

Hydrogen Production by Catalytic Ethanol Steam Reforming

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ABSTRACT A new promising way to utilize the dilute solution of ethanol is the reforming process of ethanol to produce hydrogen gas that can then be passed through a molten carbonate fuel cell to generate electricity. In this research the rate expression for the ethanol steam reforming reaction at 400 and 650 °C under atmospheric pressure was attempted. The effect of temperature on reaction conversion was also studied. Experiments were conducted in a fixed bed reactor over Ni/Al₂O₃ catalyst. The experimental results show that as W/F ratio increases, the H₂ yield increases for both reforming temperatures at 400 and 650°C but at higher reforming temperature a certain W/F ratio (~ 6 gm cat.-hr/mole) is needed to maintain low CH₄ yield. In addition thermal cracking reaction plays an important role at 650 °C. Therefore, the use of high temperature internal ethanol steam reformer in fuel cell is not practical and a pre-converter unit is recommended. The reaction rate obtained at 400°C reaction temperature under atmospheric pressure is

$$-r_{C_2H_5OH} = 280075 P_{EtOH}^{2.52} P_{H_2O}^7$$

KEYWORDS: hydrogen, steam reforming, ethanol, fuel cell.

INTRODUCTION

Since the infrastructure of Thailand is based on agriculture, raw materials, such as cassava, molasses and corn, are available for fermentation to produce dilute ethanol solution. There are many ways to utilize concentrated ethanol especially as a fuel source eg gasoline blender. To obtain high concentration of ethanol, however, the dilute solution of ethanol from fermenter must be dehydrated to a very low moisture content product. Distillation and azeotropic separation contributed to the shortcomings of ethanol as a fuel. A new promising way to utilize the dilute solution of ethanol is the reforming process of ethanol to produce hydrogen gas that can then be passed through a molten carbonate fuel cell (MCFC) to generate electricity.¹

Steam reforming of hydrocarbons has been investigated extensively since 1888. There are several books and papers, namely those of Twigg, Rostrup-Nielsen and Van Hook, that give a good overview of the steam reforming process and its historical development.²

Many kinetic studies of steam reforming reaction have been conducted with methane, some with LPG, n-hexane, toluene and C₆-hydrocarbon except ethanol. Methane steam reaction kinetics published by Akers and Camp³ shows the first order of methane disappearance rate. Several rate expressions were

announced for methane steam reforming, for instance:

$$-r_{CH_4} = 127e^{(-3.778/RT)} P_{CH_4}$$

$$-r_{CH_4} = 1.04 \times 10^4 e^{(-20,000/RT)} P_{CH_4}$$

$$-r_{CH_4} = 1.78 \times 10^7 e^{(-29,000/RT)} P_{CH_4} P_{H_2O}^{0.5}$$

Kunattippong S et al⁴ found the power-law rate expression of the maximum activity of the dry impregnated catalyst to be $1.83 \times P_{CH_4}^{1.27} P_{H_2O}^{1.24}$ for methane steam reforming.

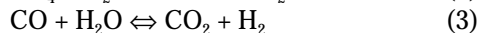
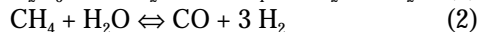
Steam reforming of LPG over Ni/Al₂O₃ reported by Vitayasuwan P and Vithitsan T⁵ shows that its rate expression was in the form of

$$-r_{LPG} = k [LPG]^{2.2} [H_2O]^{6.4}$$

$$k = 0.05 e^{(-28052/RT)}$$

The mechanism of steam reforming of higher hydrocarbons is more complex. Therdthianwong A et al⁶ are the early group who worked on the ethanol steam reforming over Ni/Al₂O₃ catalyst in a fixed bed reactor by studying the influence of temperature, steam to carbon ratio and feed rate of dilute ethanol solution on steam reforming reaction.

