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Thermodynamic Analysis for a Blend of Methanol and Urea Water Solutions to Produce Hydrogen-Rich Gas

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Keywords：urea water solution, methanol, steam reforming, hydrogen-rich gas, thermodynamic analysis, experimental validation

ABSTRACT

The article uses a thermodynamic investigation of the steam reforming of methanol (SRM) using either urea water solution (UWS) or pure water. This process examines hydrogen-rich gas production, hydrogen yield, and carbon creation. The SRM with UWS produces a higher hydrogen-rich gas and achieves greater reforming efficiency than SRM without UWS. With a water-to-methanol ratio of 5 at 700 °C using UWS, the maximum hydrogen yield reaches 4.4 mole/mole MeOH, resulting in the highest reforming efficiency of 117.9%. As the temperature exceeds 250 °C, carbon production declines significantly despite adding UWS. Although the carbon production with UWS is greater than that of non-used UWS, there is a slight difference. Comparing hydrogen and CO concentration with reference results for no UWS SRM validates the analysis's reliability. The results supported by an experiment show that the hydrogen-rich gas yield can increase when the UWS as a reactant replaces pure steam for methanol-reforming.

INTRODUCTION

The impacts of air pollution and greenhouse gasses on human health and climate change have intensified have started to emphasize the creation and use of alternative energy sources. As an alternative energy source, hydrogen is an excellent energy courier on the planet since it is abundant and pure (Mazloomi et el. 2012). Consequently, the fundamental technologies for producing, storing, and moving hydrogen energy and their applications have emerged. Other categories of hydrogen generation technologies include electrolysis, reformation, and bio-hydrogen synthesis. Many varied fuel cell systems and industries have exploited the reformation technology used to create hydrogen (Lamy et al., 2020), including the explorations of methane reforming systems (Chao et al., 2011) (Chang et al., 2019), ethanol steam reformers (Sheu et al., 2022), and methanol steam reformers (Huang et al., 2013) (Perng et al., 2021).

The application of hydrogen has long been considered one of the best solutions for environmental protection and reducing greenhouse gas emissions. Compared to combustion engines, hydrogen can be available in fuel cell systems, operating with lower noise and vibration levels while offering higher fuel efficiency (Wu, 2016) (Jiang et al., 2022). As a fuel, the hydrogen syngas produced during reforming can increase an engine's combustion efficiency owing to its characteristics of fast diffusion, rapid flame propagation, and low ignition energy (Shadidi et al., 2021) (Wu et al., 2016). Due to its convenience regarding transportation and storage, methanol performs well in reforming for the creation of hydrogen (Gautam et al., 2020). Almost all of the methanol generated currently arises from fossil fuels. However, bio-methanol from renewable sources like wind, solar, geothermal, hydro, biomass, and so on, and processes are chemically identical to methanol but lead to lower greenhouse emissions and no depletion of the fossil fuel supply. Because it is a spread method of energy production, it also offers the most potential as a biofuel for power generation (Sun et al., 2020).

The four methanol-reforming processes employed to produce hydrogen include

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decomposition, partial oxidation reforming, steam reforming, and auto-thermal reforming (Perng et al., 2013). The SRM shows the most widely used method to create hydrogen and has the highest efficiency. The process likewise delivers a lot of H_2 while emitting very little CO. However, because the reaction is endothermic, the methanol steam reforming technique needs a supplied heat source (Chen et al., 2011). Several studies have discussed methanol reformation and its application in fuel cells (Perng et al., 2019) and internal combustion engines (Wu et al., 2016). Ouyang et al. (2017) found the optimum combination of less CO concentration, more hydrogen concentration, and greater methanol conversion efficiency in the SRM by genetic algorithm via a neural network. Their results indicated that the optimum reaction temperature was 267 ^oC, the optimum carried gas flow rate was 40 cm^3/min, and the optimum steam-to-carbonate (S/C) ratio was 1.1. Faungnawakij et al. (2006) examined SRM using a thermodynamic technique that varied the S/C ratio, pressure, reaction temperature, and product species. The methanol acquired complete conversion as the temperature was over 200 ^oC. The temperature for the coke-free zone fell with a raised S/C ratio. The pressure had a minimal effect on the complete conversion of methanol. Tahir et al. (2022) explored hydrogen generation during methanol-phenol blend steam reforming via thermodynamic analysis with test work. The maximum hydrogen production occurred at 700 ^oC with a ratio of methanol to phenol to steam, 0.1:0.9:20. Rodrigues et al. (2022) investigated the methanol and dimethyl ether through steam reforming to produce hydrogen with a thermodynamic evaluation. The reforming during lower temperatures and an S/C ratio over two could generate the maximum hydrogen of 99.9%.

