



Thermodynamic analysis and experimental study of hydrogen production from oxidative reforming of n-butanol

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HIGHLIGHTS

- A Gibbs free energy minimization method was applied for thermodynamic analysis.
- Experiments were carried out using Ni- and Rh-Al₂O₃ catalysts.
- Thermoneutral conditions obtained at OBR of 2.70–2.80 at 700 °C and 2.65–2.75 at 800 °C.
- The thermodynamic predictions were in good agreement with experimental results.

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ABSTRACT

A Gibbs free energy minimization method was applied to analyze the thermodynamics of hydrogen production via oxidative reforming of n-butanol. The conditions studied were a temperature range of 300–1100 °C under atmospheric pressure with steam to n-butanol molar feed ratios (SBR) ranging from 0 to 12 and oxygen to n-butanol molar feed ratios (OBR) of 0–6. The thermoneutral conditions can be obtained at OBR of 2.70–2.80 at 700 °C and 2.65–2.75 at 800 °C, respectively. The maximum hydrogen yield of 5.56 mol/mol_{Butanol} can be achieved at 700 °C with SBR of 12, conditions under which carbon formation and methane generation are predicted to be relatively low. The thermodynamic predictions were in good agreement with experimental results using Ni/Al₂O₃ and Rh/Al₂O₃ catalysts, from which the reaction was studied at different SBR, OBR, and temperatures. Under atmospheric pressure at 700 °C with OBR of 2.70 and SBR of 9, the product yields from the reaction in the presence of Rh/Al₂O₃ were close to the thermodynamic values.

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1. Introduction

In response to the energy crisis and environmental concerns, new energy supply technologies are being researched to utilize renewable energy sources in an efficient and environmentally-friendly manner [1]. Hydrogen is considered to be an attractive replacement for fuels among these alternative energy technologies. Hydrogen can be utilized in fuel cells for example to produce electricity at high efficiencies (40–60% depending on fuel cell type) with clean exhaust [2]. Hydrogen can be produced by coal gasification, steam and dry reforming, partial oxidation, electrolysis and thermal decomposition of water as well as fermentation processes.

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Conventionally, steam reforming is applied commercially to produce hydrogen from hydrocarbons (e.g. reactions of natural gas (methane) with steam under high temperatures) for diverse applications such as ammonia and methanol production. Steam reforming is a strongly endothermic reaction ($\Delta H^\circ_{298.15} = 206.2$ and $558.3 \text{ kJ mol}^{-1}$ for natural gas and n-butanol steam reforming respectively [3,4]), thus, in conventional steam reforming of, some of the natural gas is used to supply heat for reaction. This affects both the costs of hydrogen production and time spent during start up [5]. Oxidative reforming, in which steam reforming and exothermic partial oxidation simultaneously occur, was developed as a possible solution for reducing these costs [6]. In this process, the heat released during the partial oxidation can reduce the endothermic energy requirement for steam reforming reaction to proceed.

While natural gas is conventionally used for commercial hydrogen production, catalytic developments over the last few decades have enabled use of increasingly heavier hydrocarbon feedstocks up to naphtha, biomass derived compounds such as bio-methanol [7–9], ethanol [10–12], glycerol [13–15], methane [16], bio-oil [17,18] and dimethyl ether [19,20] are also viewed as potential sources for hydrogen production. n-Butanol can be another choice of renewable fuel. Bio-butanol, is sometimes called biogasoline, can be derived from biomass feedstocks. Recent studies have shown that n-butanol can also be used to produce hydrogen [21–26]. However, due to complex multiple reactions in the oxidative reforming of n-butanol, the purity of the hydrogen product is affected by numerous undesirable side reactions e.g. reverse water gas shift, methanation and the Boudouard reaction (disproportionation of carbon monoxide to carbon dioxide and carbon). In order to achieve industrially acceptable production efficiencies and product purities, it is necessary to know the effect of temperatures, steam to n-butanol molar feed ratios (SBR) and oxygen to n-butanol feed ratios (OBR); on the product composition. A thermodynamics analysis of the process can be pursued to understand if the process is feasible and industrially significant.

Catalytic performance of other catalysts towards the butanol steam reforming had been experimentally studied previously by other researchers. Medrano [27] studied steam reforming of butanol using Ni/Al. It was found that Ni/Al with 28.5 wt.% gave 75% conversion, roughly, when using 14.7 ratio of SBR at 650 °C. Cai [28] studied catalytic performance of monometallic and bimetallic catalysts towards steam reforming of bio-butanol for hydrogen production at 500 °C, SBR = 3 and OBR = 1.5. The results showed that conversion of bio-butanol over bimetallic catalysts; CoPd/ZnO (97%), CoRh/ZnO (95%), CoRu/ZnO (90%), and CoIr/ZnO (84%); were higher than that of monometallic catalyst, Co/ZnO (78%). Harju [29] investigated steam reforming of n-butanol over ZrO₂ and Rh–ZrO₂ catalyst at temperature range from 500 to 700 °C. ZrO₂ gave lower conversion of butanol, compared to Rh–ZrO₂ at all temperatures. Conversion of butanol over ZrO₂ at 500, 600 and 700 °C were 50%, 82%, and 84%, respectively, while Rh–ZrO₂ gave 80% conversion of butanol at 500 °C and showed complete conversion at 600 and 700 °C.

