MISSOURI S&T

CENTER FOR INFRASTRUCTURE ENGINEERING STUDIES

Control of Ethanol Dehydration in the Supercritical Water Reforming of Ethanol into Hydrogen

by

Jonathan E. Wenzel, Jason W. Picou and Sunggyu Lee

UTC
R166

A University Transportation Center Program
at Missouri University of Science & Technology

Disclaimer

Technical Report Documentation Page

1. Report No.

UTC R166

2. Government Accession No.

3. Recipient's Catalog No.

4. Title and Subtitle

Control of Ethanol Dehydration in the Supercritical Water Reforming of Ethanol into Hydrogen

5. Report Date

February 2008

6. Performing Organization Code

7. Author/s

Jonathan E. Wenzel, Jason W. Picou and Sunggyu Lee

8. Performing Organization Report No.

00010045

9. Performing Organization Name and Address

Center for Infrastructure Engineering Studies/UTC program
Missouri University of Science & Technology
220 Engineering Research Lab
Rolla, MO 65409

10. Work Unit No. (TRAIS)

11. Contract or Grant No.

DTRS98-G-0021

12. Sponsoring Organization Name and Address

U.S. Department of Transportation
Research and Special Programs Administration
400 7th Street, SW
Washington, DC 20590-0001

13. Type of Report and Period Covered

Final

14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

Ethanol, a renewable resource, may be reformed non-catalytically into hydrogen by a novel process utilizing supercritical water which acts synergistically as a solvent and as a reactant. Ethanol reformed by this process does not require energy-intensive separation following fermentation or subsequent distillation. In addition this novel process produces little or no carbon build-up inside the reactor even after days of continuous operation. The principal reactions that occur are: (1) direct reformation of ethanol into hydrogen and carbon oxides, (2) pyrolytic decomposition of ethanol into hydrogen, methane, and carbon oxides, and (3) dehydration of ethanol. Dehydration of ethanol occurs as an undesired reaction in the non-catalytic reformation of ethanol to hydrogen. A preliminary series of supercritical water reformation of ethanol experiments were conducted to validate a novel 400 mL Haynes Alloy 230 tubular reactor for supercritical water reformation process. It is found that the ethanol dehydration reaction is present as a side reaction even in the water-rich mixture of the current process and its byproduct ethylene further undergoes hydrogenation reaction with the process ultimate product, hydrogen, producing ethane. Experiments were performed between 857 K and 1042 K at 24 MPa. The effects of temperature and space time upon molar concentration of ethylene and ethane in the gaseous ambient products are discussed. The optimal process conditions that minimize this wasteful ethane formation are found and experimentally demonstrated

17. Key Words

Transportation faculty, workforce development

18. Distribution Statement

No restrictions. This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

19. Security Classification (of this report)

unclassified

20. Security Classification (of this page)

unclassified

21. No. Of Pages

8

22. Price

Form DOT F 1700.7 (8-72)

Control of Ethanol Dehydration in the Supercritical Water Reforming of Ethanol into Hydrogen

Jonathan E. Wenzel, Jason W. Picou and Sunggyu Lee, Missouri University of Science and Technology

Abstract

Ethanol, a renewable resource, may be reformed non-catalytically into hydrogen by a novel process utilizing supercritical water which acts synergistically as a solvent and as a reactant. Ethanol reformed by this process does not require energy-intensive separation following fermentation or subsequent distillation. In addition this novel process produces little or no carbon build-up inside the reactor even after days of continuous operation. The principal reactions that occur are: (1) direct reformation of ethanol into hydrogen and carbon oxides, (2) pyrolytic decomposition of ethanol into hydrogen, methane, and carbon oxides, and (3) dehydration of ethanol. Dehydration of ethanol occurs as an undesired reaction in the non-catalytic reformation of ethanol to hydrogen. A preliminary series of supercritical water reformation of ethanol experiments were conducted to validate a novel 400 mL Haynes Alloy 230 tubular reactor for supercritical water reformation process. It is found that the ethanol dehydration reaction is present as a side reaction even in the water-rich mixture of the current process and its byproduct ethylene further undergoes hydrogenation reaction with the process ultimate product, hydrogen, producing ethane. Experiments were performed between 857 K and 1042 K at 24 MPa. The effects of temperature and space time upon molar concentration of ethylene and ethane in the gaseous ambient products are discussed. The optimal process conditions that minimize this wasteful ethane formation are found and experimentally demonstrated.

