Effects of Water to Sucrose Ratio and Pressure on Hydrogen Production During Supercritical Water Reformation of Sucrose

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Abstract

Sucrose, a renewable resource derived from sugarcane or sugar beet, was reformed to hydrogen using supercritical water as a novel reacting medium that acts both as a solvent and a reactant. Supercritical water has been demonstrated as an effective reformation medium for a variety of hydrocarbons including renewable energy sources derived from bioethanol and biodiesel. Temperature and space time were held constant while reactor pressure was varied from 17.94 to 30.90 MPa in a 400 mL Hanyes Alloy 230 tubular reactor and the resultant effect on gaseous hydrogen production was investigated. In addition, the water to sucrose mass ratio was varied from 9 to 28 and the effects on gaseous hydrogen production explored.

Introduction

On-site generation of hydrogen from a variety of feedstocks, both renewable and nonrenewable, may become an essential step in moving towards a hydrogen-based economy. In this regard, the potential for hydrogen production from bio-based or agricultural feedstocks bears some nontrivial significances to the sustainable energy future. A number of studies have been conducted on supercritical water reformation of glucose, fructose, and biomass; however, after an extensive search of the literature no experimental data was found on supercritical water reformation of sucrose. This process is non-catalytic thereby eliminating the problems inherent with the conventional catalytic reformation including catalyst fouling due to coking and catalyst deactivation resulting from sulfur and organonitrogen poisoning. This study was intended to determine the effects of subcritical and supercritical pressures of water on the hydrogen yield which is the ratio of the moles of hydrogen produced to the moles of sucrose fed. In addition, the concentration effects of the feed water to sucrose mixture on hydrogen yield were investigated.

Background

Sucrose is a twelve carbon disaccharide comprised of two six carbon monosaccharides, glucose and fructose. Based, in part, on studies involving supercritical water reformation of glucose and fructose, experimental procedures and operating conditions were determined for these experiments. Studies involving supercritical water reformation of common biomass products such as corn husk, sawdust, and switch grass were additionally considered as the breakdown of the cellulistic structure of these different forms of biomass results in the formation of many glucose molecules which could be broken down further using supercritical water.[1]

Experimental Section

Solution Preparation

The feed sucrose solutions were prepared as shown in Table 1:

Table 1: Sucrose and Deionized Water Amounts Used in Solution Preparation

Runs	Sucrose (g)	DI water (L)	Water to sucrose mass ratio
N/A	1682	15.14	9
WSS-254 – WSS-258	754	6.79	18
WSS-259 – WSS-263	1000	9.00	18
WSS-264	333	6.00	27
WSS-265	1110	10.00	9
WSS-266 – WSS-267	808	15.00	18
WSS-268 – WSS-269	646	12.00	18

It was noted that if feed solutions were left out for more than a few days wild yeast in the air partially fermented the feed solutions. As a result, feed solutions were prepared immediately before the experiments were conducted.

Apparatus

The supercritical water reformation experiments were carried out in a custom-designed experimental process unit, a schematic process flow diagram of which is shown in Figure 1. The unit is comprised of five main components: reactant feed system, Haynes Alloy 230 reactor, ceramic reactor heaters and insulators, integrated heat exchanger, product sample collection system, and data acquisition and control system. The reactant feed system consists of an Eldex high-pressure reciprocating micro-metering pump. Sucrose solutions were fed using a model BBB-4 pump capable of up to 100 mL/min at 34.47 MPa. The balance used for solution mass measurement was an Arlyn-610C with a range of 0-44 kg and reading increments of 0.01 kg. Four zone ceramic heaters were used to heat the reactor. Sample ports on the system allowed for collection of various liquid and gaseous products.[2,3,4]