In the present work, the thermodynamics analysis of n-butanol oxidative reforming process under various operating conditions was carried out with the aim of maximizing the hydrogen yield. The total Gibbs free energy minimization method was adopted to estimate the equilibrium composition over a range of temperatures, SBRs and OBRs at atmospheric pressure while maximizing the hydrogen yield and minimizing carbon formation. Product distribution and heat consumptions were examined under thermoneutral conditions. Experimental n-butanol oxidative reforming was also performed to check the robustness of the predictions. The experimental operating conditions of reaction temperature, SBR and OBR were selected based on the thermodynamic analyses using Ni/Al₂O₃ and Rh/Al₂O₃ (5% Ni and Rh, respectively) as catalysts.

2. Methods

2.1. Computational thermodynamic analysis

Calculation of equilibrium chemical compositions can be performed by either calculating the equilibrium constant or minimization of the total Gibbs free energy. Calculation of equilibrium chemical compositions for reactions with solid components is difficult to perform by calculation of the equilibrium constant since information of the associated chemical reactions is also required. However, by minimization of the total Gibbs free energy (which

can be applied to the reacting system including condensed components and non-reacting components) it may be easily achieved. Therefore, the Gibbs free energy minimization method was chosen for this study. The total Gibbs free energy of a system is given by the sum of the partial molar Gibbs free energy of a species *i* multiplied by the number of moles of a species *i* according to Eq. (1) [11,21,30,31]:

$$G_T = \sum_{i=1}^m n_i G_i = \sum_{i=1}^m n_{ii} = \sum_{i=1}^m n_i G_i^\circ + RT \sum_{i=1}^m n_i \ln \frac{f_i}{f_i^\circ} \quad (1)$$

where G_T is the total Gibbs free energy. G_i is the partial molar Gibbs free energy of species *i*. G_i° is the standard Gibbs free energy of species *i*. n_i is the mole of species *i*. μ_i is the chemical potential of species *i*. f_i is the fugacity of species *i*. f_i° is the standard-state fugacity of species *i*. R is the molar gas constant and T is the temperature of system.

The assumptions for the reaction equilibrium in gas phase used were:

$$f_i = y_i P \quad (2)$$

$$f_i^\circ = P^\circ \quad (3)$$

$$G_i^\circ = \Delta G_{fi}^\circ \quad (4)$$

Using Lagrange's undetermined multiplier method, the minimum Gibbs free energy of each gaseous species and that of the total system can be expressed according to Eqs. (5) and (6), respectively:

$$\Delta G_{fi}^\circ + RT \ln \frac{y_i P}{P^\circ} + \sum_k \lambda_k a_{ik} = 0 \quad (5)$$

$$\sum_{i=1}^N n_i \left(\Delta G_{fi}^\circ + RT \ln \frac{y_i P}{P^\circ} + \sum_k \lambda_k a_{ik} \right) = 0 \quad (6)$$

The constraints of elemental balance as Eq. (7):

$$\sum_{i=1}^N n_i a_{ik} = A_k \quad (7)$$

where G_{fi}° is the standard Gibbs function of formation of species *i*. P° is the standard-state pressure of 101.3 kPa. y_i is the gas phase mole fraction. i is the fugacity coefficient of species *i*. λ_k is the Lagrange multiplier. a_{ik} is the number of atoms of the element *k* present in each molecule of species *i* and A_k is the total mass of element *k* in the feed (where *i* and *k* represent compound and element in the compound, respectively). Eq. (8) illustrates the Gibbs energy of carbon when the solid carbon occurs in the system utilizing the vapor–solid equilibrium:

$$G_{C(g)} = G_{C(s)} \cong G_{fC(s)}^\circ = 0 \quad (8)$$

Substituting Eq. (1) with Eq. (5) for gaseous species and with Eq. (8) for solid species gives the minimization function of Gibbs-energy for the following Eq. (9) which is the equation of this vapor–solid system:

$$\sum_{i=1}^{N-1} n_i \left(\Delta G_{fi}^\circ + RT \ln \frac{y_i P}{P^\circ} + \sum_k \lambda_k a_{ik} \right) + (n_C \Delta G_{fC(s)}^\circ) = 0 \quad (9)$$

where $G_{C(g)}$ is the partial molar Gibbs free energy of gaseous carbon. $G_{C(s)}$ is the molar Gibbs free energy of solid carbon. $G_{fC(s)}^\circ$ is the standard Gibbs function of formation of solid carbon and n_C is the number of moles of carbon.