Introduction

Ethanol is a widely available chemical feedstock produced from domestic sources that is a gateway fuel towards energy independence in the United States. Ethanol is commonly used as an oxygenated additive in gasoline in replacement of MTBE for air quality control. An alternative means of utilizing ethanol as an energy source is converting ethanol into hydrogen for use in internal combustion engines and fuel cells. Ethanol is conventionally reformed into hydrogen by means of steam-reforming in the presence of a catalyst. Catalytic reformation of ethanol is susceptible to catalyst poisoning by feedstock impurities, catalyst degradation, coking, and the production of several undesirable products in addition to hydrogen.[1] A novel, non-catalytic, approach to reforming ethanol into hydrogen is to use supercritical water as a reaction medium. In this approach supercritical water acts synergistically both as a solvent and as a reactant.[2] This process is not susceptible to many of the pitfalls of catalytic reformation and was originally developed for the reformation of military logistic fuel (JP-8) to hydrogen.[3] Another advantage supercritical water reformation has over catalytic steam reforming is that supercritical water is denser by orders of magnitude than steam requiring smaller reactor volumes than catalytic reactors.

The reformation products of supercritical water reformation of ethanol include hydrogen, carbon oxides, methane, and ethane. This process completely converts ethanol into gaseous products with no noticeable coking or fouling and with only trace amounts of carbonaceous species in the liquid effluent. In addition most of the carbon oxides are in the form of carbon dioxide thus eliminating the need for a separate water gas shift reactor. In previous work, using a 1-liter tubular Inconel 625 Grade 1 reactor, three principle reactions were determined to occur in the supercritical water reformation of ethanol into hydrogen: (1) direct reformation of ethanol into hydrogen and carbon oxides, (2) pyrolytic decomposition of ethanol into hydrogen, methane, and carbon oxides, and (3) dehydration of ethanol.[2] Kinetic parameters were also regressed for the direct reformation reaction and the pyrolytic decomposition reaction.[4] The third, undesired reaction, dehydration of ethanol to form ethylene and subsequent hydrogenation of ethylene to form ethane was studied in further detail as part of the validation of a novel 400 mL Haynes Alloy 230 tubular reactor for supercritical water reformation of military logistic fuel.

Background

Water is in a supercritical state when its pressure is greater than 22.064 MPa and its temperature is greater than 374°C, as shown in Figure 1.[5] Above these conditions water exhibits both liquid and gas-like properties with heat capacity, thermal conductivity, viscosity, and electrolytic conductivity varying with temperature and pressure. In addition supercritical water has a low dielectric constant in comparison to ambient water, making it a non-polar solvent. As a result water can form a Type I supercritical mixture with ethanol at temperatures and pressures below water's critical point and a continuous critical mixture curve, Figure 2.[6]

