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On-Site Generation of Hydrogen from Ethanol

by

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On-Site Generation of Hydrogen from Ethanol

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Abstract

Supercritical water is a synergistic, non-catalytic media for the reformation of crude ethanol feedstocks into hydrogen. The kinetics of the supercritical water reformation of ethanol was experimentally studied in a tubular reactor made of Inconel 625 alloy. The high enthalpy level of supercritical water and the extraordinary solubility of reaction components in supercritical water allow the reformation reaction to proceed without the presence of a heterogeneous catalyst. The principal reactions are pyrolytic decomposition and reformation of ethanol, which are competing in nature. The products of both reactions are quite similar yielding both hydrogen and carbon oxides, except that the former reaction also generates methane which undergoes further reformation in the supercritical water medium. The competitive nature of the reformation and pyrolytic decomposition reactions along with the water gas shift reaction in the supercritical reformation process was elucidated from a mechanistic standpoint. Kinetic rate information as well as the optimal process operating conditions were obtained for the supercritical water reformation process.

Introduction

The production of energy from bio-based feedstocks is an integral component towards energy independence in the United States. In order to evolve towards a hydrogen-based economy, several technological issues have to be addressed including the production of hydrogen from domestic sources, especially renewable resources. One means of producing hydrogen is by reforming ethanol, a renewable agricultural product. Ethanol may be steam-reformed into hydrogen by means of catalysis; however catalysts are susceptible to poisoning, coking, degradation, and also may produce several undesirable by-products in addition to hydrogen¹. In addition catalytic reformation of ethanol may also require additional process steps such as water gas shift and secondary methane reforming.

An alternative to catalytic reformation of ethanol to hydrogen is a novel noncatalytic approach using supercritical water, where supercritical water acts synergistically as a potent solvent and as an energetic reactant. The original process was initially developed for reforming military logistic fuel (JP-8) to hydrogen² but has also been demonstrated to be capable of reforming ethanol into hydrogen as well. The resultant products of reformation were hydrogen, carbon oxides, methane, and ethane, with no noticeable coking and a complete conversion of ethanol to gaseous species. In order to optimize this novel process it is necessary to elucidate the reaction pathways by which ethanol is reformed and to determine kinetic parameters. In addition the experimental data obtained was analyzed to determine possible optimal operating conditions. The experiments were conducted in a 1-liter tubular Inconel 625 (Grade 1) reactor between 630°C and 710°C at 24.2 MPa.

Background

Supercritical Fluids

Chemical species, water included, have three distinguishable phases: solid, liquid, and gas. The phase boundaries for the phases of water are illustrated in Figure 1 which was derived from correlations printed in a circular³. When water is above both its critical temperature, $T_c=374^\circ\text{C}$, and pressure, $P_c=22.4\text{ MPa}$, the phase separation between liquid and gas becomes indistinguishable and is considered a supercritical fluid.

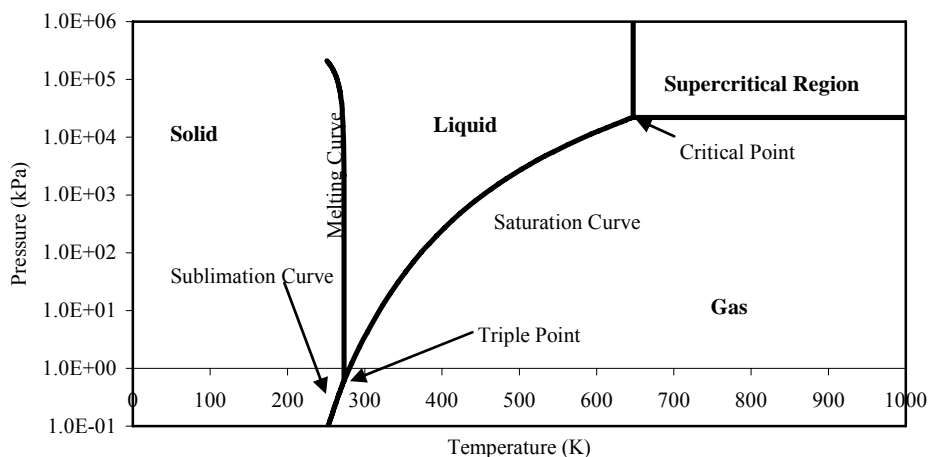


Figure 1 Phase diagram for water.

Above the critical point, water will exhibit both liquid-like and gas-like properties which are dependent upon temperature and pressure. Heat capacity, thermal conductivity, viscosity, and electrolytic conductivity can be varied by changing the temperature and pressure of supercritical water. In addition as temperature and pressure of water increase up to the critical point of water, the dielectric constant drastically decreases. At supercritical conditions, water is no longer a polar solvent and can readily dissolve a variety of nonpolar compounds and form supercritical mixtures. Binary supercritical mixtures such as ethanol and water have a continuous critical mixture curve, as shown in Figure 2⁴.