2.1.1. Reactions involved in the n-butanol oxidative reforming

During oxidative reforming, the steam reforming reaction occurs simultaneously with the oxidation reaction. Other reactions such as the water gas shift reaction, gasification, hydrogenation, decomposition, Boudouard reaction, partial oxidation reaction as well as oxidation reactions may also occur simultaneously some of which may be undesirable. The possible reaction routes of n-butanol oxidative reforming are shown in Table 1 [11]. Ten species including n-butanol ($C_4H_{10}O$), water (H_2O), oxygen (O_2), hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), ethylene (C_2H_4) and butyric aldehyde (C_4H_8O), as well as elemental carbon (graphite, C) as a solid were included in the simulation.

2.1.2. Estimation of heat and Gibbs free energies of possible reactions

PTC Mathcad Prime 2.0 program was applied for component enthalpy calculation where ΔG_f and ΔH_f are the standard Gibbs free energy of formation and enthalpy of formation in J/mol, respectively. [Table 2](#) represents possible reactions and their heat and Gibbs free energies at 300, 500, 700, 900 and 1100 °C.

From the result, Butanol steam reforming (R-2), Butanol decomposition (R-3), Methane decomposition (R-4), Boudouard reaction (R-5), Water-gas shift reaction (R-6), Hydrogenation of carbon monoxide (R-7), Hydrogenation of carbon dioxide (R-8), Hydrogenation of carbon monoxide (R-9), Hydrogenation of coke (R-10), Carbon monoxide reduction reaction (R-13), Carbon monoxide reduction reaction (R-14), Dehydrogenation of butanol (R-17), Oxidation of butanol (R-20), Oxidation of methane (R-22) and Partial oxidation of carbon monoxide (R-24) were found at 300 °C while Butanol steam reforming (R-1) was active at 500 °C. At 700 °C, the occurring reactions were Butanol steam reforming (R-1), Butanol steam reforming (R-2), Butanol decomposition (R-3), Methane decomposition (R-4), Boudouard reaction (R-5), Water-gas shift reaction (R-6), Methane steam reforming (R-11), Methane dry reforming (R-12), Coke gasification (R-16), Dehydrogenation of butanol (R-17), Oxidation of butanol (R-20), Oxidation of methane

Table 1
Key reactions of n-butanol oxidative reforming [21].

Reaction No.	Equation	Reaction
1	$C_4H_{10}O + 3H_2O \rightarrow 4CO + 8H_2$	Butanol steam reforming
2	$C_4H_{10}O + 7H_2O \rightarrow 4CO_2 + 12H_2$	
3	$C_4H_{10}O \rightarrow CO + 2CH_4 + H_2 + C$	Butanol decomposition
4	$CH_4 \rightarrow C + 2H_2$	Methane decomposition
5	$2CO \rightarrow C + CO_2$	Boudouard reaction
6	$CO + H_2O \rightarrow CO_2 + H_2$	Water-gas shift reaction
7	$CO + 3H_2 \rightarrow CH_4 + H_2O$	Hydrogenation of carbon monoxide
8	$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$	Hydrogenation of carbon dioxide
9	$2CO + 2H_2 \rightarrow CO_2 + CH_4$	Hydrogenation of carbon monoxide
10	$C + 2H_2 \rightarrow CH_4$	Hydrogenation of coke
11	$CH_4 + H_2O \rightarrow CO + 3H_2$	Methane steam reforming
12	$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	Methane dry reforming
13	$CO + H_2 \rightarrow C + H_2O$	Carbon monoxide reduction reaction
14	$2CO + 2H_2 \rightarrow 2C + 2H_2O$	
15	$CO_2 + H_2 \rightarrow CO + H_2O$	Reverse water-gas shift reaction
16	$C + H_2O \rightarrow CO + H_2$	Coke gasification
17	$C_4H_{10}O \rightarrow C_4H_8O + H_2$	Dehydrogenation of butanol
18	$C_4H_8O \rightarrow CO + CH_4 + C_2H_4$	Butyric aldehyde decomposition
19	$C_2H_4 \rightarrow \text{POLYMER} \leftrightarrow C + 2H_2$	Pyrolysis of ethylene
20	$C_4H_{10}O + 6O_2 \rightarrow 4CO_2 + 5H_2O$	Oxidation of butanol
21	$C_4H_{10}O + \alpha O_2 \rightarrow \beta CO + \gamma CO_2 + 5H_2$	Partial oxidation of butanol
22	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	Oxidation of methane
23	$CH_4 + \alpha O_2 \rightarrow \beta CO + \gamma CO_2 + 2H_2$	Partial oxidation of methane
24	$CO + 0.5O_2 \rightarrow CO_2$	Partial oxidation of carbon monoxide

Table 2
Calculation of heat and Gibbs free energy of possible reactions.