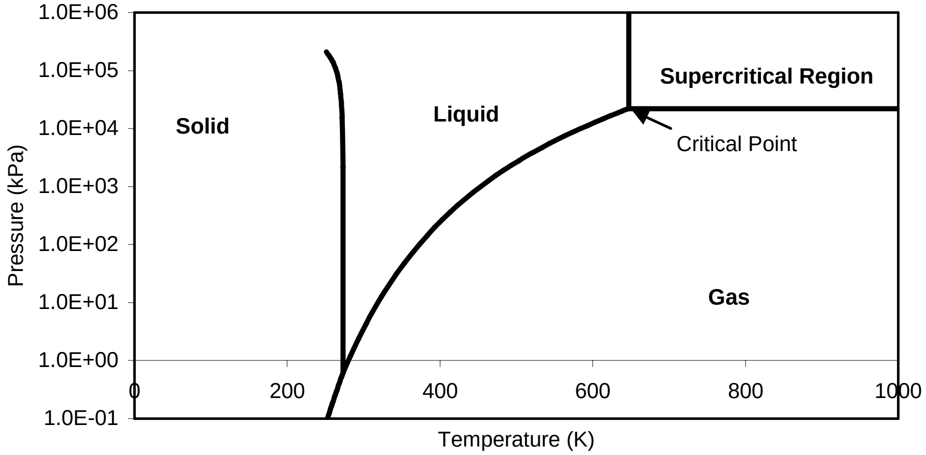

Figure 1: *Phase diagram for water.*

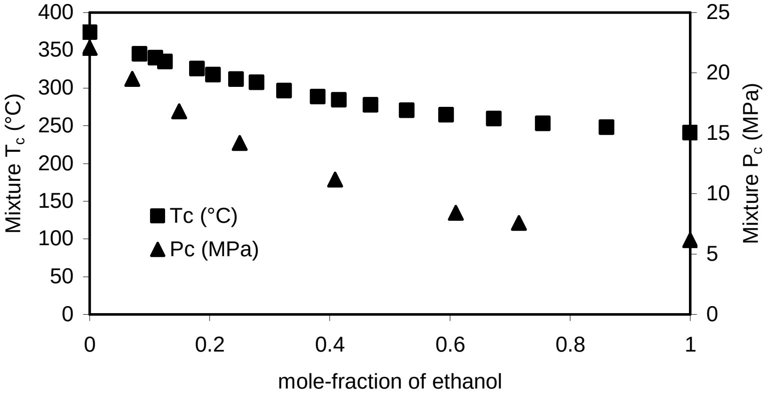

Figure 2: *Experimentally determined critical points of ethanol-water mixtures.*

There are three principal concurrent chemical reactions that occur in supercritical water reformation of ethanol: direct supercritical water reformation, pyrolytic decomposition of ethanol, and dehydration of ethanol. The direct supercritical water reformation reaction is

$$C_2H_5OH + 3\ H_2O \rightarrow 2CO_2 + 6H_2 \qquad (1)$$

On the other hand, the decomposition of ethanol is the summation of the dehydrogenation of ethanol (2) to form acetaldehyde and the decarbonylation of acetaldehyde (3) to form methane and carbon monoxide. Carbon monoxide is then subsequently converted into carbon dioxide by the water gas shift reaction:

dehydrogenation: $C_2H_5OH \rightarrow C_2H_4O + H_2$ (2)
decarbonylation: $C_2H_4O \rightarrow CH_4 + CO$ (3)
water gas shift: $CO + H_2O \rightarrow CO_2 + H_2$ (4)

This reduces to an overall stoichiometric equation:

$$C_2H_5OH + H_2O \rightarrow CH_4 + CO_2 + 2H_2 \qquad (5)$$

In addition, ethanol can be dehydrated to form ethylene which subsequently reacts with hydrogen to form ethane:

dehydration: $C_2H_5OH \rightarrow C_2H_4 + H_2O$ (6)
hydrogenation: $C_2H_4 + H_2 \rightarrow C_2H_6$ (7)

According to Arita et al. (2003)[7], at 773 K in a sealed quartz reactor the principal products of supercritical water reformation of ethanol are acetaldehyde, methane, carbon oxides, ethylene, and ethane. However, the decarbonylation reaction occurs very quickly, in supercritical water reformation in an Inconel 625 Grade 1 reactor acetaldehyde concentrations become negligible[2] above 873 K and in catalyzed systems acetaldehyde concentrations become negligible above 923 K.[8]

Experimental Section

Chemicals

The feed ethanol used for this work was 95% ethanol by volume with the balance being water. The feed water used for this work was distilled and deionized. The carrier gas for the gas chromatograph was Ultra Pure Carrier Grade (UPC 5.5) Argon with a purity of 99.9995%.