Since urea is an excellent hydrogen courier, it is gaining popularity (Rollinson et al., 2011). It is an organic compound of H, C, O, and N to produce 0.086 kgs of hydrogen per dm^3. It is more than the hydrogen depository (0.070 kgs per dm^3) in liquid at 21 K, as well as the hydrogen depository (0.043 kgs per dm^3) with a pressure of 800 kg/cm^2 (Lan et al., 2010). Urea is colorless, stable, nonpoisonous, and simple to move and store. Water, ethanol, glycerin, and other liquids can all dissolve it. In addition to ammonia and carbon dioxide, municipal wastewater can also make commercial urea. Over 90% of the urea generated annually is utilized as fertilizer, amounting to a billion tons (Matijaševic et al., 2010). Diesel engine vehicles must have selective catalytic reduction systems (SCR), which cut NOx emissions, to meet Euro 5 emission standards (Yim et al., 2004). The SCR uses the Adblue delivered into the exhaust system to convert the NO_X, employing the selective catalyst to convert nitrogen and water. The Adblue contains 32.5 percent urea and 67.5 percent by-weight de-ionized water. Urea has several benefits, such as being non-flammable, non-explosive, and affordable, while having a lower hydrogen content than liquid ammonia and methanol. Since it meets the U.S. Department of Energy's definition of a hydrogen courier having a hydrogen content of more than 5 % by weight, it is particularly well suited for automotive applications (Satyapol et al., 2007). To produce syngas at 600 ^oC, Rollinson et al. (2010) built a stuffed-bed reactor with urea processing steam reforming. According to their report, each mole of urea produced 3 moles of hydrogen. Furukawa et al. (2015) assessed the urea steam reforming process using several catalyst types containing non-noble and noble metals. They discovered that a catalyst based on ruthenium (Ru/Al_2O_3) catalyst produced a higher hydrogen yield than other catalysts. Lin and Wu (2020) explored biogas steam reforming with and without UWS and hydrogen-rich syngas generation with methane concentration via a thermodynamic study. Adding UWS instead of water steam promotes the generation of hydrogen and carbon monoxide with a slighter carbon dioxide increase than the steam reforming of biogas at above 800 ^oC. The reaction temperature of 700 ^oC could have the maximum hydrogen production and reforming efficiency.

According to the papers above, earlier research on hydrogen production from methanol reformation has solely examined the impacts of varied catalysts. Few investigations investigated the production of hydrogen by combining methanol and UWS. As a result, this work proposes an innovative method of hydrogen production via reforming methanol coupled with the UWS rather than decomposing urea alone. Using the thermodynamic study of Gibbs minimization as an approach to equilibrium compares the syngas generation in the SRM combined with or without UWS. This work also performs a test using Ru/Al_2O_3 as the SRM catalyst to certify the findings of the thermodynamic investigation in the SRM mixed with UWS.

CHEMICAL EQUILIBRIUM METHOD

Scholars (Faungnawakij et al. 2006), (Tahir et al. 2022), (Rodrigues et al. 2022) have widely applied the Gibbs minimization as a method of equilibrium to predict chemical system reaction parameters and assess syngas generation and carbon formation. The assumptions of the Gibbs free energy minimization approach are the given reaction at constant temperature and pressure. The limitations show that Gibbs Free energy does not deal with the kinetics of the problem without getting to know the rate of the reaction. The study then minimizes the Gibbs free energy with the constrained conditions (Eq. (1)) to determine the equilibrium state. Eq. (1) represents atom conservation as

$$b_i - b_i^0 = 0, \quad i=1,\cdots\cdots,1 \tag{1}$$

where b_i represents the i^{th} element number in the roducts products $= \sum_{j=1}^{n} a_{ij} n_j$ products , in which a_{ij} denotes the i^{th} element's atom number in species j, and b_i^0 is the i^{th} element number in the reactants.

Define B as $$B = G + \sum_{i=1}^{l} \lambda_i (b_i - b_i^0)$$

where G denotes Gibbs free energy, λ_i represents Lagrangian multiplier. The following equation is the calculus of variation method for equilibrium state at constant temperature and pressure.

$$\delta B = \sum_{i=1}^{n} (\mu_j + \sum_{i=1}^{l} \lambda_i a_{ij}) \delta n_i + \sum_{i=1}^{l} (b_i - b_i^0) \delta \lambda_i = 0 \quad (2)$$

Eq. (3) gets for gaseous species under low pressure dealing δn_i and $\delta \lambda_i$ as independent variables from Eq. (2).

$$\mu_j^0 + R_u T (\ln \frac{n_j}{n} + \ln \frac{P}{P_0}) + \sum_{i=1}^{l} \lambda_i a_{ij} = 0, \quad j=1,\ldots, n \ (3)$$

where μ_j^0 represents the j^{th} species' chemical potential at standard state, R_u denotes the universal gas constant, T represents temperature, n_j signifies the j^{th} species' molar number, N represents gas mixture molar number, p denotes pressure, and P_0 is standard pressure referred to as 101.3 kPa.

For the total system with gaseous species and solid-phase carbon, the minimum Gibbs free energy becomes

$$\sum_{j=1}^{n-1} n_j (\mu_j^0 + R_u T (\ln \frac{n_j}{n} + \ln \frac{P}{P_0}) + \sum_{i=1}^{l} \lambda_i a_{ij}) + n_c \mu_c^0 = 0 \ (4)$$

Solving the nonlinear equations (3), (4), and (1) can achieve the product species under different temperatures. As urea is unavailable, the atom elements are only C, H, O, and l=3. When UWS is available, the elements are C, H, N, O, with l=4. The calculations ponder the possibility of producing ethane (C_2H_6), ethylene(C_2H_4), acetylene (C_2H_2), carbon dioxide (CO_2), methane (CH_4), hydrogen (H_2), ammonia (NH_3), carbon monoxide (CO), solid carbon (C), and isocyanic acid (HNCO). This study used the commercial program HSC to calculate hydrogen-rich gas generation during the reforming process.