The suitable steam to carbon ratio was reported to be 9.23 or 15% (by volume) ethanol concentration. The following reactions were proposed as the main possible reactions to describe the steam reforming of ethanol:



The study evidenced the potential of using ethanol steam reforming to produce hydrogen for the carbonate fuel cell process. However, coke formation problem of the catalyst at high temperature, 650°C, was reported. This deposited carbon could reduce the fuel cell efficiency and cause the difficulty in catalyst changing. Hence a pre-converter unit operated at lower temperature, ie 400°C, as an external reformer unit was suggested to convert ethanol solution to hydrogen, methane and carbon dioxide before feeding these intermediate gases into the internal reformer of a fuel cell system. Steam reforming of methane in the internal reformer can lessen the coke deposit problem by controlling the steam to carbon ratio to be around 3-4.

As mentioned, although the condition of 650°C under atmospheric pressure was suggested as the operating condition of an internal reformer of a fuel cell, the ethanol pre-converter is necessary for preventing coke formation on the catalyst inside the fuel cell. The internal steam reformer inside the fuel cell is needed since the heat generated by electrochemical reaction of fuel cell can be used for steam reforming, which is an endothermic reaction. Therefore this research was then aimed to study the hydrogen production at the pre-converter temperature, 400°C, as well as the simple rate expression of ethanol reforming over the commercial catalyst assuming that reaction (1) is a controlling step. Moreover, the reforming temperature influence on conversion was also studied. Experiments were conducted to provide data for simple rate expression analysis and the STATISTICA® program was applied to determine the power-law rate of the reaction.

EXPERIMENTAL

Materials and Apparatus

Ethanol solution was prepared by diluting 97% Ethanol (Lab grade provided by Merck Co.Ltd.) with deionized water. The reforming catalyst, nickel supported on alumina, a commercial product of a catalyst company, was used. It was crushed into small granules with 2-4 mm size.

The experiment was carried out in a 1.27 x 40 cm (diameter x length) fixed bed reactor made of 316-stainless steel and assembled with SWAGELOK® fittings. For each experimental test, fresh catalyst was reduced *in situ* by high-purity hydrogen gas (99.9%) for 4 hours. Then the prepared ethanol solution was fed by electromagnetic dosing pump, LMI MILTON ROY model A962-161S, to a temperature controlled pre-heater unit. The pre-heater unit vaporized the dilute ethanol solution prior to sending further to the temperature controlled reactor unit. A removable gas distributor was used to uniformly distribute gas and support the catalyst in the reactor. After the reactor unit, several U-shape gas sample tubes were used to gather both liquid and gas samples. The condensable effluent gas such as water and ethanol vapor liquid sample was condensed in an ice bath. Schematic flow diagram of equipment is shown in Figure 1.

The reactant and gas products were analyzed with FID, Shimadzu model 9 A, and TCD, Shimadzu model 14 A, gas chromatography. H₂, O₂, CO, and CH₄ product concentrations were analyzed using molecular sieve 5A column whereas porapak Q column was used to analyze CO₂, CH₄ and C₂H₄ composition.

Experimental Set Up

There were 3 sets of experiment in this work. The first one involved the determination of conditions for reforming reaction at 650°C. 30% by vol of ethanol solution was chosen for this study. Temperature of the pre-heater and reactor units in this experiment were set at 400 and 650°C, respectively. In an attempt to search for the simple rate equation, the differential analysis of the obtained reaction data was applied and the experiments with different W/F ratio were performed. Ethanol flow rate was varied while keeping W/F ratio constant to examine the external mass transport limitation.⁷

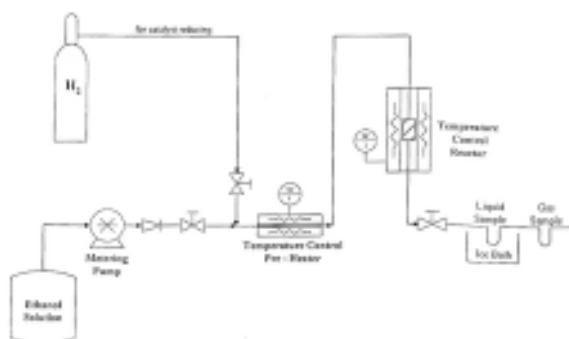


Fig 1. Laboratory flow diagram of ethanol steam reforming.