Apparatus

Experiments were conducted using a custom-designed Haynes® Alloy 230 supercritical water reformation reactor system. This system consists of a feed system, integrated heat exchanger for heat recovery, reactor, sample collection system, and data acquisition and control system. A schematic process flow diagram is shown in Figure 3. The feed system consists of micrometering pumps for water and ethanol and provides accurate feed-rate measurements for material balances. The reactor is tubular with an internal volume of 383 mL and constructed of Haynes® Alloy 230 permitting supercritical water experiments to be conducted at pressures and temperatures up to 36.3 MPa at 800°C. Various sampling systems allow for the collection of gaseous and liquid effluent from the reactor at ambient conditions for compositional analysis and material balances. A wet-test meter is used for determining the gaseous effluent flow rate.

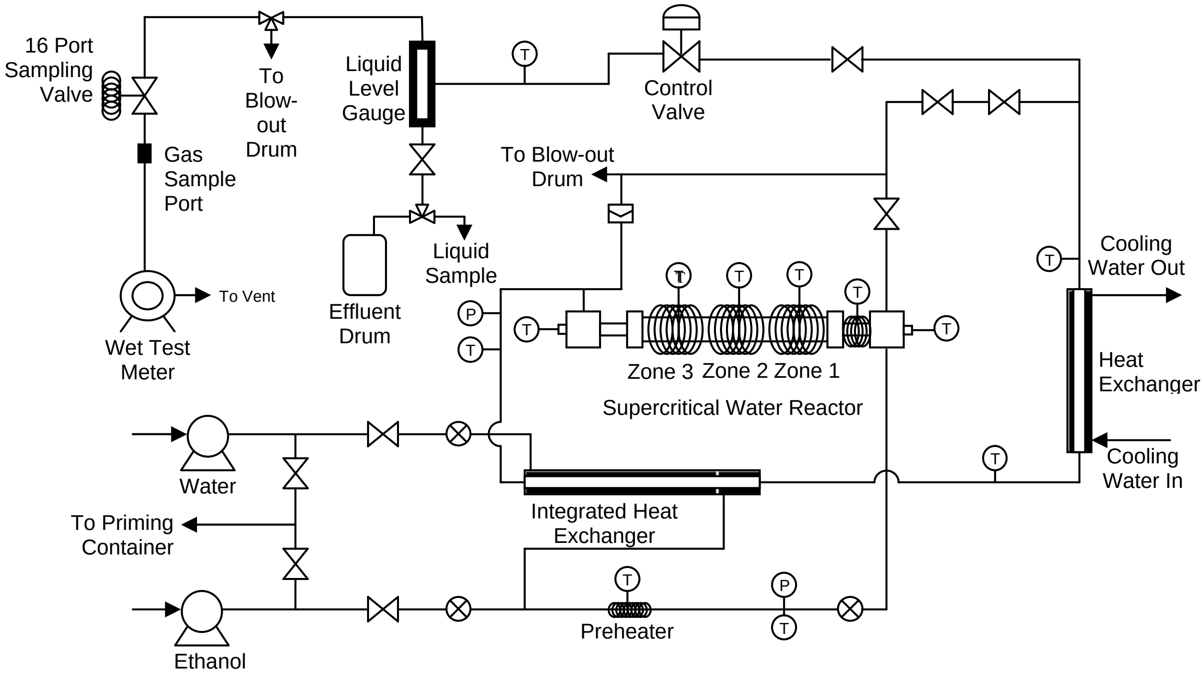

Figure 3: *A schematic of supercritical water reformation system at MS&T.*

Analysis of the gaseous effluent was performed using a HP 5890 Series A gas chromatograph with a thermal conductivity detector. Liquid effluent was analyzed for total carbon content using a Dohrmann DC-190 TOC.

Procedure

Experiments were performed according to the following procedure: start-up of the system to operating conditions, sample and data collection, and shut-down of the system. To start-up the system, the supercritical water reactor (SWR) was heated and once the internal temperature of SWR approached the operating temperature, water was fed into the reactor. Once the SWR inlet temperature and integrated heat exchanger temperature stabilized, the experimental run started by feeding ethanol into the reactor. Depending on the experimental run's residence time, the production of gaseous effluent would reach a steady flow-rate half an hour after ethanol was fed into the reactor. During an experiment, multiple gas and liquid samples were collected and reactant fed rates and effluent flow rates were recorded. The data acquisition and control software recorded temperature and pressure at various locations in the system. At the conclusion of an experimental run, additional experiments were conducted by changing experimental conditions and allowing the system to stabilize. To shut-down the system, the reactor was slowly depressurized and allowed to cool.