No	Reaction	At 300 °C			At 500 °C			At 700 °C			At 900 °C			At 1100 °C		
		ΔH (J/mol)	ΔG (J/mol)		ΔH (J/mol)	ΔG (J/mol)		ΔH (J/mol)	ΔG (J/mol)		ΔH (J/mol)	ΔG (J/mol)		ΔH (J/mol)	ΔG (J/mol)	
1	Butanol steam reforming	6.38×10^5	1.32×10^4		6.48×10^5	-2.07×10^5		6.52×10^5	-4.28×10^5		6.52×10^5	-6.50×10^5		6.48×10^5	-8.72×10^5	
2	Butanol steam reforming	4.82×10^5	-5.74×10^4		4.99×10^5	-2.50×10^5		5.11×10^5	-4.45×10^5		5.18×10^5	-6.43×10^5		5.22×10^5	-8.41×10^5	
3	Butanol decomposition	7.03×10^4	-1.97×10^5		6.89×10^4	-2.91×10^5		6.63×10^4	-3.83×10^5		6.32×10^4	-4.75×10^5		5.96×10^4	-5.67×10^5	
4	Methane decomposition	-3.16×10^5	-3.68×10^5		-3.14×10^5	-3.87×10^5		-3.13×10^5	-4.06×10^5		-3.12×10^5	-4.26×10^5		-3.13×10^5	-4.45×10^5	
5	Boudouard reaction	-1.73×10^5	-7.09×10^4		-1.73×10^5	-3.54×10^4		-1.71×10^5	-1.96×10^5		-1.69×10^5	3.46×10^4		-1.67×10^5	6.92×10^4	
6	Water–gas shift reaction	-3.91×10^4	-1.77×10^4		-3.73×10^4	-1.07×10^4		-3.54×10^4	-4.14×10^3		-3.35×10^4	1.96×10^3		-3.16×10^4	7.76×10^3	
7	Hydrogenation of carbon monoxide	-2.17×10^5	-7.86×10^4		-2.22×10^5	-2.95×10^4		-2.25×10^5	2.06×10^4		-2.26×10^5	7.12×10^4		-2.27×10^5	1.22×10^5	
8	Hydrogenation of carbon dioxide	-1.78×10^5	-6.10×10^4		-1.85×10^5	-1.88×10^4		-1.90×10^5	2.48×10^4		-1.93×10^5	6.92×10^4		-1.95×10^5	1.14×10^5	
9	Hydrogenation of carbon monoxide	-2.56×10^5	-9.63×10^4		-2.59×10^5	-4.02×10^4		-2.60×10^5	1.65×10^4		-2.60×10^5	7.32×10^4		-2.58×10^5	1.30×10^5	
10	Hydrogenation of coke	-8.23×10^4	-2.54×10^4		-8.65×10^4	-4.79×10^3		-8.90×10^4	1.67×10^4		-9.04×10^4	3.86×10^4		-9.11×10^4	6.06×10^4	
11	Methane steam reforming	2.17×10^5	7.86×10^4		2.22×10^5	2.95×10^4		2.25×10^5	-2.06×10^4		2.26×10^5	-7.12×10^4		2.27×10^5	-1.22×10^5	
12	Methane dry reforming	2.56×10^5	9.63×10^4		2.59×10^5	4.02×10^4		2.60×10^5	-1.65×10^4		2.60×10^5	-7.32×10^4		2.58×10^5	-1.30×10^5	
13	Carbon monoxide reduction reaction	-1.34×10^5	-5.33×10^4		-1.35×10^5	-2.47×10^4		-1.36×10^5	3.94×10^3		-1.36×10^5	3.26×10^4		-1.35×10^5	6.14×10^4	
14	Carbon monoxide reduction reaction	-2.69×10^5	-1.07×10^5		-2.71×10^5	-4.95×10^4		-2.72×10^5	7.88×10^3		-2.72×10^5	6.53×10^4		-2.71×10^5	1.23×10^5	
15	Reverse water–gas shift reaction	3.91×10^4	1.77×10^4		3.73×10^4	1.07×10^4		3.54×10^4	4.14×10^3		3.35×10^4	-1.96×10^4		3.16×10^4	-7.76×10^3	
16	Coke gasification	1.34×10^5	5.33×10^4		1.35×10^5	2.47×10^4		1.36×10^5	-3.94×10^3		1.36×10^5	-3.26×10^4		1.35×10^5	-6.14×10^4	
17	Dehydrogenation of butanol	9.04×10^4	-3.46×10^5		9.25×10^4	-4.98×10^5		9.48×10^4	-6.51×10^5		9.72×10^4	-8.05×10^5		9.94×10^4	-9.59×10^5	
18	Butyric aldehyde decomposition	1.07×10^5	2.60×10^5		1.04×10^5	3.14×10^5		9.91×10^4	3.69×10^5		9.36×10^4	4.25×10^5		8.74×10^4	4.81×10^5	
19	Oxidation of butanol	-2.45×10^6	-2.64×10^6		-2.46×10^6	-2.71×10^6		-2.46×10^6	-2.78×10^6		-2.47×10^6	-2.84×10^6		-2.47×10^6	-2.90×10^6	
20	Oxidation of methane	-8.00×10^5	-8.01×10^5		-8.00×10^5	-8.01×10^5		-8.01×10^5	-8.01×10^5		-8.03×10^5	-8.02×10^5		-8.04×10^5	-8.01×10^5	
21	Partial oxidation of carbon monoxide	-2.84×10^5	2.33×10^5		-2.84×10^5	-2.16×10^5		-2.83×10^5	-1.98×10^5		-2.82×10^5	-1.81×10^5		-2.81×10^5	-1.64×10^5	