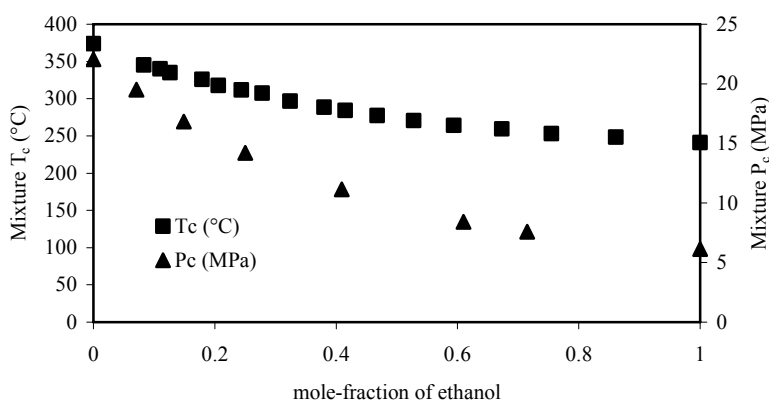


Figure 2 Experimentally determined critical points of ethanol-water mixtures

An accurate determination of the ethanol-water critical loci is necessary for ascertaining if the operating conditions for reforming ethanol are indeed supercritical. In addition an accurate estimate of the ethanol-water mixture density at experimental conditions is important for determining reactor residence time. Ethanol-water mixture densities for this work were calculated using the Peng-Robinson-Stryjek-Vera equation of state (PRSV-2 EOS). In order to optimize the predictive abilities of PRSV-2 EOS a binary interaction parameter, $k_{ij}=-0.051866$, was used⁵. Critical properties of various compounds of interest are presented in Table 1⁶.

Table 1 Critical and Physical Properties of Some Species Present in Ethanol Reforming

Species	H ₂ O	CH ₃ CH ₂ OH	H ₂	CO	CO ₂	CH ₄	C ₂ H ₆
CAS #	7732-18-5	64-17-5	1333-74-0	630-08-0	124-38-9	74-82-8	74-84-0

MW	18.015	46.069	2.016	28.01	44.01	16.043	30.07
T _c (K)	647.14	513.92	32.98	132.85	304.12	190.56	305.32
P _c (bar)	220.64	61.48	12.93	34.94	73.74	45.99	48.72
V _c (cm ³ ·mol ⁻¹)	55.95	167	64.2	93.1	94.07	95.6	145.5
Z _c	0.229	0.24	0.303	0.292	0.274	0.286	0.279
w	0.344	0.649	-0.217	0.045	0.225	0.011	0.099

Reaction Pathways for Ethanol Reformation

The overall reformation reaction of ethanol may be written as:



Several mechanistic reactions for the catalytic reformation of ethanol have been elucidated. The first steps in these various pathways include:

1. Dehydration of ethanol to ethylene



2. Pyrolytic decomposition of ethanol to methane, carbon monoxide, and hydrogen



3. Dehydrogenation of ethanol to acetaldehyde



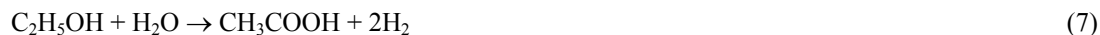
4. Decomposition of ethanol to acetone



5. Reforming of ethanol to syngas



6. Formation of acetic acid by dissociative absorption of water



Coking hampers several catalytic efforts by polymerization of ethylene and methylene radicals to polycyclic aromatic hydrocarbons, by the decomposition of methane, or by the Boudouard reaction. Other disadvantages of using catalysts for reforming are that some catalysts will become deactivated in a short period of time, are susceptible to poisoning, fouling, and degradation⁷.

Noncatalytic reforming of ethanol using supercritical water has several distinct advantages: the inherent problems of using catalysts are avoided; carbon fouling is eliminated, supercritical water is denser than steam allowing for a smaller reactor volume, and single-pass conversion of ethanol is near 100%. In the reformation of ethanol using supercritical water, the reformation pathways that were elucidated for catalytic reforming may be narrowed down substantially. There are three principal reactions concurrently occurring in the supercritical water reformation of ethanol.

1. Direct supercritical water reformation of ethanol



2. Pyrolytic decomposition of ethanol which is followed by the reformation of methane and the water gas shift reaction



3. Dehydration of ethanol to ethylene followed by hydrogenation of ethylene to ethane



Of the three competing reactions, the first is most desirable, while the second reaction also generates gaseous products which are similar to the reformation products. The dehydration of ethanol, if not controlled properly, can lead to the formation of coking precursors via further dehydrogenation and cyclization polymerization of ethylene, acetylene, and methylene radicals. However, coking due to ethylene precursors is typically avoided by the hydrogenation of ethylene to ethane, which has the drawback of consuming hydrogen, the desired product. Further, both ethane and ethylene can also be reformed by reacting with supercritical water, thus producing hydrogen and carbon oxides.