Results and Discussion

As part of an evaluation of the Haynes® Alloy 230 reactor, seven ethanol reformation experiments were performed. The experiments were carried out between 850 and 1050 K at a constant pressure of 24.2 MPa. At the conclusion of the experiments the reactor was opened for inspection and found to be free of carbon deposits. The test conditions, ambient reactor effluent gas flow rate, and compositions on a water free basis are listed in Table 1. Table 2 lists the mole fractions of the reactor effluent.

Table 1: Supercritical Water Reformation Conditions and Ambient Gas Effluent Concentrations

Run ID	T / K	EtOH / $g\cdot min^{-1}$	H_2O / $g\cdot min^{-1}$	P / MPa	Gas Rate / $L\cdot min^{-1}$	H_2 / mol-%	CO / mol-%	CH_4 / mol-%	CO_2 / mol-%	C_2H_6 / mol-%	C_2H_4 / mol-%
WE_135	858	0.7	18.8	24.0	0.35	30.8%	26.3%	27.5%	1.7%	9.3%	4.2%
WE_137	896	0.9	20.5	24.2	0.90	25.4%	34.7%	31.2%	1.1%	11.2%	0.7%
WE_138	911	0.9	18.9	24.2	1.10	26.2%	32.9%	29.4%	2.9%	11.1%	0.0%
WE_139	960	0.9	20.1	24.2	1.22	34.4%	20.1%	30.1%	10.5%	9.1%	0.0%
WE_140	1020	0.8	20.8	24.2	1.49	41.6%	4.7%	29.6%	18.8%	4.6%	0.0%
WE_143	1042	0.9	18.8	24.1	1.48	41.9%	1.4%	30.5%	21.1%	2.3%	0.0%
WE_141	1019	0.4	10.5	24.2	0.71	42.4%	1.2%	30.1%	21.5%	3.1%	0.0%

Table 2: Supercritical Water Reformation Feed and Effluent Mole Fractions Acetaldehyde Free Basis

	Reactor Feed			Reactor Effluent Acetaldehyde Free Basis						
Run ID	T / K	EtOH / mol-%	H_2O / mol-%	H_2O / mol-%	H_2 / mol-%	CO / mol-%	CH_4 / mol-%	CO_2 / mol-%	C_2H_6 / mol-%	C_2H_4 / mol-%
WE_135	858	1.37%	98.63%	98.69%	0.40%	0.34%	0.36%	0.02%	0.12%	0.06%
WE_137	896	1.61%	98.39%	96.86%	0.77%	1.04%	0.94%	0.03%	0.34%	0.02%
WE_138	911	1.77%	98.23%	95.88%	1.05%	1.32%	1.18%	0.12%	0.45%	0.00%
WE_139	960	1.76%	98.24%	95.69%	1.42%	0.83%	1.25%	0.43%	0.38%	0.00%
WE_140	1020	1.49%	98.51%	95.12%	2.04%	0.23%	1.46%	0.92%	0.23%	0.00%
WE_143	1042	1.44%	98.56%	95.42%	1.98%	0.06%	1.40%	1.00%	0.14%	0.00%
WE_141	1019	1.76%	98.24%	94.76%	2.26%	0.08%	1.64%	1.14%	0.12%	0.00%

It is important to note that one of the test conditions, Run ID WE_135, is below 873 K. In previous supercritical water reformation studies at temperatures between 773 K and 873 K, ethanol was completely dehydrogenated to form acetaldehyde though there remained detectable quantities of acetaldehyde since the decarbonylation of acetaldehyde did not proceed to completion.[2, 7] Based on an atomic carbon balance in Table 3 between the carbon fed as ethanol and the carbon exiting the reactor as gaseous species at ambient conditions, and the lack of a solid product, it is evident that a there is a liquid product collected ambient conditions for Run WE_135, acetaldehyde. In addition, total carbon analysis of the liquid effluent of Run ID WE_137 had a total carbon content of 2274 ppm, which is indicative that acetaldehyde was not completely converted by the decarbonylation reaction. Closure of the carbon balance at higher temperatures suggests that the decarbonylation reaction has proceeded to close to completion.