(R-22) and Partial oxidation of carbon monoxide (R-24). At higher temperature range, from 900 to 1100 °C, the spontaneous reactions were Butanol steam reforming (R-1), Butanol steam reforming (R-2), Butanol decomposition (R-3), Methane decomposition (R-4), Methane steam reforming (R-11), Methane dry reforming (R-12), Reverse water gas shift active (R-15), Coke gasification (R-16), Dehydrogenation of butanol (R-17), Oxidation of butanol (R-20), Oxidation of methane (R-22) and Partial oxidation of carbon monoxide (R-24).

This result is in good agreement with Nahar [21], our simulation results, and experimental ref in the next section. It can be seen that the more hydrogen was produced from 700 to 1100 °C, compared to at 500 °C, due to Methane steam reforming (R-11), Methane dry reforming (R-12) and Coke gasification (R-16).

2.1.3. Simulation operating conditions

The Aspen Plus program was used to perform all the equilibrium composition calculations. “Gibbs reactor” in the software was commonly used to calculate product compositions and heat of overall reaction in a reacting system under the condition of minimization of Gibbs free energy. The Soave Redlich Kwong method was selected for the simulations. The production of hydrogen and other compounds from n-butanol oxidative reforming were investigated at atmospheric pressure and temperatures from 300 to 1100 °C, SBR between 0 and 12, and OBR between 0 and 6. To evaluate process performance of the equilibrium conversions of n-butanol (Eq. (10)) and product yield of species *i* (Eq. (11)), the following equations were used:

$$X_e (\%) = \frac{(F_{B_{in}} - F_{B_{out}})}{F_{B_{in}}} \times 100 \quad (10)$$

$$Y_i (\%) = \frac{F_{i_{out}}}{F_{B_{in}}} \quad (11)$$

where X_e is the equilibrium conversion of n-butanol. Y_i is the yield of product species *i*. $F_{B_{in}}$ is the molar flow rate of n-butanol at the inlet. $F_{B_{out}}$ is the molar flow rate of n-butanol at the outlet and $F_{i_{out}}$ is the molar flow rates of species *i* at the outlet.

2.2. Experimental study of the n-butanol oxidative reforming

To evaluate the thermodynamic predictions, experimental n-butanol oxidative reforming was performed using Ni/Al₂O₃ and Rh/Al₂O₃ (5% Ni and Rh) as the catalysts in a tube reactor.

2.2.1. Catalyst preparation and characterizations

The catalysts were prepared by impregnating α -Al₂O₃ (Aldrich) with Ni(NO₃)₃ and Rh(NO₃)₃ (Aldrich), respectively. After stirring, the solution was dried and calcined at 1000 °C for 6 h. Both catalysts were then reduced using 10% hydrogen in helium at 700 °C for 6 h before use. The weight content of Ni and Rh was determined by X-ray fluorescence (XRF) analysis. The reducibility percentages of metals was measured and calculated from the degree of H₂ uptakes from the temperature-programmed reduction (TPR) test using 5% H₂ with the total flow rate of 100 cm³ min⁻¹ and temperature from room temperature to 500 °C, while the dispersion percentage of metals was identified from the volumetric H₂ chemisorption measurement using a chemisorption analyzer. Lastly, the catalyst specific surface areas were obtained from BET measurements. All physicochemical properties of the synthesized catalysts are presented in Table 3.

2.2.2. Apparatus and procedures

For the catalytic testing, the feed gases i.e. He (as carrier gas) and O₂ were controlled by 2 mass flow controllers, whereas

Table 3

Physicochemical properties of prepared catalysts.

Catalyst	BET surface (m ² g ⁻¹)	Metal-load ^a (wt.%)	Metal-red ^b (%)	Metal-disp ^c (%)
Rh/Al ₂ O ₃	44.7	5.06	96.5	7.25
Ni/Al ₂ O ₃	43.8	5.11	95.8	7.11

^a Measured from X-ray fluorescence analysis.

^b Metal reducibility (measured from temperature-programmed reduction (TPR) with 5% hydrogen).