Table 1 indicates methanol and urea properties. Set the H_2O/MeOH molar ratio from 1 to 5 to compute all the products in the methanol-reforming reaction mixed with and without UWS. The UWS is feasible with the Adblue of 32.5 wt% or 0.144 mole-urea/ mole-H_2O. Calculating the creation of hydrogen and carbon reaction formulas in the SRM combined with UWS, monoxide appears concurrently with carbon generation. Eq. (5) indicates the overall chemical reaction formulas in the SRM combined with UWS, where ν_1, ν_2, ν_3, ν_4, ν_5, ν_6, ν_7, and the methanol-reforming reaction mixed with and without UWS. The equilibrium calculation uses a reaction temperature range of 0 °C to 800 °C at normal atmospheric pressure. Urea decomposition, HNCO hydrolysis, NH_3 cracking, a water-gas shift reaction, and hydro-nitrogen cracking show the five primary processes in urea syngas generation (Furukawa et al. 2015). Eq. (6) indicates the overall reaction equation in MeOH reforming with pure steam, where ν_1', ν_2', ν_3', ν_4', ν_5', ν_6' denote the product's moles. H_2O and UWS in Eq. (5) to Eq. (6) show gas phases.

$$CH_3OH_{(l)} + xH_2O_{(g)} + z(NH_2)_2CO_{(g)} \rightarrow \nu_1 H_2 + \nu_2 CO + \nu_3 CO_2 + \nu_4 CH_4 + \nu_5 N_2 + \nu_6 H_2O + \nu_7 C + \nu_8 CH_3OH \ (5)$$

where $z=0.144x$.

$$CH_3OH_{(l)} + xH_2O_{(g)} \rightarrow \nu_1' H_2 + \nu_2' CO + \nu_3' O_2 + \nu_4' CH_4 + \nu_5' N_2 + \nu_6' H_2O + \nu_7' C + \nu_8' CH_3O \quad (6)$$

Table 1 Methanol and urea properties at 25 °C

	Methanol	Urea
Formula	CH_3OH	$(NH_2)_2CO$
Density (g/ml)	0.792	1.34
Molecular weight (g/mol.)	32.04	60.06
Lower heating value (MJ/kg)	19.91	10.5
Enthalpy of formation (MJ/kmole)	-201.0	-323.6

RESULTS AND DISCUSSION

The explored temperatures are 600, 700, and 800°C, owing to the theoretical reaction temperature of urea from 650 to 750 °C. Figure 1 shows that the hydrogen production using UWS water is higher than without UWS when the H_2O/MeOH ratio varies from

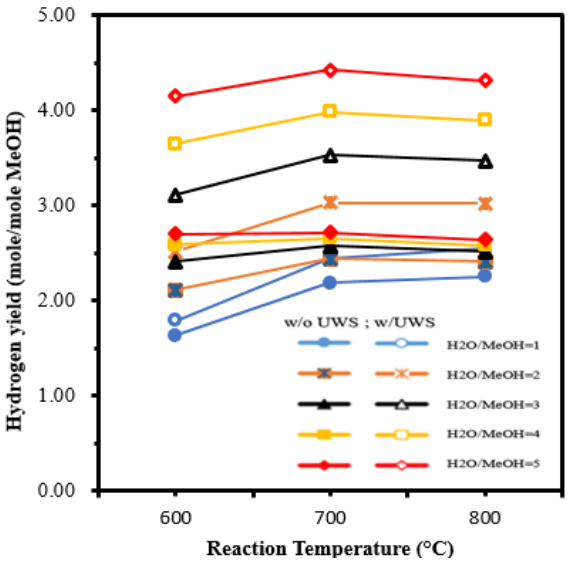


Figure 1 Hydrogen yield versus reaction temperature for with or without UWS for various H_2O/MeOH ratios.

1 to 5 because the UWS carries more hydrogen atoms (Eq. (7) and Eq. (8)). The more urea solution is in the blend, the more hydrogen production increases due to having more hydrogen atoms (Eq. (7). The hydrogen production rises with an increase in temperature till the temperature reaches 700 ºC because the higher temperature promotes the reaction rate. However, for the same H_2O/MeOH ratio, the difference in hydrogen production between 700 ºC and 800 ºC is slight despite adding urea solution because more H_2O production affects the equilibrium. For reaction temperatures at 600ºC, the hydrogen output reaches 2.41 moles as the H_2O/MeOH ratio is 3 for no UWS. When combined with the UWS, 0.43 mole of urea is soluble in 3 moles of H_2O to generate 3.31 moles of hydrogen during the reforming process. As the reforming undergoes UWS at 700 ºC, the hydrogen production is 3.53 moles or 1.37 times that of no UWS. When the H_2O/MeOH ratio reaches 5, the hydrogen output from the SRM without UWS at 700 ºC gets 2.71 moles. The hydrogen output of methanol combined with UWS can theoretically get 4.42 moles or 1.63 times that of pure steam. As a result, without pondering supplied heat, for x moles $H_2O_{(g)}$, the reactants contain (4+2x+4z) moles H in methanol with UWS (in Eq. (5)), but the reactants contain (4+2x) moles H in methanol solution (in Eq. (6)). Therefore, methanol with UWS can produce more hydrogen for the same product compositions. It can apply to conditions with a bountiful heat supply, such as enough waste heat from combustion engines. Eq. (7) and Eq. (8) are steam-reforming processes of urea and methanol with endothermic reactions.