The presence of ethylene and ethane are indicative that ethanol is being dehydrogenated, which is remarkable given that the molar ratio of water to ethanol is approximately 60 for the experiments considered. The production of ethylene and ethane as a by-product in the supercritical water reformation of ethanol is a concern due to multiple reasons. First, ethanol is being consumed in reactions that do not produce hydrogen. Second, ethylene could potentially be polymerized producing coke and fouling a reactor. In addition when ethylene is hydrogenated to ethane, hydrogen, the desired product, is consumed. Hence, it is desirable to limit the amount of ethylene and ethane produced. It should be also noted that both ethylene and ethane can be reformed to generate hydrogen in the supercritical water reformation process; however, its kinetic rate is slower than that of the ethanol reformation at the conditions studied in this paper.

Table 3: Atomic Carbon Balance on Carbon exiting the Reactor as a Gaseous Species at Ambient Conditions

Run ID	T / K	Carbon In mmol·min^{-1}	Carbon Out mmol·min^{-1}	Closure
WE_135	858	29.0	11.5	40%
WE_137	896	37.4	32.4	87%
WE_138	911	37.7	38.5	102%
WE_139	960	40.1	38.2	95%
WE_140	1020	35.0	36.9	105%
WE_143	1042	17.0	16.7	98%
WE_141	1019	37.4	34.0	91%

At temperatures of 896 K and below, detectable amounts of ethylene are observed, whereas at higher temperatures ethylene concentrations are below detection limits. When comparing runs WE_135 and WE_137 it is apparent that the hydrogenation of ethylene to ethane is less active at lower temperatures. It may be possible that either the hydrogenation reaction is less active due to lower temperatures or at the lower temperature experiments the mole fraction of hydrogen was lower (Table 2). It is likely that both circumstances are contributing to the detectable presence of ethylene which merits further study. In experiments at temperatures of 911 K and above, all the ethanol fed is converted to gaseous products and ethylene is completely hydrogenated into ethane. In addition at higher temperatures more gaseous effluent is produced as shown in Table 1 and ethane is less abundant. This is indicative that ethanol is preferentially being reformed instead of being dehydrated. The effect of temperature upon the combined mole fractions of ethylene and ethane are shown in Figure 4.

