biomass energy is transforming it into fuel, especially gaseous fuel, i.e. synfuel gases. One of the promising technologies for the conversion of biomass into gaseous fuel is supercritical water gasification [1]-[5]. Supercritical water has many unique features, including high critical temperature (647.4 K), high critical pressure (22 MPa), low in hydrogen-bond concentration and other typical characteristics of supercritical fluids, making it a promising, and sometimes ideal, medium for the reactions of organics. Numerous organic matters have undergone various reactions in supercritical water, e.g. alkanes [6]-[8], organic wastes [9], polymeric wastes [10], [11], coal [12], etc.

The ideal gasification reaction for typical biomass, e.g. glucose or fructose, in supercritical water is:



Previous investigations [13], [14] have shown that gasification of biomass in supercritical water approaches the ideal gasification reaction of biomass, producing dry product gases with hydrogen content higher than 60%. However, most studies to date have focused on gasification of biomass without addition of oxidizing agent, which is quite endothermic and hence is impractical for commercial processes because of the need of massive external energy supply. With addition of oxidizing agent of less than the needed amount for complete

oxidation, the gasification of biomass in supercritical water may proceed with little or no external energy input, and the process is named supercritical water partial oxidation (SCWPO).

Typical biomass, like wood, contains up to 40 % of cellulose, which can be chemically or biochemically converted into glucose, the building block of cellulose. As a result, studies of the transformation of biomass into fuels or chemicals have mostly chosen glucose as the model compound. On the contrary, fructose is employed as a model compound for biomass in this study. Fructose has the same chemical formula as glucose. Hence, it will be interesting to compare the results of its gasification in supercritical water with those of glucose, for thermodynamic equilibrium modeling [14] predicts identical results for both. Aside from also being abundant in nature, fructose has one more helpful feature than glucose, more soluble in water than other monosaccharides. In the present work, the SCWPO of fructose was investigated experimentally to evaluate applicability of supercritical water processes to biomass gasification. The effect of two major operating parameters, the reaction temperature and the dosage of oxidizing agent, on the product gas composition, yield and heating value was also examined.

## II. EXPERIMENTAL METHOD

### A. Materials

Reagent-grade fructose and hydrogen peroxide aqueous solution, 30 wt. % H<sub>2</sub>O<sub>2</sub>(aq), were employed as the organic reactant and the oxidizing agent, respectively. De-ionized water was used as the water source for SCW.

### B. Apparatus and Procedures

All experimental runs were conducted with a batch-type 16-ml autoclave reactor. The reactor is placed in a furnace and its top is connected to a main valve, which in turn connects the product collection and separation unit. The autoclave, tubing and valves are all made of cold-worked 316L stainless steel rated 140 MPa at room temperature. The reactor system was estimated to withstand pressure up to 30 MPa at 873 K, the highest operating temperature employed in this study. A typical experimental run begins by estimating the amount of reactants (including organics, oxidizing agent and de-ionized water) needed according to the target operating temperature and pressure; then, put the precisely weighed reactants into the autoclave, which is then carefully tightened and placed in the furnace. Set the target temperature on the furnace and start heating until the target temperature within the reactor is reached (in about 30 minutes). Meanwhile, temperature is recorded at a fixed interval of time. The reaction is allowed to continue for 60 minutes at the preset temperature to ensure the completion of

S. M. Chern is with the Department of Chemical Engineering, I-Shou University, Kaohsiung, 84001 Taiwan (phone: 886-7-6577711 ext3419; fax: 886-7-6578945; e-mail: smchern@isu.edu.tw).

H. Y. Cheng was an undergraduate student at the Department of Chemical Engineering, I-Shou University, Kaohsiung, 84001 Taiwan.

the reaction. Then, the furnace is turned off, and the reactor system is removed from the furnace and cooled by forced air to room temperature in about 30 minutes. At this point, the pressure inside the reactor has reduced to a few atmospheric pressures. The main valve is carefully and slowly opened and the gaseous product is collected and weighed with its volume measured by water displacement method. The reactor is opened afterwards. The liquid product is collected and weighed, and the formation of solids is only qualitatively observed.