$$H_2NCONH_{2(g)}+H_2O_{(g)}\rightarrow CO_{2(g)}+3H_{2(g)}+N_{2(g)} \quad (7)$$

where ΔH^0_{298} =80.4 kJ/mol

$$CH_3OH_{(l)}+H_2O_{(g)}\rightarrow CO_{2(g)}+3H_{2(g)} \quad (8)$$

where ΔH^0_{298} =49. 2 kJ/mol

The water-gas shift reaction is as follows.

$$CO_{(g)}+H_2O_{(g)}\rightarrow CO_{2(g)}+H_{2(g)} \quad (9)$$

where $\Delta H^0_{298K} = -41.2\ kJ/mol$

The reverse water-gas shift is as follows.

$$H_{2(g)}+CO_{2(g)}\rightarrow CO_{(g)}+HO_{2(g)} \quad (10)$$

where $\Delta H^0_{298K} = 41.2\ kJ/mol$

Figure 2 depicts that the hydrogen-rich gas generation with UWS is better than without UWS because it carries more hydrogen and carbon atoms. The more UWS is in the blend, the more hydrogen-rich gas becomes due to having more hydrogen and carbon atoms. The hydrogen-rich gas production also rises with increasing temperature until the temperature is 700ºC because higher temperature enhances the reaction rate of hydrogen syngas production. For the reforming undergoing UWS at 700 ºC, the hydrogen-rich gas production is 5.13 moles or 1.71 times that of no UWS when the H_2O/MeOH ratio reaches 5. The equilibrium reaction is disturbed because H_2O generation increases as the

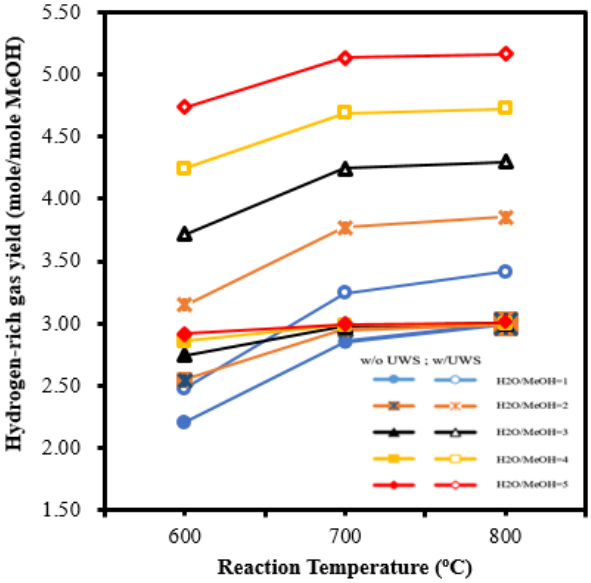


Figure 2 Hydrogen-rich gas yield versus reaction temperature for with or without UWS for various H_2O/MeOH ratios.

Figure 3 displays that the hydrogen concentration ranging from 600 to 800 ºC for no UWS are close to those shown in reference Faungnawakij et al. (2006), as depicted in Figure 3 at an H_2O/MeOH ratio of 1, 3, and 5. More UWS will decrease the hydrogen concentration for 700 and 800 ºC, but the difference is low. The difference is due to the more hydrogen and nitrogen production adding UWS. With the same ratio of methanol to water, the hydrogen concentration of adding UWS will be lower than that without adding UWS because of the produced nitrogen to dilute hydrogen. For the reforming undergoing UWS at 700 ºC, the hydrogen concentration is 64.4% moles or 0.88 times that of no

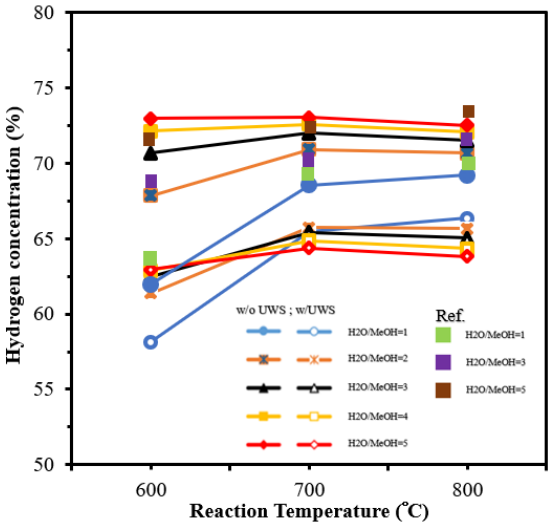


Figure 3 Hydrogen concentration versus reaction temperature for with or without UWS for various H_2O/MeOH ratios.

UWS when the H_2O/MeOH ratio reaches 5. Figure 4 indicates a hydrogen-rich gas concentration map with or without UWS varying reaction temperature. Adding UWS for the reaction produces nitrogen, so the more UWS decreases the hydrogen-rich gas concentration. The hydrogen-rich gas's concentration in UWS is less than that in urea-free water because more UWS creates more nitrogen in a blend of the same ratio of H_2O and MeOH. The hydrogen-rich gas's concentration declines with a rise in the H_2O and MeOH ratio, whether adding UWS because of the raised carbon monoxide and methane concentration. Since urea contains carbon, it will produce carbon monoxide after the reaction.