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 and Procedure

Experiments were conducted using a custom-designed Inconel 625 (Grade 1) supercritical water reformation reactor system. This system consists of a feed system, integrated heat exchanger, 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 integrated heat exchanger allows for heat recovery from the effluent of the reactor by heating the water being fed to the reactor. The tubular reactor is constructed of Inconel 625 which permits supercritical water experiments to be conducted over a wide range of pressures and temperatures up to 24.2 MPa at 710°C, or up to 33.6 MPa at 650°C. The internal reactor volume is 926 mL. 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. During operation, the data acquisition and control system collects temperature and pressure data and controls the temperature and pressure inside the reactor.

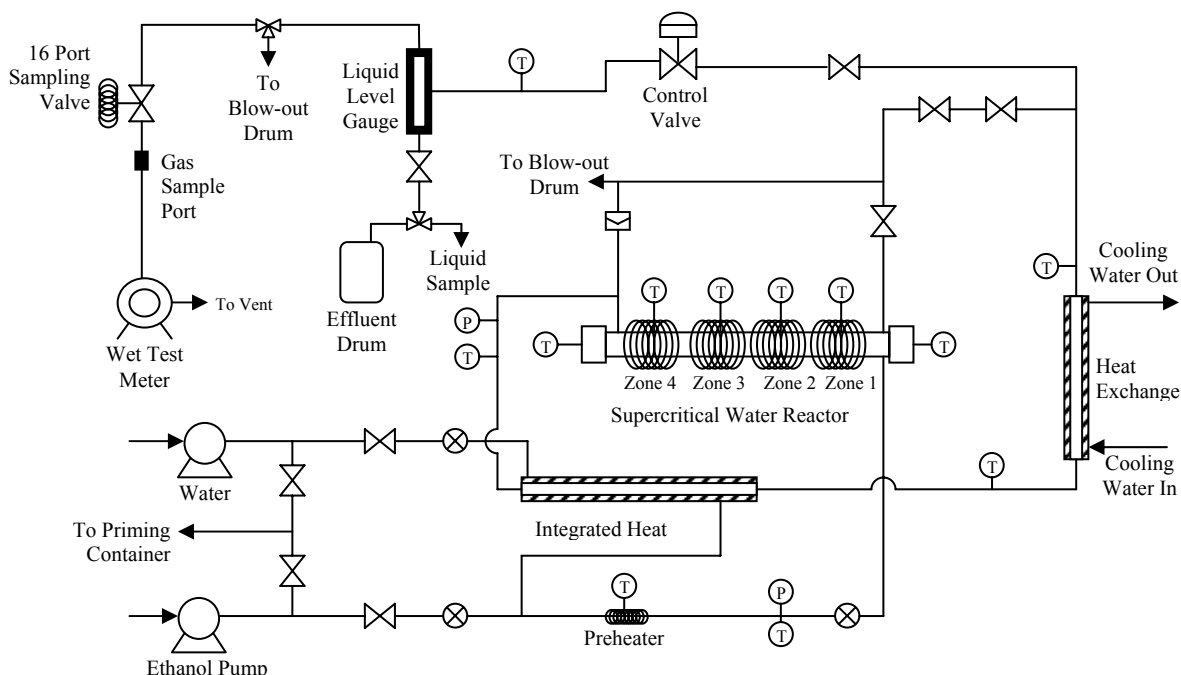


Figure 3 A schematic of supercritical water reformation system at UMR

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) is heated and once the internal temperature of SWR approaches the operating temperature, water is fed into the reactor. Once the SWR inlet temperature and integrated heat exchanger temperature stabilizes, the experimental run starts by feeding ethanol into the reactor. Depending on the experimental run's residence time, the production of gaseous effluent should reach a steady flow-rate half an hour after ethanol is fed into the reactor. During an experiment, multiple gas and liquid samples are collected. In addition, water and ethanol flow rates, liquid effluent flow rates, and gas effluent flow rates are recorded. The data acquisition and control software records temperature and pressure at various locations in the system. An experimental run typically lasts 90 minutes. At the conclusion of an experimental run, additional experiments may be conducted by setting the new run conditions and allowing at least 60 minutes for system to stabilize. To shut-down the system, all heaters are turned off and the reactor is slowly depressurized.

Experimental

A central composite circumscribed (CCC) design of experiments (DOE) was conducted to determine the optimal operating conditions of the ethanol reformation process. Important process variables are based on previous work with jet fuel reformation^{2,8} and include pressure, temperature, ethanol feed rate, and water feed rate. For design of experiments pressure was fixed at 24.2 MPa. The rationale for choosing a fixed pressure for the design matrix is based on the preliminary experimental results with JP-8 reformation, which indicate that as long as the supercritical condition is assured, further increase in pressure does not exhibit a favorable effect on the process conversion efficiency⁸. The three remaining variables for the CCC DOE are shown in Table 2. Temperature was centered at $670 \pm 20^\circ\text{C}$, ethanol flow rate at $1.000 \pm 0.375 \text{ g}\cdot\text{min}^{-1}$, and water flow rate at $12 \pm 3 \text{ g}\cdot\text{min}^{-1}$. For these experiments α was set to 2. Three center-point experiments were also performed for an error estimate.