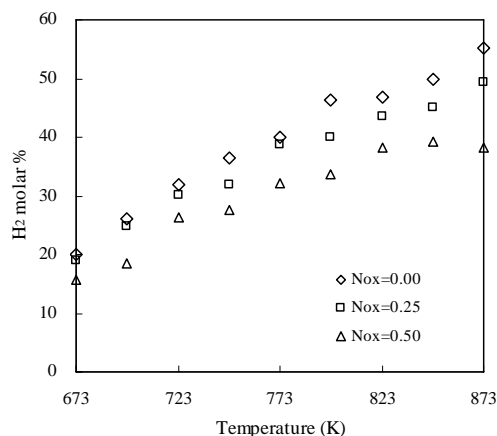


Fig. 1 H<sub>2</sub> concentration in product gas at 25 MPa

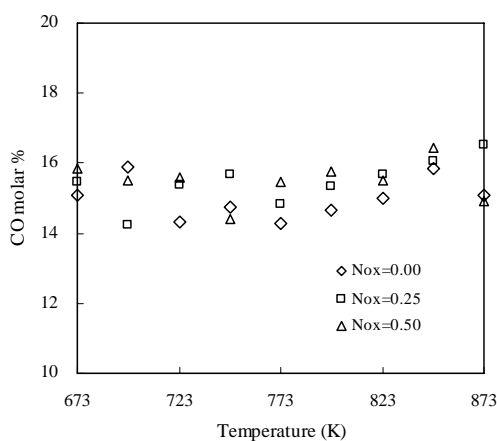


Fig. 2 CO concentration in product gas at 25 MPa

Gaseous product is measured volumetrically and analyzed for its hydrocarbons as well as H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, CO and CO<sub>2</sub> compositions with a GC-TCD (ThermoQuest TRACE 2000). The composition of hydrocarbons with two carbons or less is analyzed individually, and the composition for hydrocarbons with more than two carbons is negligibly small.

The experimental design did not incorporate a pressure gauge for direct pressure monitoring within the reactor, since no pressure measuring instruments are available which would not significantly disturb the small reactor system adopted here. Alternatively, the internal pressure of the reactor is practically estimated. The molar percentage of water in the SCW reaction environment normally exceeds 95%, so ideal solution model

applies to the water molecules and more than 95% of the total pressure is contributed by the water molecules. In the current study, the reaction pressure will be characterized by the apparent pressure,  $P_{AP}$ , which is defined as the thermodynamic equilibrium pressure exerted by water in the autoclave reactor containing only water of the amount identical to that of total water in the feed at the beginning of an experimental run. From the known amount of water and the volume of the reactor, the apparent pressure at various temperatures can be easily obtained from a steam table. In the SCW reaction environment, water molecules not only serve as the reaction solvent but also participate in the reactions to some extent. However the amount of water affected by the reactions is minor in comparison with the total amount of water present in the SCW system. Therefore, the discrepancy between the apparent pressure of water and the real reaction pressure should be no more than 5%. For instance, when the apparent pressure of water is 30 MPa, the real reaction pressure shall lie in the range of  $30 \pm 1.5$  MPa.

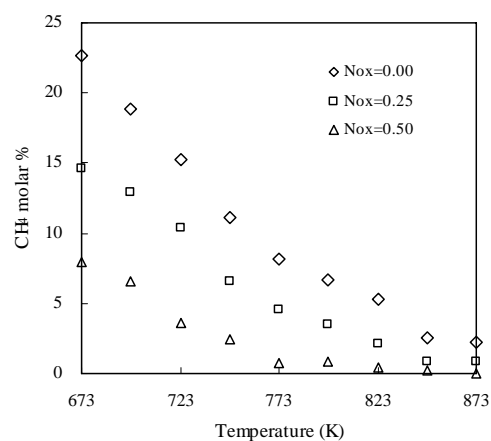


Fig. 3 CH<sub>4</sub> concentration in product gas at 25 MPa

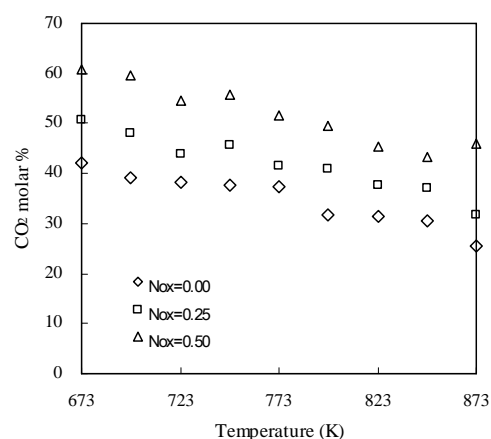


Fig. 4 CO<sub>2</sub> concentration in product gas at 25 MPa

### III. RESULTS AND DISCUSSION

A total of 54 experimental runs were successfully completed from 27 different experimental conditions. Each data point in the following figures represents an average of two data values