To study the effect of thermal cracking of ethanol at high temperature, the second experiments were set at three different temperatures, 200, 400 and 650°C in blank reactor (without catalyst). It was investigated with 5% ethanol concentration.

The third set of experiments was performed to determine the reaction rate expression at pre-converter temperature of 400°C. The recommended ethanol concentration from the work of Therdthianwong A et al, 15% vol, was applied.⁶ The temperature in the pre-heater and reactor unit was controlled at 250 and 400°C, respectively. Two feed rates, 70±1% and 140±1% ml/hr, were performed to test for interphase mass transfer resistance. At each feed rate, 4 different catalyst weights were varied.

Conversion of ethanol was calculated from the difference between inlet and outlet amount of ethanol. For each test, ethanol conversion, $X_{C_2H_5OH}$, and corresponding W/F ratio was plotted. A regression curve was determined for each plot. The reaction rate at different catalyst space time was then obtained by differentiating the regression equation.⁸ For each experiment, ethanol and steam partial pressure were obtained from effluent gas composition. Each calculated reaction rate and its corresponding effluent partial pressures of ethanol and steam were employed to determine the reaction rate equation. The STATISTICA[®] program tool was applied to estimate the proper constants, k , α and β in the rate equation $-r_{C_2H_5OH} = k(P_{C_2H_5OH})^\alpha(P_{H_2O})^\beta$

RESULTS AND DISCUSSIONS

Ethanol Conversion vs. W/F ratio at 650 °C

The first set of experiments was tested at constant temperature of 650°C because this is the operating temperature of molten carbonate fuel cell. The results at different catalyst weight per feed flow rate ratios are summarized in Table 1. Lowering catalyst weight whilst increasing feed flow rate was attempted, the results of ethanol conversion remains high (> 99%)

Table 1. Investigation for experimental condition at 650°C.

Exp ID	Catalyst Weight	Feed rate	W/F	Conversion
	gm	mol/hr		
650-A	4.99	0.3450	14.47	99.99
650-B	4.99	0.8146	6.13	99.92
650-C	0.5	0.3232	1.55	99.18
650-D	0.5	0.5639	0.89	98.59
650-E	0.1	0.3173	0.32	99.81
650-F	0.1	1.2337	0.08	99.40
650-G	0	0.3385	0.00	99.03

although W/F ratio was varied in the range of 0.0-5.0. It should be noticed that for the last experiment performed in blank reactor without catalyst, 99.03% of conversion was still obtained.

The composition of reforming gas was analyzed and the ratio of CH₄/H₂ was plotted against W/F ratio as shown in Figure 2. As W/F ratio was small, the ratio of methane to hydrogen in the effluent gas was high. In addition at high temperature (650 °C), ethanol was cracked into smaller molecules such as methane and ethylene. This was confirmed by the presence of small amount of the cracked gases found in the last gas product (650-G test).

It was suspected that thermal cracking reaction played an important role in the reforming reaction. Therefore the influence of temperature on the cracking reaction of ethanol was studied subsequently.

Investigation of Thermal Cracking Temperature

The temperature effect on thermal cracking of ethanol was studied in blank reactor. Table 2 displays the %conversion at three different temperatures. At low temperature of 200°C the ethanol did not convert at all (0% conversion). However, some extent of conversion, 13.42%, takes place when the reactor temperature was increased to 400°C. Moreover, high conversion, 97.7%, was achieved at 650°C.