Table 2 Design of experiments for supercritical water reforming

Run ID	DOE Line	T (°C)	Ethanol Flow (g·min ⁻¹)	Water Flow (g·min ⁻¹)	Run ID	DOE Line	T (°C)	Ethanol Flow (g·min ⁻¹)	Water Flow (g·min ⁻¹)
WE_I	1	650	0.625	9	WE_G	10	670	1.000	12
WE_J	2	690	0.625	9	WE_C	11	670	1.000	12
WE_D	3	650	1.375	9	WE_F	12	630	1.000	12

WE_P	4	690	1.375	9	WE_A	13	710	1.000	12
WE_Q	5	650	0.625	15	WE_N	14	670	0.250	12
WE_L	6	690	0.625	15	WE_K	15	670	1.750	12
WE_E	7	650	1.375	15	WE_M	16	670	1.000	6
WE_B	8	690	1.375	15	WE_H	17	670	1.000	18
WE_O	9	670	1.000	12					

Results and Discussion

Seventeen supercritical water reformation experiments of ethanol were conducted using the Inconel 625 reactor system and a central composite circumscribed design of experiments. The operating conditions, ambient pressure effluent rates, and gas composition are presented in Table 3. The liquid effluent collected averaged a total carbon content of 10 ppm. This is indicative that ethanol was completely converted to gaseous species. At the conclusion of the design matrix the interior of the reactor was found to be free of deposits, which indicates that the supercritical water reformation of ethanol at the conditions considered did not result in coking or fouling of the reactor. This is also reflected in an effective closure of carbon balances in Table 4, based on ethanol feed and gaseous effluent.

Table 3 Design of experiments for supercritical water reforming

Run ID	DOE Line	Observed				Effluent Rates		Outlet Gas Mole fractions				
		T (°C)	EtOH Flow (g·min ⁻¹)	H ₂ O Flow (g·min ⁻¹)	Pressure (Mpa)	Gas (L·min ⁻¹)	Liquid (g·min ⁻¹)	H ₂ (mol-%)	CO (mol-%)	CH ₄ (mol-%)	CO ₂ (mol-%)	C ₂ H ₆ (mol-%)
WE_I	1	657.6	0.52	9.3	23.96	1.18	9.04	53.1%	0.4%	19.7%	21.7%	2.1%
WE_J	2	693.4	0.61	9.3	24.24	1.44	11.06	58.2%	0.5%	16.8%	21.5%	1.6%
WE_D	3	657.1	1.55	9.2	24.19	3.19	8.85	49.7%	2.4%	22.8%	22.3%	3.0%
WE_P	4	693.5	1.55	9.3	24.20	3.20	8.95	51.0%	2.0%	23.5%	22.6%	2.0%
WE_Q	5	656.0	0.59	13.6	24.30	1.35	13.52	56.1%	0.4%	19.2%	23.4%	1.8%
WE_L	6	691.1	0.58	13.7	24.24	1.42	13.45	57.4%	0.1%	18.0%	21.3%	1.6%
WE_E	7	657.2	1.55	14.1	24.20	3.22	14.49	51.5%	1.5%	21.0%	22.8%	2.7%
WE_B	8	693.4	1.55	16.1	24.22	3.52	17.12	53.0%	1.6%	19.9%	22.5%	1.8%
WE_O	9	670.5	0.93	11.6	24.18	2.02	11.31	53.0%	0.7%	19.9%	22.7%	2.2%
WE_G	10	670.8	0.92	11.4	23.83	2.06	10.97	52.6%	0.7%	20.6%	23.4%	2.2%
WE_C	11	671.0	0.90	11.4	24.20	2.02	10.75	52.8%	1.0%	19.8%	22.9%	2.1%
WE_F	12	628.2	0.91	11.3	24.18	2.13	10.74	54.1%	0.6%	18.9%	23.0%	1.7%
WE_A	13	709.8	0.93	11.4	24.21	2.19	11.23	53.4%	1.6%	18.3%	22.4%	0.9%
WE_N	14	670.6	0.17	11.5	24.19	0.43	11.37	60.0%	0.0%	15.1%	22.7%	1.6%
WE_K	15	670.0	2.02	11.3	24.23	4.17	11.39	49.1%	1.9%	23.4%	22.2%	3.1%
WE_M	16	671.0	0.91	6.4	23.98	1.90	6.19	49.4%	1.3%	23.0%	21.5%	2.4%
WE_H	17	668.2	0.90	19.7	24.18	2.16	17.80	54.1%	0.7%	18.4%	22.9%	2.2%

Mechanistic Elucidation

The supercritical water reformation of ethanol produces hydrogen and carbon monoxide, which further reacts with supercritical water via the forward water gas shift reaction as:



The resultant reaction, direct reformation of ethanol, is a combination of these two reactions



Based on the experimental results of Table 3, the extent of the water gas shift reaction in the supercritical water reformation process under the conditions studied is found to be quite significant, typically ranging over 90%. This experimental result is noteworthy, since the water gas shift reaction in this process proceeds without an aid of any heterogeneous catalyst. Further, the result indicates that the forward water gas shift reaction at the conditions studied proceeds without being limited by chemical equilibrium. If all ethanol molecules fed were converted solely via this reaction (1), the molar ratios of CH₄/CO₂ and H₂/CO₂ would become 0:1 and 3:1, respectively.