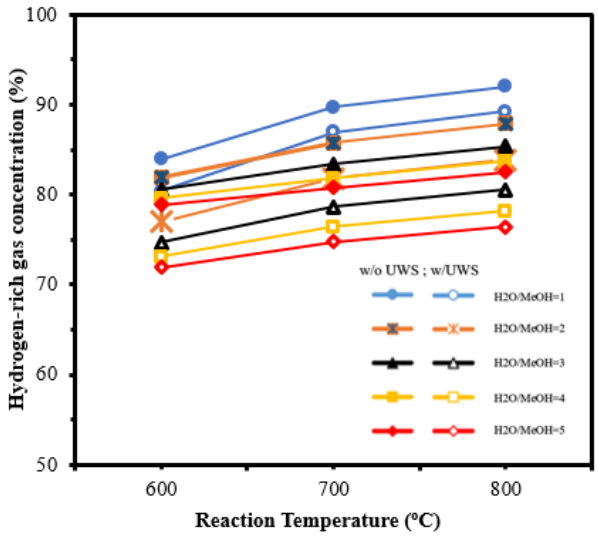


Figure 4 Hydrogen-rich gas concentration versus reaction temperature for with or without UWS

The carbon monoxide concentration rises with increasing temperature (Figure 5) because of the

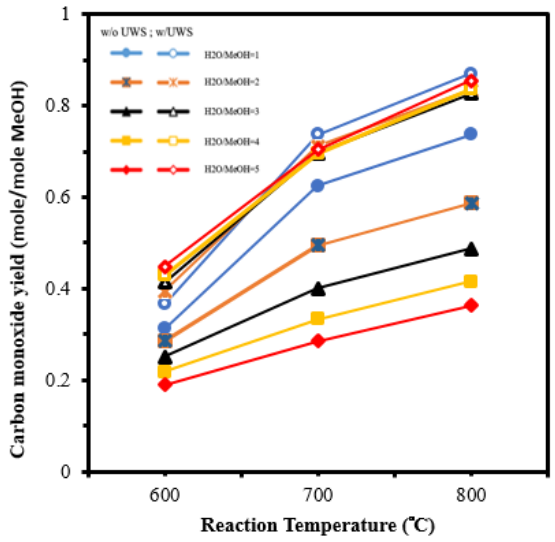


Figure 5 Carbon monoxide yield versus reaction temperature with or without UWS

raised reverse water gas shift reaction (Eq. (10)). The carbon monoxide yield with UWS is higher than without UWS. The more UWS in the blend generates a higher carbon monoxide yield, and the difference is low at temperatures of 700 and 800 °C. Figure 6 depicts that the carbon monoxide concentration ranging from 600 to 800 °C for no UWS are more similar to those shown in reference (Faungnawakij et al. 2006), as depicted in Figure 6 at an H_2O/MeOH

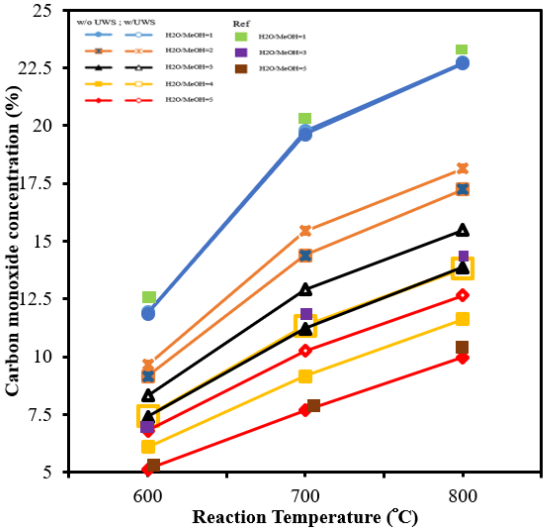


Figure 6 Carbon monoxide concentration versus reaction temperature

ratio of 1, 3, and 5. The carbon monoxide concentration declines with increasing the H_2O and MeOH ratio for no UWS because of the raised water gas shift reaction (Eq. (9)) and dimethyl ether decomposition. For adding UWS, the more the H_2O/MeOH ratio is, the more other products will be produced, such as nitrogen, so the carbon monoxide concentration decreases. For the same ratio of H_2O and MeOH, the carbon monoxide yield is higher than the yield of other products owing to the contained carbon, so the concentration of carbon monoxide with UWS will be higher than that of non-used UWS.

Carbon deposits impede the reforming reaction. Figure 7 displays that increasing the H_2O/MeOH ratio leads to a decline in the carbon formation temperature because more steam could provide more steam as a reactant to react with carbon and produce CO. The coal gasification reaction occurs at high temperatures to remove the carbon in the reforming. The reaction equations are as follows:

$$C_{(s)}+H_2O_{(g)}\rightarrow CO_{(g)}+H_{2(g)} \quad (11)$$

$$C_{(s)}+CO_{2\,(g)}\rightarrow 2CO_{(g)} \quad (12)$$

The higher H_2O will also reaction with CH_4, and the reaction equation is expressed as follows.

$$CH_{4(g)}+H_2O_{(g)}\rightarrow CO_{(g)}+3H_{2(g)} \quad (13)$$

When adding UWS, the temperature at which carbon forms is higher than when using pure water because of more carbon content for the same