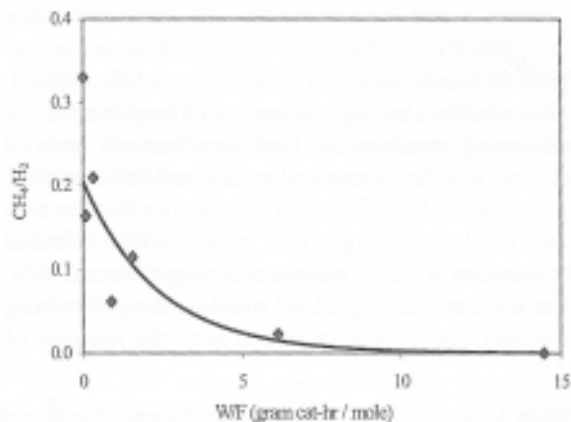
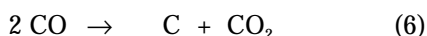
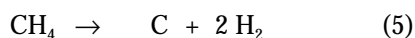
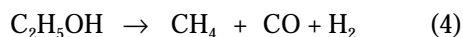


Fig 2. CH₄/H₂ ratio vs W/F at 650°C.

Table 2. Temperature effect on thermal cracking of ethanol.

Exp ID	Reactor Temp °C	Conversion %
200-Blank	200	0.00
400-Blank	400	13.42
650-Blank	650	97.71

These experimental results confirmed that thermal cracking of ethanol was increased as temperature increased and the main cracking products were methane and carbon monoxide. Methane and carbon monoxide were further cracked to carbon because the higher coke deposited on reactor wall was observed as the reactor temperature was higher. The coke formation problem at high temperature became considerable. Thermal cracking and coke formation reactions possibly follow the reactions:



H₂ Production and Rate Expression at 400 °C

The hydrogen production and rate expression at the temperature of pre-converter, 400 °C were obtained. The dry gas composition results were used to calculate yield and partial pressure of ethanol and steam at the reactor exit. Table 3 summarizes the reaction rate, partial pressure and yield results. H₂ and CH₄ yield were defined as the mole of H₂ and CH₄ produced divided by mole of ethanol in feed, respectively.

The CH₄ and H₂ yield for two different reforming temperatures (400 and 650 °C) are compared in Figures 3 and 4 respectively. At high reforming temperature (650 °C) the CH₄ yield decreased as W/F ratio increased whereas the H₂ yield increased. This shows the significance of temperature on reforming reaction. At high temperature, most of ethanol was firstly cracked to CH₄ and subsequently converted to H₂ if the residence time for the reaction was sufficient (high W/F ratio). The ethanol conversion at 650 °C was quite constant around 99%. On the contrary, the CH₄ yield at low reforming temperature slightly increased with the increase of

W/F ratio and approached a constant after W/F of ~1. This is the result of the increase of conversion as W/F ratio increased. At low W/F ratio the conversion of ethanol was quite low, therefore most of produced CH₄ was catalytically converted to H₂. As W/F ratio increased (residence time was longer) the CH₄ conversion to H₂ was enhanced as seen the results in Table 3. However, the increase of H₂ yield with the increase of W/F ratio was observed at both reforming temperatures.

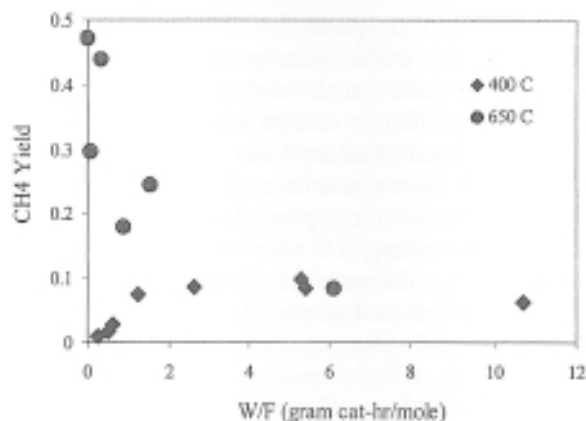


Fig 3. CH₄ yield varying with W/F ratio at 400 and 650 °C.

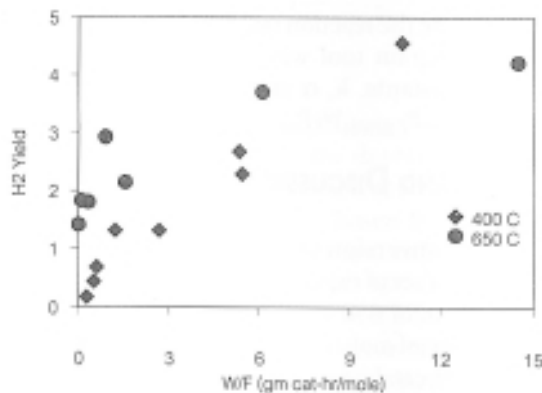


Fig 4. H₂ yield varying with W/F ratio at 400 °C and 650 °C.