Table 4 Residence time, ethanol to water ratio, molar ratios, and carbon balance

Run ID	DOE Line	T (°C)	τ (sec)	C ₂ H ₅ OH/H ₂ O			Carbon Balance	
				(by mass)	H ₂ /CO _x	H ₂ /CH ₄	CH ₄ /CO _x	Closure

WE_I	1	657.6	356.09	5.4%	2.403	2.696	0.891	98.0%
WE_J	2	693.4	339.41	6.4%	2.647	3.463	0.764	92.0%
WE_D	3	657.1	348.49	16.5%	2.011	2.184	0.921	103.0%
WE_P	4	693.5	324.10	16.2%	2.070	2.168	0.955	101.4%
WE_Q	5	656.0	249.80	4.2%	2.361	2.921	0.808	99.8%
WE_L	6	691.1	235.08	4.1%	2.696	3.187	0.846	98.1%
WE_E	7	657.2	232.79	10.7%	2.121	2.450	0.866	99.0%
WE_B	8	693.4	193.67	9.4%	2.204	2.664	0.827	101.0%
WE_O	9	670.5	281.27	7.9%	2.260	2.660	0.850	96.9%
WE_G	10	670.8	280.55	7.9%	2.188	2.558	0.855	103.0%
WE_C	11	671.0	285.33	7.7%	2.209	2.668	0.828	100.3%
WE_F	12	628.2	307.78	7.8%	2.288	2.862	0.799	100.9%
WE_A	13	709.8	268.34	8.0%	2.227	2.910	0.765	97.2%
WE_N	14	670.6	290.75	1.5%	2.640	3.963	0.666	96.8%
WE_K	15	670.0	275.47	17.4%	2.040	2.098	0.972	103.5%
WE_M	16	671.0	486.19	13.8%	2.166	2.143	1.011	98.8%
WE_H	17	668.2	168.15	4.4%	2.297	2.937	0.782	104.9%

The presence of methane in the effluent gas, in relatively high concentrations, between 15.1 and 23.5 mol-%, suggests ethanol is also being decomposed:

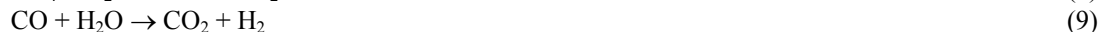


The resultant stoichiometric equation from combining the two reactions reduces to



If all ethanol molecules fed were converted by this reaction, the molar ratios of CH_4/CO_2 and H_2/CO_2 would be 1:1 and 2:1, respectively. Further, more importantly, the molar ratio of H_2/CH_4 would become 2:1. The ratio of H_2/CH_4 has an extra significance, since the goal of reformation, whether it involves ethanol or hydrocarbons as a starting reactant, is to produce more hydrogen than methane. Therefore, the ratio of H_2/CH_4 , which is the selectivity of hydrogen as a product, may be directly used as an optimization variable, as long as the conversion of ethanol is complete or near complete.

At higher temperatures, methane can be further reacted via methane reformation and subsequent water gas shift reaction^{2, 8}:



The resultant stoichiometric equation combining all three reactions, i.e., Eqns (3), (8), and (9), would become essentially the same as the direct reformation reaction of ethanol as:



As a result, a vital question regarding the mechanistic pathway for noncatalytic ethanol reformation in the supercritical water medium now becomes whether the reformation reaction proceeds via direct reformation, reaction (1), to produce hydrogen and carbon dioxide, or indirectly via methane reformation (3, 8, & 9) to produce hydrogen and carbon dioxide. Based on the preliminary study of JP-8 reformation kinetics⁸, it was found that the reformation of methane at temperatures lower than 690°C is not appreciably significant. Thus, the methane reformation reaction was not heavily involved in most of the design point runs, except the ones for 710°C, listed in Table 3.

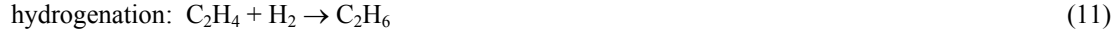
As can be clearly seen in Table 4, the molar ratios of CH_4/CO_2 and H_2/CO_2 for all experimental runs range between 0-1:1 and 2-3:1, respectively. This further indicates that the both reactions represented by Eq. (1) and Eq. (12) are competitively taking place in the reaction system at the conditions investigated in the current study.