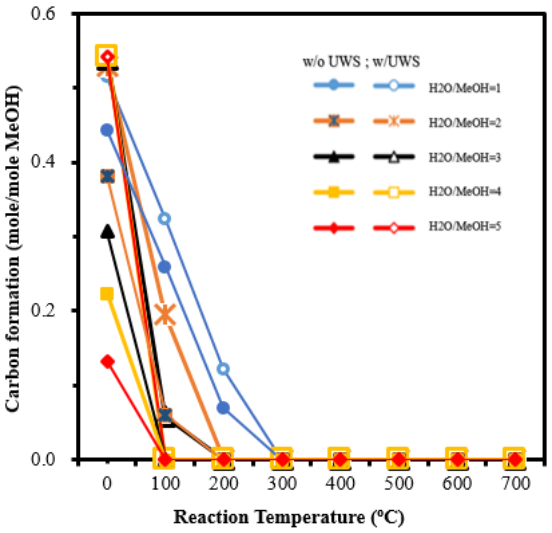
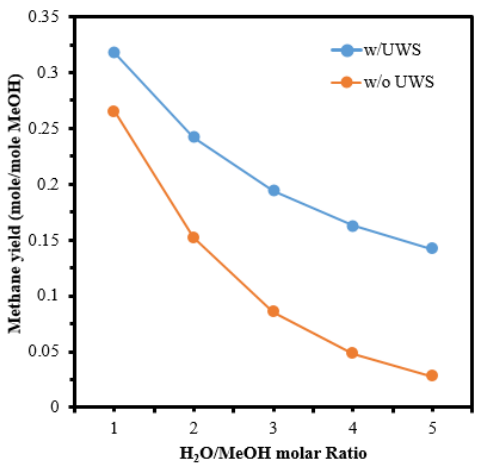
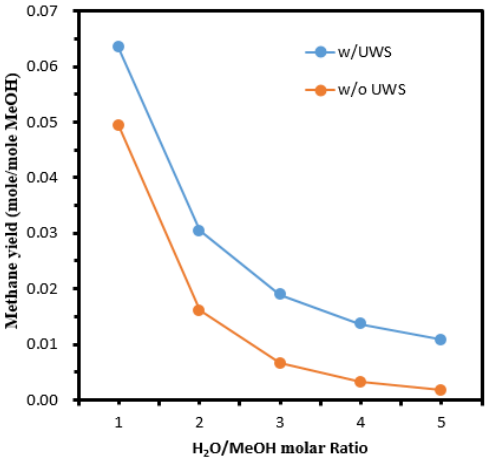


Figure 7 Carbon formation versus reaction temperature with or without UWS

H_2O/MeOH ratio. Carbon production abruptly declines to small values as the temperature exceeds 250 °C despite adding UWS. The carbon deposits do not impede the methanol-reforming reaction for adding UWS at higher reaction temperatures. Figure 8 depicts the methane yield with or without UWS changing reaction temperature. When increasing the H_2O/MeOH molar ratio, methane yield declines despite adding UWS; however, the decreasing level for no UWS is slightly higher. With UWS, there is a higher methane production than without UWS because urea contains carbon. The methane yield is minimal as the reaction temperature is at 700 °C in Figure 8(b) because more reformatted methane is feasible at high temperatures. Employing Eq. (14) calculates the reforming efficiency of the SRM mixed with and without UWS. At identical conditions, as the urea mole fraction $n_{(NH_2)_2CO}$ becomes zero without UWS and the H_2O/MeOH represents 5,



(a)



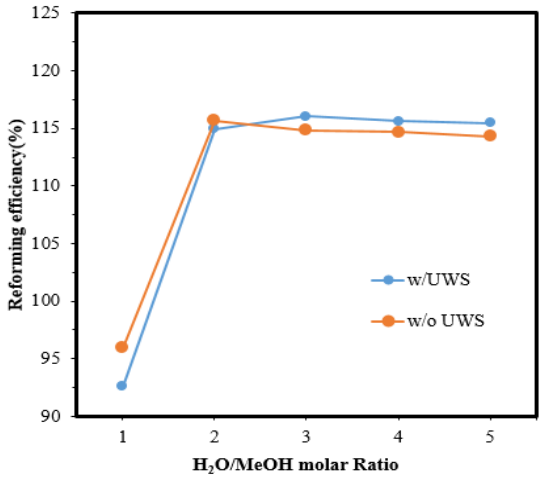
(b)

Figure 8 Methane formation with and without UWS for (a) reaction temperature, 600 °C, and (b) reaction temperature, 700 °C.

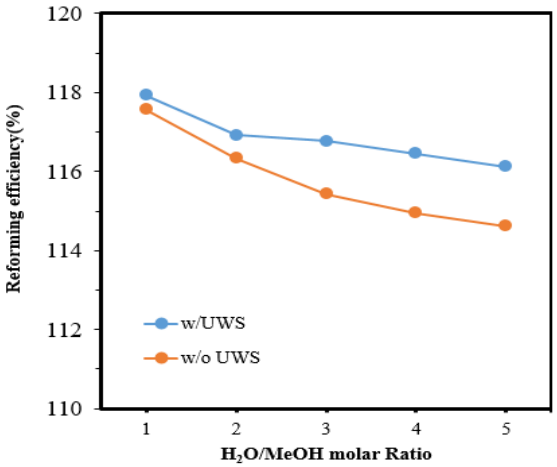
$n_{(NH_2)_2CO}$ gets 0.72 moles with AUS.