Table 3. Reaction results of ethanol steam reforming at 400 °C.

Exp ID	W/F	Reaction Rate (mole/g cat-hr)	P _{EIOHP} (atm)	P _{H₂O} (atm)	H ₂ Yield	CH ₄ Yield	Conversion %
400-A	0.26	96.559	0.0508	0.9371	0.176	0.010	4.67
400-E	0.53	47.392	0.0393	0.9334	0.432	0.016	20.9
400-B	0.61	41.221	0.0398	0.9104	0.683	0.0292	28.3
400-F	1.23	20.245	0.0291	0.8689	1.329	0.0745	47.9
400-C	2.66	9.376	0.0311	0.8560	1.326	0.0861	50.7
400-G	5.31	4.701	0.0136	0.7822	2.691	0.0975	75.8
400-D	5.44	4.594	0.0067	0.8247	2.299	0.084	88.6
400-H	10.73	2.327	0.0003	0.7094	4.558	0.0625	99.5

In all experiments at 400 °C, it was also observed that the dry effluent gas contains more than 70 % by volume of hydrogen gas for all cases but the methane yield was changed with conversion shown in Figure 5. The change in CH₄ yield was resulted from two competing reactions; one is the thermal cracking of ethanol to produce CH₄ and the other is the CH₄-steam reforming to consume CH₄. The trend hence would follow the one that dominates another. At low conversion the CH₄ yield was increased as conversion of ethanol increased and thermal cracking plays important role. But after ~60% conversion CH₄ further reacted with steam to form H₂ and CO as seen the decrease of CH₄ yield.

The results at each W/F ratio and its corresponding conversion are plotted in Figure 6. As W/F ratio was increased, the conversion of ethanol to gas products were increased. A regression of the plot was determined. The differentiating of this regression equation or finding the slope of the curve yields the reaction rate. Eventually, the reaction rate of each experiment can be represented by

$$-r_{C_2H_5OH} = 24.981 / (W/F) \quad (7)$$

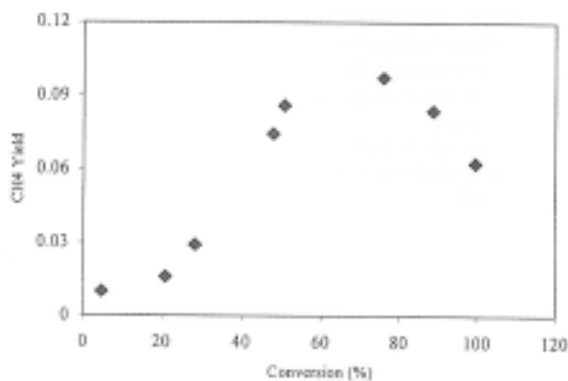


Fig 5. CH₄ yield vs conversion at 400°C.

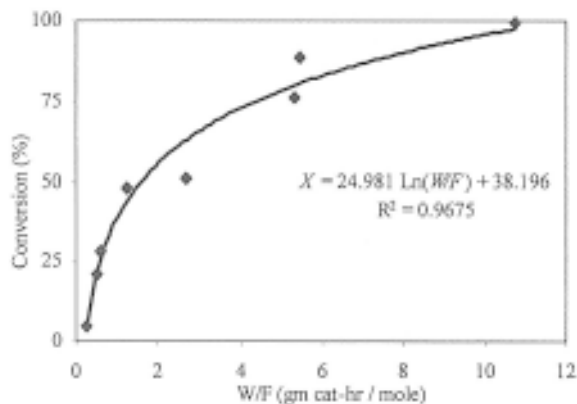
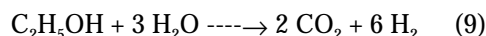


Fig 6. Conversion vs W/F of ethanol steam reforming at 400 °C.