Carbon monoxide appears in relative low concentrations, between 0 and 2.4 mol-%. Since carbon monoxide does not appear in equal molar quantities as methane and that there is an abundant presence of carbon dioxide is indicative that the water gas shift reaction is active at the conditions tested:



It is important to note that the water gas shift reaction is a reversible reaction whose equilibrium can be easily reversed by imposed conditions. At the temperatures at which the experiments were conducted, the water gas shift reaction should be limited by chemical equilibrium or occurring predominantly in the reverse direction. A possible explanation is attributable to the fact that the high concentration of water is driving the water gas shift reaction in the forward direction. Another explanation is due to the fact that there may be more than one phase in the reactor, a hydrogen rich phase and a hydrogen poor phase that contains mostly water and carbon-containing species. If hydrogen is not present in a phase where water and carbon monoxide is present, the water gas shift reaction would proceed in the forward direction without the full influence of equilibrium limitation.

The presence of ethane suggests that there is an undesirable competing reaction, even though not dominant. Ethylene, a potential coking precursor, can be produced by dehydration of ethanol. If there is a sufficient amount of product hydrogen present ethylene can be hydrogenated *in situ* to form ethane by the following reactions:



Absence of acetylene in the product stream also indicates that the reaction environment is more hydrogenating rather than dehydrogenating ethylene.

Kinetics

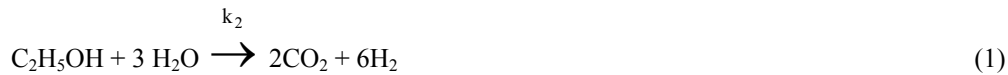
Since all of the reactant, ethanol, was consumed in the reformation reactions, the kinetic model is based on carbon balances and the conversion of ethanol to methane and the conversion of ethanol to hydrogen. Global first-order kinetics is assumed for the pyrolytic decomposition of ethanol to methane:



with the rate of disappearance of ethanol for the decomposition reaction as

$$-\frac{dC_A}{dt} = k_1 C_A \quad (13)$$

For the direct reformation of ethanol into carbon dioxide a multiplicative factor of the molar ratio of ethanol to water, Φ^n , is included in the global first-order rate expression:



with the rate of disappearance of ethanol for the reformation reaction:

$$-\frac{dC_A}{dt} = k_2 \Phi^n C_A \quad (14)$$

The overall rate expression for the disappearance of ethanol is

$$-\frac{dC_A}{dt} = k_1 C_A + k_2 \Phi^n C_A \quad (15)$$

with the integrated rate expression as follows:

$$C_A = C_{A0} \exp[-(k_1 + \Phi^n k_2)t] \quad (16)$$

the rates of generation of methane and hydrogen may be expressed as a function of the concentration of ethanol and are

$$\frac{dC_E}{dt} = k_1 C_A \quad (17)$$

$$\frac{dC_C}{dt} = 2k_1 C_A + 6k_2 \Phi^n C_A \quad (18)$$

by substituting (16) into equations (17) and (18) and integrating, the expressions for the concentrations of hydrogen and methane are

$$C_C = C_{A0} \frac{2k_1 + 6\Phi^n k_2}{k_1 + \Phi^n k_2} \left(1 - \exp\left[-(k_1 + \Phi^n k_2)t\right]\right) \quad (19)$$

$$C_E = C_{A0} \frac{k_1}{k_1 + \Phi^n k_2} \left(1 - \exp\left[-(k_1 + \Phi^n k_2)t\right]\right) \quad (20)$$

where C_{A0} is the initial concentration of ethanol, k_1 and k_2 are first order rate constants, and Φ^n is the molar ratio of ethanol to water. These equations can be solved simultaneously to find the rate constants k_1 and k_2 by setting C_{A0} as the inlet concentration of ethanol in moles per liter, C_E is the outlet concentration of methane in moles per liter, and C_C is the outlet concentration hydrogen.

The rate coefficients may then be regressed using a commercially available software package such as Maple. The calculated rate coefficients for the decomposition reaction and the reformation reaction are tabulated in Table 5.

Table 5 Calculated rate coefficients for the pyrolytic decomposition (1) and direct reformation (2) reactions.

Run ID	DOE Line	$\Phi^{1.5}$	T^{-1}/K^{-1}	k_1	k_2
WE_I	1	3.084E-03	1.074E-03	0.260636	0.030229
WE_J	10	5.424E-03	1.059E-03	0.334345	0.031075
WE_D	11	5.249E-03	1.059E-03	0.301882	0.033630
WE_P	12	5.354E-03	1.109E-03	0.272997	0.039233
WE_Q	13	5.522E-03	1.017E-03	0.302477	0.045853
WE_L	14	4.301E-04	1.060E-03	0.246838	0.080759
WE_E	15	1.778E-02	1.060E-03	0.317803	0.005209
WE_B	16	1.255E-02	1.059E-03	0.190206	0.004518
WE_O	17	2.292E-03	1.062E-03	0.553869	0.086538
WE_G	2	3.987E-03	1.035E-03	0.202829	0.049462
WE_C	3	1.637E-02	1.075E-03	0.238523	0.007298
WE_F	4	1.592E-02	1.035E-03	0.284378	0.007959
WE_A	5	2.138E-03	1.076E-03	0.363529	0.055794
WE_N	6	2.059E-03	1.037E-03	0.395480	0.078271
WE_K	7	8.586E-03	1.075E-03	0.341979	0.025633
WE_M	8	7.073E-03	1.035E-03	0.447696	0.049562
WE_H	9	5.431E-03	1.060E-03	0.288272	0.031716