from two runs of identical experimental conditions. The major operating parameters are reaction temperature and dosage of the oxidizing agent. The operating temperature (furnace set temperature) ranged from 673 K to 873 K, and the amount of oxidizing agent used were 0, 0.25 and 0.5 stoichiometric oxygen,  $N_{ox}$ . One stoichiometric oxygen is defined as the amount of oxidizing agent necessary to completely oxidize the organic reactants, quite similar to the concept of chemical oxygen demand for the water treatment. The reactant concentration was fixed at 0.1 M (moles of organic reactant per liter of total water in the feed), and reaction pressure, at 25 MPa.

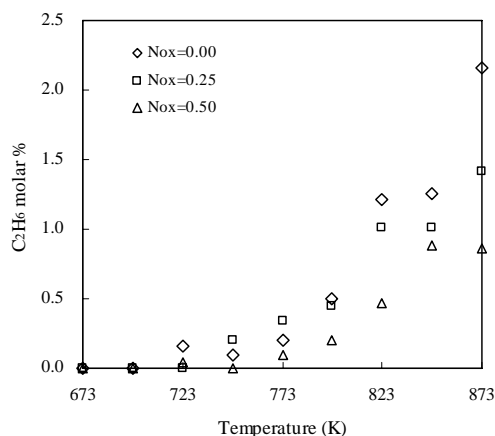


Fig. 5  $C_2H_6$  concentration in product gas at 25 MPa

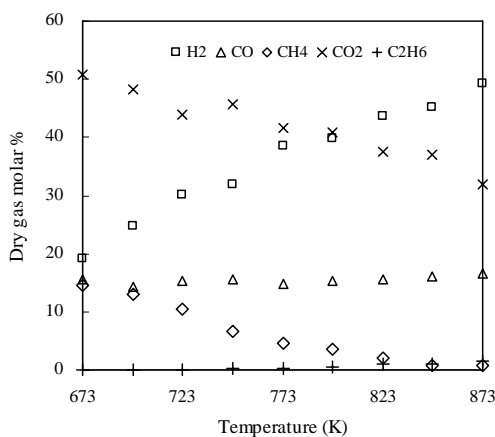


Fig. 6 Dry gas composition at 25 MPa and 0.25  $N_{ox}$

The gaseous product from the SCWPO was found to consist mainly of  $CO_2$ ,  $H_2$ ,  $CO$ ,  $CH_4$  and  $C_2H_6$  in order of decreasing amount. The gaseous hydrocarbons of three to five carbon atoms were found to be negligibly scarce in the product gas. The liquid product was weighed and visually inspected. Solid residues were generally not present in the product. Figs. 1 through 5 present the dry gas compositions for  $H_2$ ,  $CO$ ,  $CH_4$ ,  $CO_2$  and  $C_2H_6$ , respectively, against reaction temperature, with dosage of oxidizing agent as the parameter. As seen from Fig. 1, the molar concentration of hydrogen in the dry gas increases

with temperature all the way from about 20 % at 673 K to about 50 % at 873 K. As expected, the hydrogen content decreases with increasing dosage of oxidizing agent, since more hydrogen gas is oxidized with the increase. The  $CO$  content of the dry product gas presented in Fig. 2 ranges between 14 and 16 % and shows no specific trend versus reaction temperature and the dosage of oxidizing agent. The  $CH_4$  content of the dry product gas, presented in Fig. 3, exhibits a roughly exponential decreasing trend with reaction temperature. It is also markedly reduced by the increase in dosage of oxidizing agent. The level of  $CO_2$  is seen in Fig. 4 to decrease steadily with increasing temperature and to increase with increasing dosage of oxidizing agent. The former may be due to more external heating and less oxidation at higher temperature and the latter can be easily understood to result from increased oxidation at higher dosage of oxidizing agent. The high level of  $CO_2$  is undesirable since  $CO_2$  has no energy content. The  $C_2H_6$  content in the dry product gas is generally low, as shown in Fig. 5, especially at low temperature, and is seen to show increasing trend with temperature. It is also seen to be adversely affected by the increase in dosage of oxidizing agent.