^c Metal dispersion (measured from the volumetric H₂ chemisorption measurement using chemisorption analyzer).

n-butanol and H₂O were introduced by the heated syringe pump (with the reactant feed flow rate of 2.54 cm³ h⁻¹) and vaporized by our designed quartz vaporizer-mixer system. All feeds were introduced to a 10-mm diameter quartz reactor, which is mounted vertically inside the tubular furnace. The catalyst (100 mg) was loaded in the quartz reactor, which was packed with a small amount of quartz wool to prevent the catalyst from moving. To avoid any limitations by intraparticle diffusion, the total gas flow was 100 cm³ min⁻¹ to give a constant residence time of 5×10^{-3} g min cm⁻³ in all experiments. Preliminary experiments were carried out to find suitable conditions in which internal and external mass transfer effects are not predominant. Considering the effect of external mass transfer, we kept the total flow rate constant at 100 cm³ min⁻¹ under a constant residence time in all testing. The suitable average sizes of catalysts were also verified in order to confirm that the experiments were carried out within the region of isothermal kinetics. Based on the verification, the catalyst particle size diameter was between 100 and 200 μ m in all experiments. In the catalytic testing reactor, a Type-K thermocouple was placed into the annular space between the reactor and the furnace. This thermocouple was mounted on the tubular reactor in close contact with the catalyst bed to minimize the temperature difference between the catalyst bed and the thermocouple. Another Type-K thermocouple, which is covered with small closed-end quartz rod to prevent any catalytic reactivity of the thermocouple during the reaction, was inserted in the middle of the quartz tube in order to re-check the possible temperature gradient. The recorded values showed that the maximum temperature fluctuation during the reaction was always ± 1.0 °C or less from the temperature specified for the reaction. The operating conditions i.e. reaction temperatures, SBR and OBR were selected based on the results of the thermodynamic analyses.

After the reactions, the exit gas mixture was transferred via trace-heated lines to the analysis section, which consists of a Porapak Q column Shimadzu 14B gas chromatograph (GC) and a mass spectrometer (MS). The mass spectrometer in which the sampling of the exit gas was done by a quartz capillary and differential pumping was used for the transient and carbon formation experiments, whereas the gas chromatography was applied in order to investigate the steady state condition experiments and to recheck the results from the mass spectrometer. In the present work, the catalyst activity was defined in terms of conversion and product yields.

2.2.3. Measurement of carbon formation

The oxidation reaction was applied to investigate the amount of carbon formed on the catalyst surface by introducing 10% O₂ in He into the system at 900 °C, after purging with helium. The amount of carbon formation on the surface of catalysts was determined by measuring the CO and CO₂ yields from the test. The calibrations of CO and CO₂ productions were performed by injecting a known amount of these calibration gases from a loop, in an injection valve in the bypass line. The response factors were obtained by dividing

the number of moles for each component over the respective areas under the peaks. It is noted that the spent sample was further tested with TGA-MS (PerkinElmer, USA) at the maximum temperature of 1000 °C to ensure that no carbon formation remains on the surface of the catalyst; and no weight loss or CO/CO₂ productions were detected from all catalysts after the oxidation reaction.

3. Results and discussion

This section presents the result of the thermodynamic analyses and the optimal conditions for hydrogen production followed by the experimental results.

3.1. Computational thermodynamic analysis

3.1.1. Effect of operating conditions on the hydrogen production

The thermodynamic analyses predicted that, during n-butanol oxidative reforming, hydrogen can be produced from steam reforming of n-butanol, shown as reaction 1 (R-1) and reaction 2 (R-2) in Table 1, decomposition of n-butanol (R-3), methane decomposition (R-4), water–gas shift reaction (R-6), steam and dry reforming of methane (R-11, R-12), coke gasification (R-16), dehydrogenation of n-butanol (R-17), pyrolysis of ethylene (R-19), oxidation reaction (R-20), and partial oxidation (R-21), whereas hydrogen can be utilized in the hydrogenation reaction (R-7 to R-10), carbon monoxide reduction reaction (R-13, R-14) and reverse water gas shift reaction (R-15). Fig. 1 shows the hydrogen yield as a function of SBR and OBR at different temperatures. Fig. 1 shows that hydrogen yield increased with increasing temperature and/or SBR, whereas it decreased with increasing OBR.

The reaction temperature is predicted to strongly influence the reforming reaction, an endothermic reaction. The hydrogen yield increased with increasing temperature, especially at 700 °C. The amount of hydrogen produced at 500 °C was relatively low compared to that produced at temperatures between 700 and 800 °C. At low temperatures, the hydrogen yield was low due to hydrogenation occurring, in which hydrogen reacts with carbon monoxide, carbon dioxide, and coke to form methane (R-7 to R-10); these reactions are favored at low temperature. With increasing temperature, the hydrogen yield increased due to steam reforming (R-11) and dry reforming of methane at temperatures above 600 °C [21]. Similarly, methane decomposition (R-4) and the reverse water–gas shift reaction (R-15) are favored at high temperature. Thus, the hydrogen yield decreased at temperatures higher than 800 °C, this is expected to be due to acceleration of the reverse water gas shift (R-15) [15]. Increased SBR is predicted to result in an increase in hydrogen yield; this is probably due to addition of water shifting the equilibrium towards n-butanol in the reforming reaction (R-1, R-2), water gas shift reaction (R-6), and coke gasification (R-16). Fig. 1 demonstrates that SBR of 9–12 was suitable for the steam reforming of n-butanol when the OBR was maintained at zero. The hydrogen production yields at SBR of 9–12 are close to each other but significantly different from the hydrogen production yield at SBR of 6. These results agreed with previous studies by Nahar et al. [21].