The Arrhenius activation energy is defined by

$$k = A e^{-E_a/R T} \quad (21)$$

where k is the rate coefficient, A is the frequency factor, E_a is the activation energy, R is the gas law constant, and T is absolute temperature. The activation energy may be determined by linear regression of the natural log of the rate coefficient versus the inverse of the temperature. The natural log of the mean of the rate coefficient for the pyrolytic decomposition reaction and the direct reformation reaction at the design of experiment's test temperatures are plotted in Figure 4.

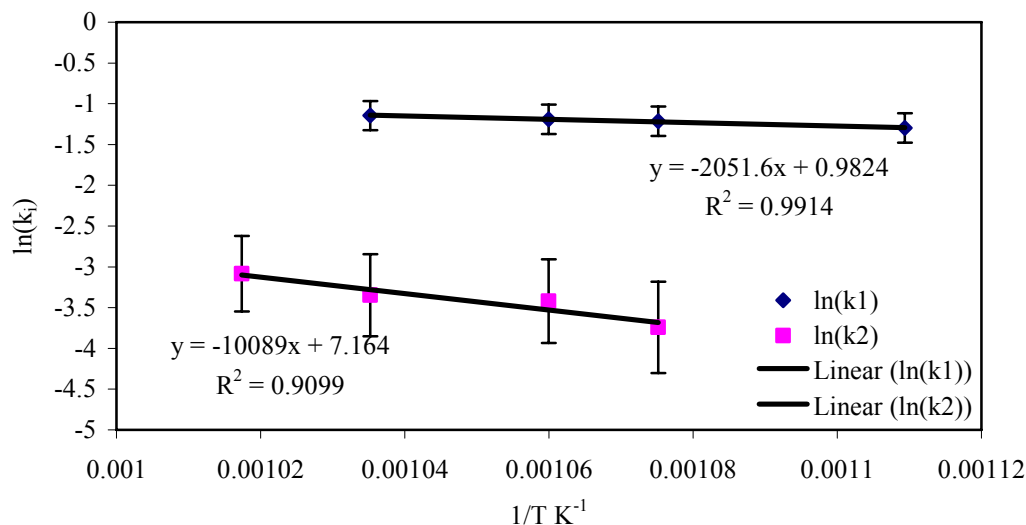


Figure 4: Arrhenius plot for the pyrolytic decomposition reaction (1) and the direct reformation reaction (2).

The rate constant k_1 represents the pyrolytic decomposition reaction and k_2 represents the direct reformation reaction. The error bars were determined from the standard error of the average log of the rate constant at each temperature. For the pyrolytic reformation reaction, k_1 , the greatest standard error was 0.18. For the direct reformation reaction, k_2 , the standard error was 0.50. Based on the linear best fit of the Arrhenius plot, the Arrhenius activation energy and frequency factor values are obtained as shown in Table 6.

Table 6 Arrhenius activation energy.

	E_A (kJ/mol)	A	R^2
pyrolytic decomposition	17.1	2.67	0.99
direct reformation	83.9	1290	0.91

Optimal Process Conditions

The three process conditions tested in the DOE were temperature, ethanol feed rate, and water feed rate with a fixed pressure. For this particular process it is desirable to maximize hydrogen production. The effectiveness of hydrogen generation is evaluated by statistical analysis of the molar ratio of hydrogen produced versus ethanol fed into the reactor. An analysis of variance of the factorial portion of the DOE, Table 7, shows that only the main effects, temperature, ethanol flow rate, and water flow rate, are statically significant in terms of hydrogen production with $p \leq 0.05$. The interactive effects were not statically significant. This may be due to the long residence times used for this design since the feed ethanol was completely converted as evidenced by practically no carbon content in the liquid phase of the reactor effluent. Table 8 shows the estimated effects and corresponding p-values.