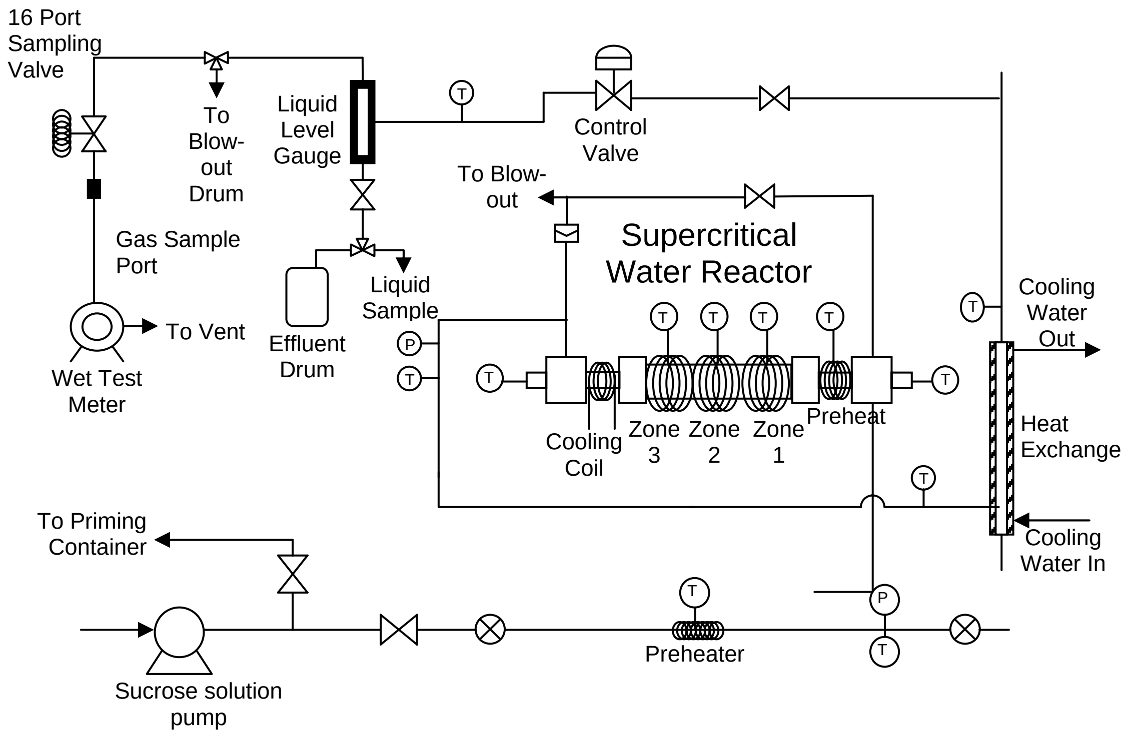

Figure 1: *Process flow diagram of supercritical water reformation unit at MS&T.*

Procedure

The reformation experiments were conducted in the following manner: system start-up to operating conditions, sample and data collection, and system shut-down. System start-up involved bringing the internal temperature and pressure of the supercritical water reactor (SWR) to desired operating conditions. Once the operating temperature was reached water was fed into the system at a desired flow rate and the temperature and pressure were allowed to stabilize before the sucrose solutions were fed into the reactor. The experimental run was started after the temperature, pressure, and reactant flow rates were stabilized. The data acquisition system based on Labview software recorded inlet and outlet pressures, and temperatures at various locations along the system. As the experiments progressed, liquid and gaseous samples were taken for analysis. In addition, the masses of water and sucrose solution fed into the system were recorded. When an experimental run concluded, operating conditions were changed to the next run and the system allowed to stabilize. When experiments were finished the system was shut-down and the reactor was depressurized and allowed to cool.[3,4]

Results and Discussion

Four experiments were conducted to determine the effects of varying water to sucrose ratios on the hydrogen yield. The temperature was maintained between 958 and 963 K and the pressure was approximately 24.13 MPa. The solution flow rate was between 14.9 and 15.6 g/min. The results are summarized in Table 2.

Table 2: Effects of Varying Water to Sucrose Ratios on Hydrogen Yield

Run	T	P	Soln. flow	Water to sucrose ratio	Hydrogen yield
	(K)	(MPa)	(g/min)	(g water / g sucrose)	(mol/mol)
WSS-265	959	24.12	15.3	9.0	3.48
WSS-257	961	24.14	15.3	18.5	4.51
WSS-266	958	23.94	15.6	18.5	5.27
WSS-264	963	24.14	14.9	28.0	5.76

Figure 2 depicts the increase in the hydrogen yield as the water to sucrose ratio was increased. This suggests that sucrose solutions which are more dilute will produce more moles of hydrogen per mole of sucrose fed.