For rate expression determination, the proper constant of power-law rate equation was determined using STATISTICA® program and the obtained ethanol steam reforming reaction rate at 400 °C under atmospheric pressure with 98% confidence is

$$-r_{C_2H_5OH} = 280075 P_{EtOH}^{2.52} P_{H_2O}^7 \quad (8)$$

Figure 7 illustrates a good fit between the calculated reaction rate from the above expression and the obtained reaction rate. From equation (8) the ratio of H₂O partial pressure and C₂H₅OH partial pressure is ~ 2.78 which is close to 3. The high power of H₂O partial pressure compared with ethanol partial pressure in the rate expression is similar to that (power 6.4 in H₂O and 2.2 in LPG partial pressure) found by Vitayasuwan P. and Vithitsan T.⁵ It shows that the ethanol steam reforming is not an elementary reaction and could consist of mainly three reactions as proposed in equations (1) - (3). Its overall reaction can be almost represented by the irreversible reaction between one ethanol molecule and three water molecules:



Equation (9) is also proposed by the research work done by Patel.¹

Two experimental results (Exp.ID 400D and 400G shown in Table 3) at the same W/F but different feed flow rate shows the similar reaction rates. Hence the external mass transport resistance did not influence the reaction rate.

Conclusions

According to the results and discussions, the following conclusions for H₂ production by ethanol

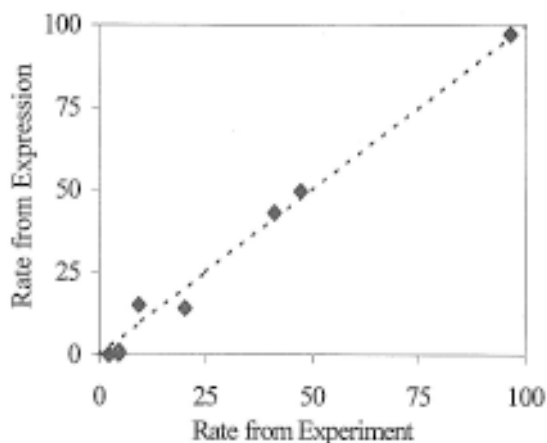


Fig 7. Diagonal chart of calculated and experimental reaction rate.

steam reforming over the commercial catalyst were made.

- a) Thermal cracking reaction of ethanol is significant at 650°C.
- b) The use of high-temperature internal ethanol steam reformer in fuel cells is not practical. A pre-converter unit at mild temperature of 400°C is recommended. The pre-converter will change the ethanol molecule to hydrogen-rich gas or methane-rich gas. These intermediate gases will create less coke deposition in the internal reformer of fuel cell.
- c) The simple rate expression of ethanol steam reforming at 400°C under atmospheric pressure is

$$-r_{C_2H_5OH} = 280075 P_{EtOH}^{2.52} P_{H_2O}^7$$

where $0.0003 < P_{EtOH} < 0.0508$ atm, $0.7094 < P_{H_2O} < 0.9371$ atm

- d) More than 70% by volume of hydrogen in effluent gas was achieved from ethanol steam reforming at 400°C under atmospheric pressure over this specific catalyst.

Since the coke formation still exists at mild temperature reaction, the catalyst improvement to reduce coke formation is now further studied.⁹ Again this work is a preliminary study for the use of ethanol to produce an alternative fuel. After obtaining a good catalyst the true kinetic expression will be investigated for designing and modeling the reformer.

NOTATION

F_A	Molar flow rate of substance A (mol/hr)
k	Reaction rate constant in equation (8) (mol/gm-cat hr atm ^{9.52})
P_A	Partial pressure of substance A (atm)
$-r_A$	Rate of disappearance of substance A (mol/gm-cat hr)
T	Temperature (°C)
W	Catalyst weight filled in the reactor (gm)
X	Conversion of the reaction (%)
α, β	Reaction order with respect to a specific substance, (dimensionless)

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