$$\text{Reforming efficiency (\%)} = \frac{(n_{H_2} \times LHV_{H_2} + n_{CO} \times LHV_{CO}) \times 100}{n_{CH_3OH} \times LHV_{CH_3OH} + n_{(NH_2)_2CO} \times LHV_{(NH_2)_2CO}} \quad (14)$$

Figure 9 depicts that the reforming efficiency increases from an H_2O/MeOH ratio of 1 to 2 but slightly varies from an H_2O/MeOH ratio of 3 to 5 at reaction temperature 600°C. The reforming efficiency increases with increasing reaction temperature due to increasing the energy of hydrogen and carbon monoxide. The reforming efficiency is higher with UWS than without UWS at varied H_2O/MeOH ratios because the reforming with UWS gets more hydrogen and CO yields. There are exceptions that for H_2O/MeOH ratios of 1 and 2 at a reaction temperature of 600 °C, the reforming efficiency without UWS is slightly larger than with UWS due to the increase in urea's energy than in hydrogen's and carbon monoxide's energy.



(a)



(b)

Figure 9 Reforming efficiency (a) with (b) without UWS varying H_2O/MeOH ratios

Test rig and its validation

Figure 10 displays the test rig to generate the hydrogen-rich gas of the SRM process for verifying the thermodynamic results. This rig consists of a reactant offer system, a reformer, a heating and temperature control system, a cooling system, a gas sampling and analysis system, and so on. The reactant offer system includes a fuel tank and a peristaltic pump (Longer Pump C9ES-DG100M). Stainless steel is feasible in this cylindrical reformer, which has 1.2 by weight percent of pelletized Ru/CeO_2 catalyst in the bottom with 5.2 mm in and 3.0 mm in height. The electric heater with asbestos prevents heat loss. The reformer shell with a ceramic heater and a tube through the reformer via exhaust gas from a diesel engine to regain the exhaust waste heat serve as the heat source for the SRM. To control the temperature of the layer filled with catalyst, use the thermocouples' signal and a PID controller with a voltage input from a thermocouple and a voltage output to the heater. After the temperature of the gas mixture decreases through the cooler, the anti-corrosion vacuum pump. Employ gas chromatography (Aglient 6850) to analyze the cooled gaseous pro ducts by the gaseous products with H_2, CO, N_2, CO_2, and CH_4. The experimental procedures are as follows:

1. Check if the related instruments work and calibrate them. Adjust setting values of required parameters for the related equipment.
2. Adjust setting values of required parameters for the related equipment.
3. Turn on the heating and temperature control system. Record the duration of the reformer to heat from ambient temperature to the required reaction temperature. The fuel can be injected into the gas preheating zone and vaporize about 12 to 15 minutes after the reformer reaches the reaction temperature. Finally, the fuel vapor enters the reformer body and reacts to produce hydrogen.
4. Connecting the reformer with the cooling system through the copper pipe pumps the high-temperature gas mixture into the cooling system and drying bottles to cool and remove excess water vapor. The end of the system is directly connected with an airtight bag to avoid pollution by the atmospheric gas during the sampling process. The gas chromatograph receives the gas mixture from an airtight bag to analyze the compositions.
5. Calculate the hydrogen-rich gas flow rate employing the carried gas flow rate and hydrogen-

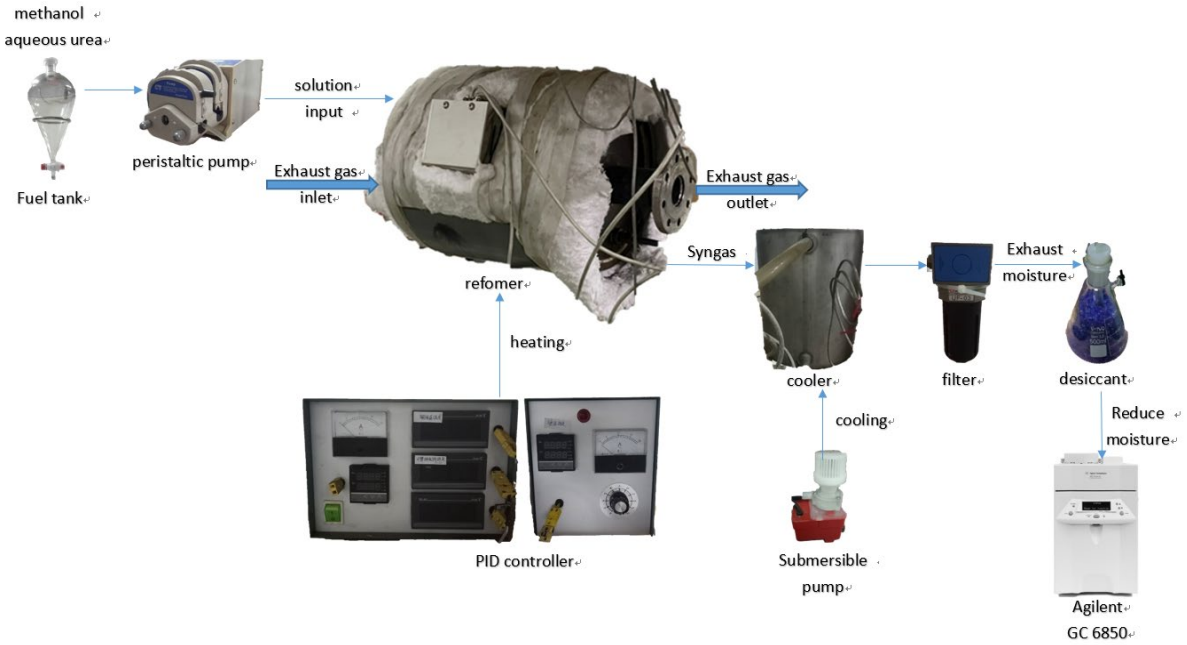
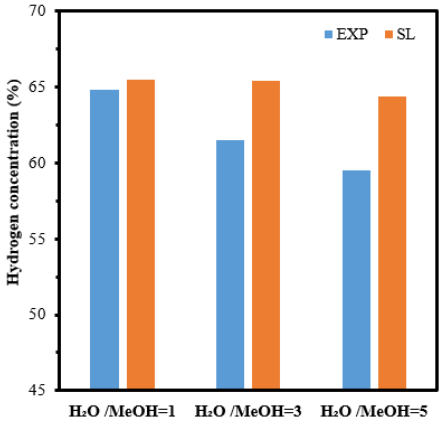