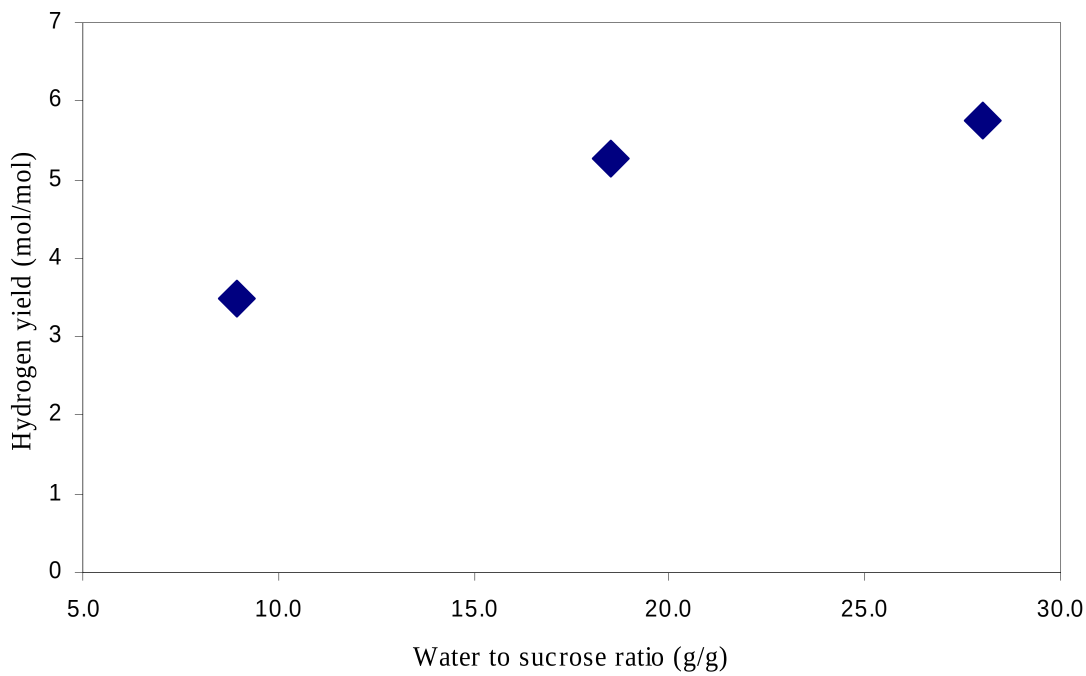

Figure 2: *Water to sucrose ratio vs. hydrogen yield.*

Four experiments were conducted to explore the effects of varying reactor pressure on the hydrogen yield. The temperature was kept between 958 and 962 K and the water/sucrose mass ratio was 18.5. The solution flow rates for these experiments were between 14.8 and 15.6 g/min. A summary of the results is presented in Table 3.

Table 3: Effects of Varying Reactor Pressure on Hydrogen Yield

Run	T	P	Soln. flow	Hydrogen yield
	(K)	(MPa)	(g/min)	(mol/mol)
WSS-259	961	17.94	15.3	2.50
WSS-266	958	23.94	15.6	5.27
WSS-268	961	27.61	14.5	6.20
WSS-269	961	30.90	14.8	6.18

Figure 3 suggests that there is a strong dependence on the hydrogen yield with experimental pressure up to 26 MPa. Beyond this point there is no significant change in the hydrogen yield. This suggest that above the critical point of pure water, 22.06 MPa, pressure has a minimal influence on hydrogen yield; however, between the subcritical and supercritical experiments the hydrogen yield more than doubled from 2.5 at 17.94 MPa to 5.27 at 23.94 MPa. This result most emphatically shows that the supercriticality of the process system is essential for the noncatalytic reformation reaction of sucrose to proceed with a high efficiency. This finding is in agreement with that with the supercritical water reformation of jet fuel.[2]