The OBR is a key parameter in oxidative reforming process since heat released from the oxidation reaction is consumed in the steam reforming reaction. Addition of oxygen shifts the equilibrium towards oxidation reactions (R-20 to R-23) which compete with the reforming reaction. Fig. 1 shows that n-butanol oxidative reforming was favored at low OBR, especially OBR ranging from

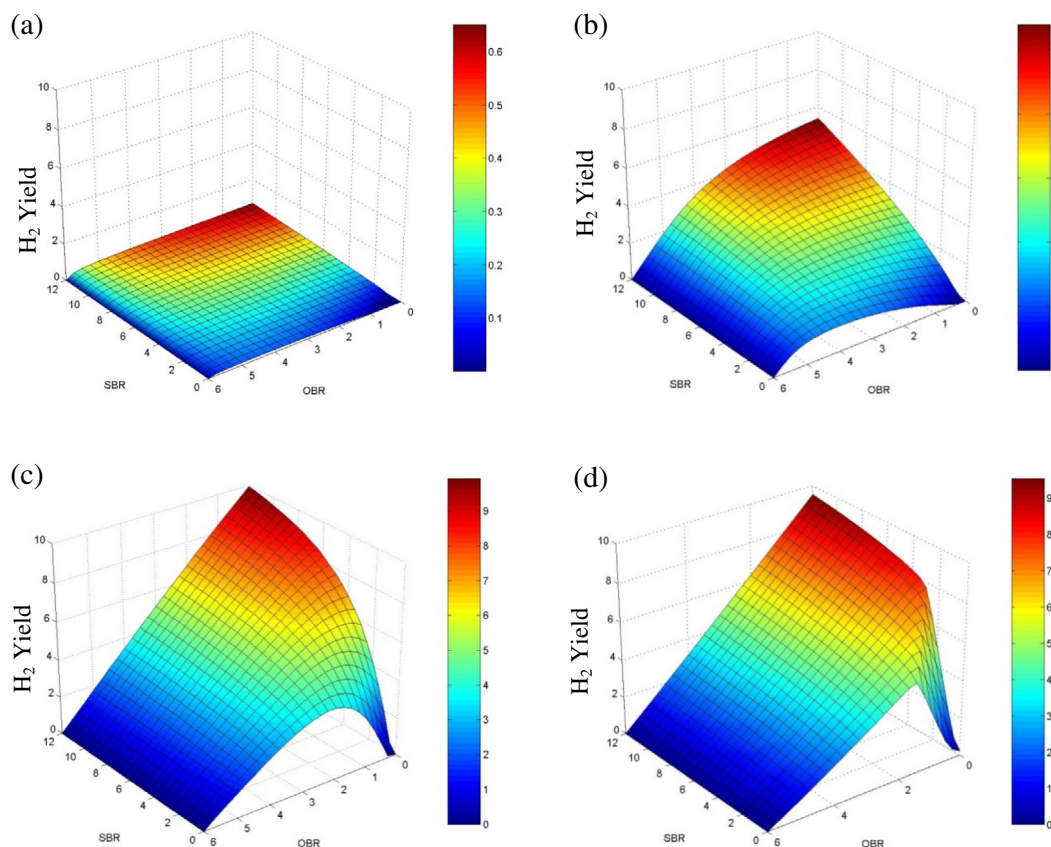


Fig. 1. Hydrogen yield as a function of SBR and OBR at 1 bar and temperatures: (a) 300 °C, (b) 500 °C, (c) 700 °C and (d) 900 °C.