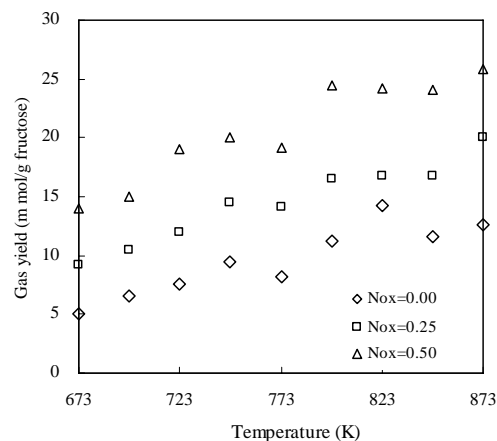


Fig. 7 Dry gas yield per mole of fructose

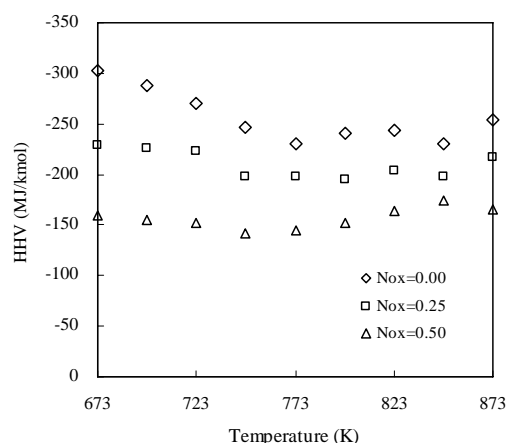


Fig. 8 HHV of dry product gas

Fig. 6 depicts a typical relative distribution of the five gas

species in the dry gas versus reaction temperature at  $N_{ox}$  of 0.25. It is seen that  $CO_2$  and  $H_2$  are the dominant species at the low temperature end and at the high temperature end, respectively.  $CO$  content is relatively stable throughout the temperature range investigated, while  $CH_4$  content is significant at low temperature and reduces to a negligible level at high temperature end. The  $C_2H_6$  content is negligibly small throughout.

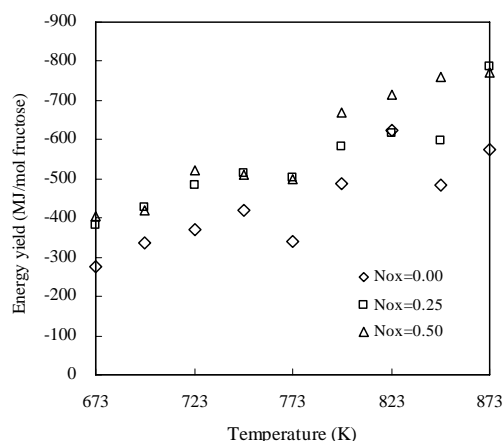


Fig. 9 HHV of dry product gas from gasification of one mol of fructose

The dry gas yield, number of moles of dry product gas produced per mole of fructose in the feed, and higher heating value (HHV) of the dry product gas are also exhibited in Figs. 7 and 8, respectively, versus major operating parameters. The dry gas yield was found to increase steadily with increasing temperature, about doubled over the temperature range investigated. It is also significantly boosted by the addition of oxidizing agent. The influence of temperature on the HHV of the dry product gas does not show distinct trends. However, the effect of dosage of oxidizing agent is seen to be more significant at the low temperature end than at the high temperature end. The HHV of the dry gas comes mainly from the contribution of the three major energy containing species,  $H_2$ ,  $CO$ , and  $CH_4$ , which generally make up more than half of the dry gas. Finally, the energy yield, defined as the HHV of dry product gas from the gasification of one mol of fructose, is illustrated in Fig. 9. The energy yield combines the effect of gas yield, shown in Fig. 7, and the effect of dry gas HHV, depicted in Fig. 8, and serves to indicate the overall performance of the gasification process. The energy yield generally increases with increasing temperature from about -350 (MJ/mol fructose) at the low temperature end to about -700 (MJ/mol fructose) at the high temperature end. It may seem that gasification at high temperature is better than that at low temperature. However, due to current experiment design, gasification at higher temperature consumes more external energy than that at lower temperature. The external energy input shall be carefully figured out and subtracted from the energy output from the gasification, before an optimal temperature is realizable. It is also evident that proper dosage of oxidizing agent favors the conversion of energy from the form of biomass into the form of

fuel gas.