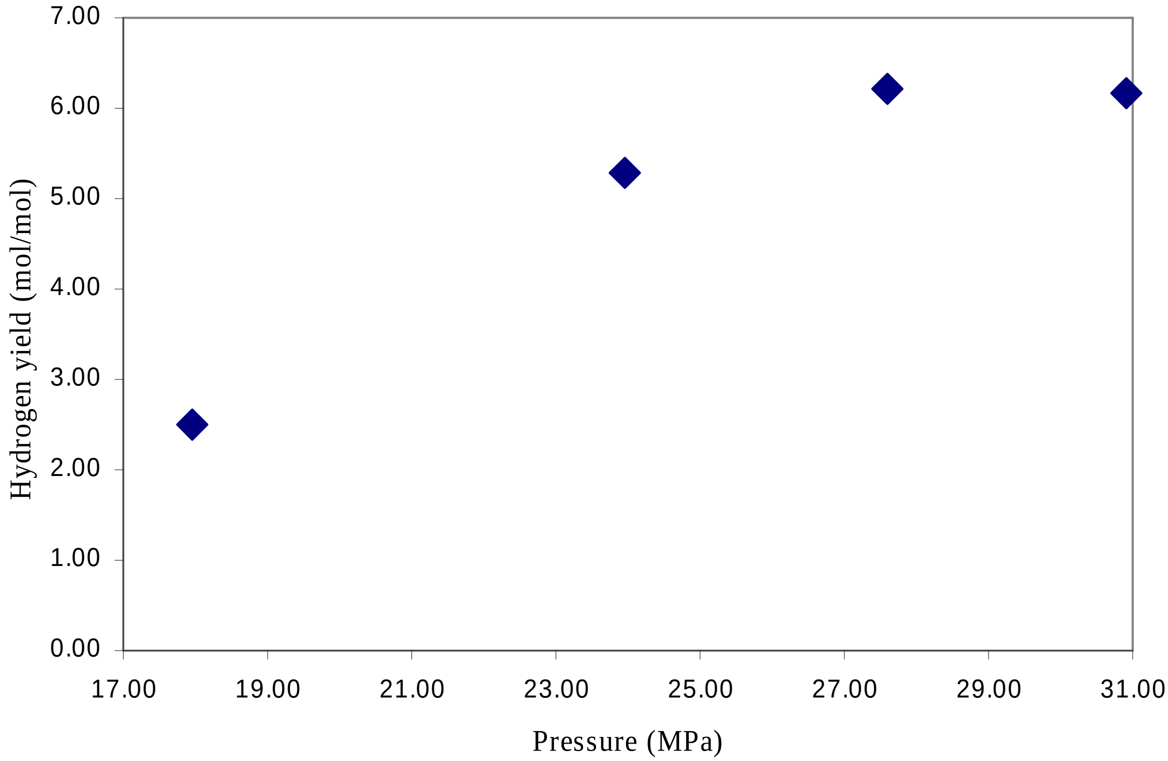

Figure 3: *Pressure vs. hydrogen yield.*

Conclusions

Four non-catalytic supercritical water reformation of sucrose experiments were conducted to determine the effects of varying water to sucrose ratios on hydrogen yield. It was found that hydrogen yields increased as the feed sucrose solution was diluted. These findings were consistent with those found during studies of supercritical water reformation of glucose.[5] A possible explanation for this finding is that sucrose molecules were able to diffuse more readily and react further to completion in more dilute solutions.

Seven reformation experiments were also conducted to examine the effects of reactor pressure on resultant hydrogen yield. It was found that the hydrogen yield increased with increasing reactor pressure up to approximately 26 MPa. Similar studies with glucose and sugarcane bagasse in a cornstarch gel have found that supercritical water reformation processes operated between approximately 25 and 35 MPa had no significant increase in hydrogen yield with increased reactor pressure.[6,7] The experiment conducted at subcritical conditions resulted in a significantly lower hydrogen yield than those performed at supercritical conditions. This provides evidence of the significance of the difference between supercritical water and subcritical water on non-catalyzed water reformation of sucrose.

References

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