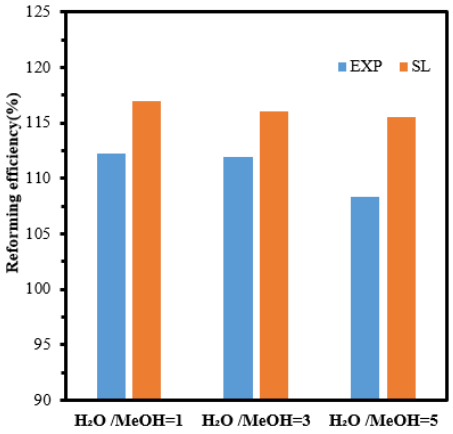
Figure 10 Experimental apparatus

rich gas concentration.

The SRM with and without UWS undergoes the work. The test factors contain methanol mass flow rate and reaction temperature with the UWS or the aqueous methanol. The mass flow rate of methanol with UWS or pure water remains constant at 13.5 g/min with helium as the carried gas at a 30 c.c./min flow when the H_2O/MeOH is 1, 3, and 5, reforming at 700 ºC. Measurements include the reaction temperature with the resultant gas concentrations. The H_2O/MeOH of 1 can produce a hydrogen-rich gas flow rate of 15.4 l/min, H_2O/MeOH of 3 can produce a hydrogen-rich gas flow rate of 15.4 l/min and H_2O/MeOH of 5 can produce a hydrogen-rich gas flow rate of 11.1 l/min. Figure 11 compares the outcomes of the experimented hydrogen concentration and reforming efficiency of methanol-reforming using UWS for various H_2O/MeOH ratios. The concentration of experiment hydrogen at H_2O/MeOH=1 is 64.84%, 5.35% larger than the concentration while blending with UWS at H_2O/MeOH=5 (59.49%). The pattern of the H_2 concentration in the simulation and experimental data is 5.35% larger than the concentration while blending with UWS at H_2O/MeOH=5 (59.49%). The pattern of the H_2 concentration in the simulation and experimental data is as consistent as H_2O/MeOH spans from 1 to 5. Because the experiments have fluid friction, finite-temperature difference heat transfer, and finite reaction rates, the experimental results for H_2yield are less than the simulation ones, and they get similar trends with H_2O/MeOH ratio. For H_2O/MeOH ranging from 1 to 5, the pattern of the reforming efficiency between simulation and experimented data is also the same. The experimental results for the reforming efficiency are lower than the theoretical ones due to less experimental H_2 yield. Future research will be required to ascertain how the catalyst and UWS concentration affect hydrogen production.



(a)



(b)

Figure 11 A comparison chart of the simulation and experiment (a) hydrogen concentration (b) reforming efficiency.

CONCLUSIONS

Because there are more hydrogen couriers throughout the reforming procedure, this work compares the hydrogen and hydrogen-rich output with methanol for UWS and no UWS. The conclusions are as follows:

Adding UWS can boost hydrogen production for the same H_2O/MeOH ratio. As urea's molarity rises, it rises as well. For steam reforming with an H_2O/MeOH ratio of 5, the hydrogen production with UWS is 63.1% higher than without UWS.

More carbon will form than in the absence of UWS because urea consists of carbon atoms. Compared to unutilized UWS, the mole with UWS will have a slightly higher carbon formation than unutilized UWS. As the temperature surpasses 250 ºC, carbon production quickly drops to a low amount despite adding UWS. It suggests that adding UWS at higher reaction temperatures should not cause the carbon deposits to inhibit the methanol-reforming reaction. Since urea is non-flammable, it contributes to the endothermic reaction throughout the reforming procedure. It can appear in a condition with an abundant heat supply, such as sufficient waste heat regained via combustion engines.

This work presented and analyzed a new concept of methanol-reforming mixed with UWS and conducted elemental verification by the cylindrical reformer. The findings demonstrated the similarity between the simulation and experiment trends. Using UWS instead of pure steam offers the benefit of promoting hydrogen-rich gas production. Further experiments will be required to realize the effect of catalysts and UWS.

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