#### IV. CONCLUSION

The gasification of fructose in SCW was investigated experimentally to evaluate the applicability of supercritical water processes to biomass gasification. Gaseous product of the gasification process mainly consists of  $H_2$ ,  $CO$ ,  $CO_2$ ,  $CH_4$  and  $C_2H_6$ . The effect of two major operating parameters, the reaction temperature (673-873 K) and the dosage of oxidizing agent (0-0.5 stoichiometric oxygen), on the product gas composition, yield and heating value was also examined, with the reaction pressure fixed at 25 MPa. It was found that higher reaction temperature and proper dosage of oxidizing agent favor the conversion of energy from the form of fructose into the form of fuel gas. Increasing reaction temperature from 673 K to 873 K approximately doubles the energy yield. The addition of oxidizing agent of 0.5  $N_{ox}$  increases the energy yield by about 30% in comparison to the case of no oxidizing agent added.

#### ACKNOWLEDGMENTS

It is grateful for the financial support from I-Shou University of Taiwan.

#### REFERENCES

- [1] M. J. Antal Jr., S. G. Allen, D. Schulman, X. Xu and R. J. Divilio, "Biomass gasification in supercritical water," *Industrial and Engineering Chemistry Research*, vol. 39, no. 11, pp. 4040-4053, 2000.
- [2] Y. Matsumura, "Evaluation of supercritical water gasification and biomethanation for wet biomass utilization in Japan," *Energy Conversion and Management*, vol. 43, no. 9-12, pp. 1301-1310, 2002.
- [3] A. Kruse, T. Henningsen, A. Smag and J. Pfeiffer, "Biomass gasification in supercritical water: Influence of the dry matter content and the formation of phenols," *Industrial and Engineering Chemistry Research*, vol. 42, no. 16, pp. 3711-3717, 2003.
- [4] M. Bagnoud-Velásquez, M. Brandenberger, F. Vogel and C. Ludwig, "Continuous catalytic hydrothermal gasification of algal biomass and case study on toxicity of aluminum as a step toward effluents recycling," *Catalysis Today*, vol. 223, pp. 35-43, 2014.
- [5] H. T. Nguyen, E. Yoda and M. Komiyama, "Catalytic supercritical water gasification of proteinaceous biomass: Catalyst performances in gasification of ethanol fermentation stillage with batch and flow reactors," *Chemical Engineering Science*, vol. 109, pp. 197-203, 2014.
- [6] T. Richter and H. Vogel, "The partial oxidation of cyclohexane in supercritical water," *Chemical Engineering and Technology*, vol. 25, no. 3, pp. 265-268, 2003.
- [7] B. Veriansyah, J. Kim, J. D. Kim and Y. W. Lee, "Hydrogen production by gasification of isooctane using supercritical water," *International Journal of Green Energy*, vol. 5, no. 4, pp. 322-333, 2008.
- [8] R. F. Susanti, L. W. Dianningrum, T. Yum, Y. Kim, Y. W. Lee and J. Kim, "High-yield hydrogen production by supercritical water gasification of various feedstocks: Alcohols, glucose, glycerol and long-chain alkanes," *Chemical Engineering Research and Design*, 2014, Article in Press.
- [9] J. García M.B., J. Sánchez-Oneto, J. R. Portela, E. Nebot Sanz and E. J. Martínez de la Ossa, "Supercritical water gasification of industrial organic wastes," *Journal of Supercritical Fluids*, vol. 46, no. 3, pp. 329-334, 2008.
- [10] Y. Park, J. T. Reaves, C. W. Curtis and C. B. Roberts, "Conversion of Tire Waste using Subcritical and Supercritical Water Oxidation," *Journal of Elastomers and Plastics*, vol. 31, no. 2, pp. 162-179, 1999.
- [11] M. Watanabe, T. Adschiri and K. Arai, "Polyethylene Decomposition via Pyrolysis and Partial Oxidation in Supercritical Water," *Kobunshi Ronbunshu*, vol. 58, no. 12, pp. 631-641, 2001.

- [12] T. Sato, P. H. Trung, T. Tomita and N. Itoh, "Effect of water density and air pressure on partial oxidation of bitumen in supercritical water," *Fuel*, vol. 95, pp. 347-351, 2012.
- [13] M. Watanabe, H. Inomata and K. Arai, "Catalytic hydrogen generation from biomass (glucose and cellulose) with ZrO<sub>2</sub> in supercritical water," *Biomass and Bioenergy*, vol. 22, no. 5, pp. 405-410, 2002.
- [14] H. Tang and K. Kitagawa, "Supercritical water gasification of biomass: Thermodynamic analysis with direct Gibbs free energy minimization," *Chemical Engineering Journal*, vol. 106, no. 3, pp. 261-267, 2005.