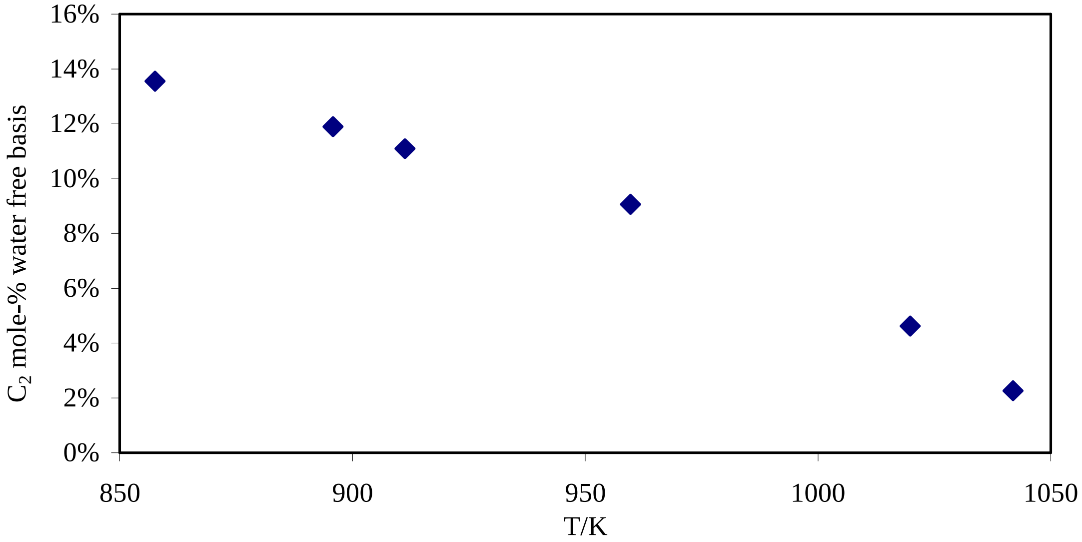

Figure 4: *Combined mole fraction of ethylene and ethane versus temperature.*

Experimental Runs WE_140 and WE_141 provide a comparison of the effect of residence time upon conversion of ethanol in supercritical water reformation. Run WE_140 has approximately half the residence time of WE_141. At an increased residence time hydrogen content of the reactor effluent increases while ethane content of the reactor effluent decreases. This may be attributable to the contributions of the ethane reformation that takes place simultaneously in the reactor, thereby deceasing the ethane concentration while increasing the hydrogen yield. Kinetic studies to determine the effect of residence time and temperature in a Haynes® Alloy 230 reactor would provide considerable insight on minimizing the ethanol dehydration reaction while maximizing ethanol reformation.

Conclusions

Supercritical water is used as a solvent and as a reactant in the non-catalytic reformation of ethanol into hydrogen. Three principal reactions that occur in the supercritical water reformation of ethanol are (1) direct reformation into hydrogen and carbon dioxide, (2) pyrolytic decomposition of ethanol into methane, carbon dioxide, and hydrogen, and (3) dehydration of ethanol. The supercritical water reformation of ethanol was studied in order to produce hydrogen from renewable feedstocks such as corn ethanol and also as part of the validation trials of a novel supercritical water reactor constructed of Haynes® Alloy 230. It was found that the undesired competing reaction in supercritical water reformation, the dehydration of ethanol is less pronounced as temperature is increased in relation to the reformation reactions when the reactant feed rates and reactor pressure are kept constant. Also an increase in reactor residence time may decrease the selectivity of the dehydration of ethanol over that of the reformation of ethanol to hydrogen.

Acknowledgments

This work was supported by a grant from National University Transportation Center (NUTC), U.S. Department of Transportation. The major parts of the experimental hardware system were developed using financial support from DRS Technical Services, Inc. The authors are also grateful for helpful comments provided by Dr. H. Bryan Lanterman.

References

1. Morgenstern, D. A.; Fornango, J. P., Low-temperature reforming of ethanol over copper-plated raney nickel: a new route to sustainable hydrogen for transportation. *Energy & Fuels* 2005, 19, 1708-1716.
2. Wenzel, J.; Picou, J.; Factor, M.; Lee, S., Kinetics of Supercritical Water Reformation of Ethanol to Hydrogen. In *Materials Science & Technology 2007 Conference and Exhibition*, Detroit, Michigan, 2007.
3. Lee, S.; Lanterman, H. B.; Wenzel, J. E.; Edwards, N.; Adams, A.; Wootton, J.; Garcia, A., Noncatalytic direct reformation of JP-8 fuel in supercritical water. *Preprints - American Chemical Society, Division of Petroleum Chemistry* 2006, 51, 487-490.
4. Wenzel, J. E.; Niemoeller, A.; Stever, M. S.; Lee, S., Kinetics of Reforming Ethanol into Hydrogen in a Supercritical Water Medium. In *2007 AIChE Annual Meeting*, Salt Lake City, Utah, 2007.
5. IAPWS *Release on the pressure along the melting and the sublimation curves of ordinary water substance*; The International Association for the Properties of Water and Steam: Milian, Italy, September, 1993; pp 1-4.
6. Hicks, C. P.; Young, C. L., The gas-liquid critical properties of binary mixtures. *Chem. Rev.* 1975, 79, 119-175.
7. Arita, T.; Nakahara, K.; Nagami, K.; Kajimotoa, O., Hydrogen generation from ethanol in supercritical water without catalyst. *Tetrahedron Letters* 2003, 44, 1083-1086.

8. Deluga, G. A.; Salge, J. R.; Schmidt, L. D.; Verykios, X. E., Renewable Hydrogen from Ethanol by Autothermal Reforming. *Science* 2004, 303, (5660), 993-997.