Table 7 Analysis of variance for hydrogen generation

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	0.503555	0.503555	0.167852	120.94	0.008
2-way Interactions	3	0.011041	0.011041	0.00368	2.65	0.286
3-way Interactions	1	0.00606	0.00606	0.00606	4.37	0.172
Curvature	1	0.009102	0.009102	0.009102	6.56	0.125
Residual Error	2	0.002776	0.002776	0.001388		
Pure Error	2	0.002776	0.002776	0.001388		
Total	10	0.532534				

Table 8 Estimated effects and test statistics for hydrogen generation

Term	Effect	Coef	SE Coef	T	P
Constant		2.2552	0.01317	171.22	0
T	0.2106	0.1053	0.01317	7.99	0.015
F _{EtOH}	-0.4297	-0.2148	0.01317	-16.31	0.004
F _{H2O}	0.151	0.0755	0.01317	5.73	0.029
T*F _{EtOH}	-0.0573	-0.0286	0.01317	-2.17	0.162
T*F _{H2O}	0.0355	0.0177	0.01317	1.35	0.31
F _{EtOH} *F _{H2O}	0.0313	0.0157	0.01317	1.19	0.356
T*F _{EtOH} *F _{H2O}	0.055	0.0275	0.01317	2.09	0.172
Ct Pt		-0.0646	0.02522	-2.56	0.125

Contour plots of the response surface for hydrogen to ethanol molar ratios were generated using Minitab® statistical software and are shown in Figure 5. Since the interactive effects are not statistically significant, conclusions cannot be drawn with statistical certainty using the contour plots. However, some trends may be inferred: hydrogen production is highest at higher temperatures, at higher water flow rates, and at lower ethanol flow rates tested.

The flow rate of water and ethanol affect both residence time and ethanol feed concentration (water to ethanol ratio). Since more hydrogen appears to be produced at the lowest ethanol flow rates, it is apparent that higher water to ethanol ratios allow for more hydrogen to be produced. This is also consistent with the fact that the highest water-to-ethanol feed ratio generates the highest molar ratio of hydrogen-to-methane in the product stream, thus maximizing the reformation efficiency. Please see Run WE_N of Table 4.

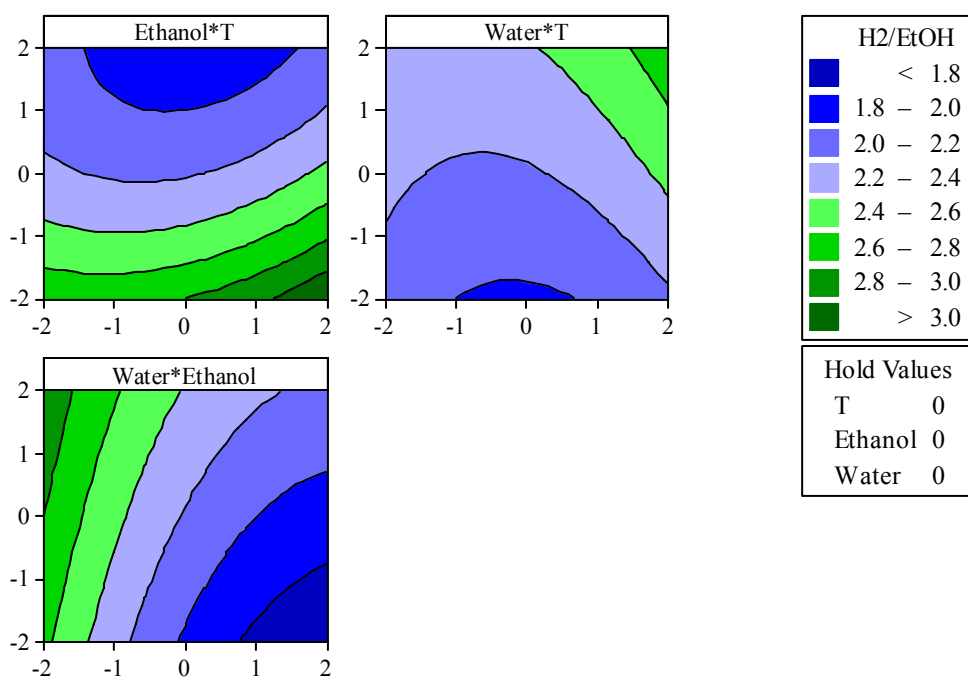


Figure 5 Contour plots of DOE for hydrogen to ethanol molar ratio, clockwise starting with the top left contour plot: (1) ethanol flow rate versus temperature with water flow held constant, (2) water flow rate versus temperature, ethanol flow held constant, (3) water flow rate versus ethanol flow rate, temperature held constant.

Conclusions

Ethanol can be reformed to hydrogen using supercritical water both as a reaction medium and as a solvent. Supercritical water reformation of ethanol requires no catalyst and is not susceptible to carbon fouling. Ethanol reacts in supercritical water by three different pathways: direct reformation of ethanol to hydrogen and carbon dioxide; decomposition to methane, carbon monoxide, and hydrogen; and dehydration followed by hydrogenation to form ethane. Experiments were performed at 24.2 MPa at temperatures between 630°C and 710°C at various ethanol and water feed rates. Ethanol was completely converted to gaseous products with hydrogen mole fractions between 49% and 60% with the balance in order of concentration being methane, carbon dioxide, ethane, and

carbon monoxide. Based on the experimental results and experience, further study is warranted on gas purification to ultra-pure hydrogen, energy integration, and process economic analysis.

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