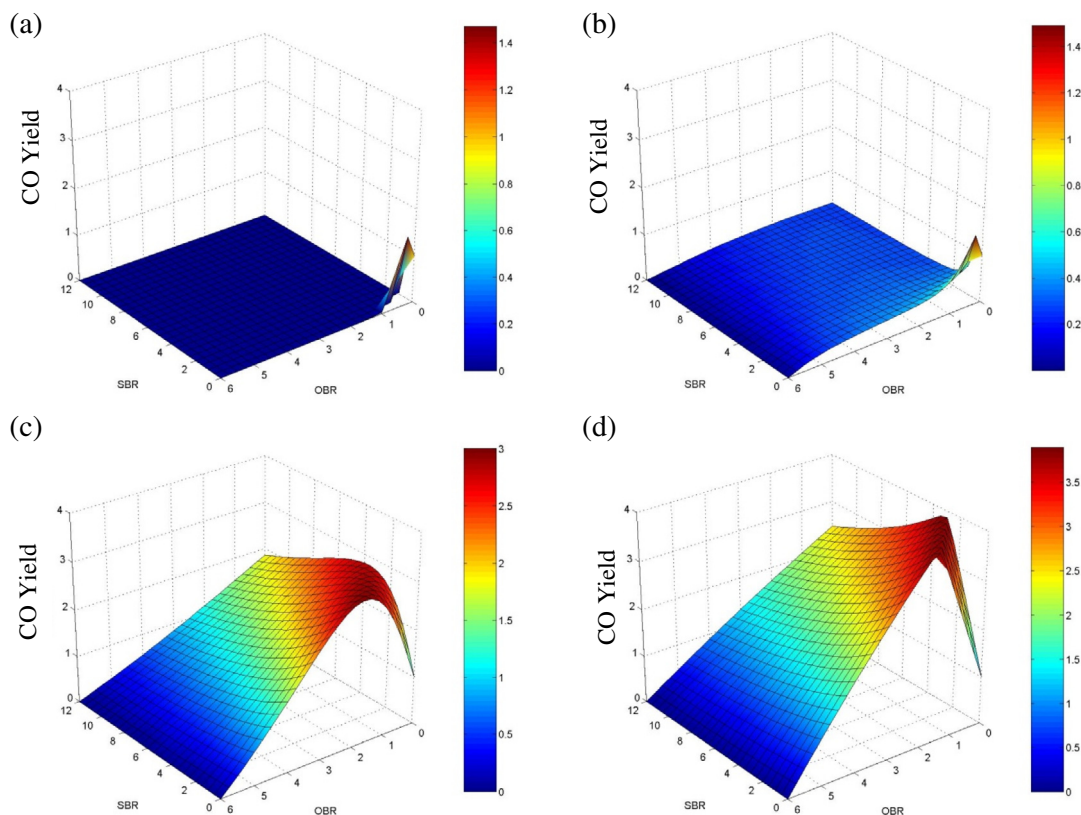


Fig. 2. Carbon monoxide yield as a function of SBR and OBR at 1 bar and temperatures: (a) 300 °C, (b) 500 °C, (c) 700 °C and (d) 900 °C.

1.5 to 3. Under these conditions, the thermoneutral condition was examined; this will be discussed in Section 3.1.3.

3.1.2. Effect of operating conditions on other product distributions

In the n-butanol oxidative reforming process, carbon monoxide can be produced by steam reforming of n-butanol (R-1); n-butanol decomposition (R-3); steam and dry reforming of methane (R-11, R-12); the reverse water gas shift reaction (R-15); coke gasification (R-16); and butyric aldehyde decomposition (R-18); while it can be consumed in the Boudouard reaction (R-5); water gas shift reaction (R-6); hydrogenation of carbon monoxide (R-7, R-9); carbon monoxide reduction (R-13, R-14) and carbon monoxide partial oxidation (R-24).

For fuel cell applications, the carbon monoxide content should be minimized. The carbon monoxide yield as a function of SBR and OBR under different temperatures is shown in Fig. 2. The figure indicates that carbon monoxide yield increased with increasing temperatures, whereas it decreased with increasing SBR and/or OBR.

At low temperatures, carbon monoxide production was low since it can be consumed in the Boudouard reaction (R-5), hydrogenation of carbon monoxide (R-7, R-9), and also carbon monoxide reduction reactions (R-13, R-14) which are all favored at low temperature. Increasing temperatures increased carbon monoxide yields as a result of steam and dry reforming of methane (R-11, R-12), reverse water gas shift (R-15), and coke gasification (R-16). The maximum carbon monoxide yield was 2.8 at 900–1100 °C, whereas carbon monoxide yield was about 1.8–2.2 at 700–800 °C and 0–0.2 at 300–500 °C for SBR of 12.

These results suggest that carbon monoxide formation can be inhibited at low temperatures. In addition, increased amounts of SBR are predicted to have no effect on carbon monoxide yield at

low temperatures. This could be due to its complete consumption during hydrogenation of carbon monoxide to methane and the carbon monoxide reduction reaction. Whereas, an inverse relation to carbon monoxide yield at high temperatures was predicted, due to increased amounts of steam feed shifting the equilibrium towards the water gas shift and reverse water gas shift reaction to the hydrogen product as discussed above. The maximum carbon monoxide yield was 2.8 for SBR of 3, whereas carbon monoxide yield was 1.8 at SBR of 12 at 700 °C. This suggests that at high temperature carbon monoxide production can be reduced by increasing SBR.

Increased OBR results in a shifting of the equilibrium in the oxidation and partial oxidation reactions (R-20 to R-23) which can produce carbon monoxide. However, the carbon monoxide produced can also react with the oxygen via carbon monoxide partial oxidation (R-24) resulting in a decrease in carbon monoxide yield [32]. Therefore, it can be seen that an increase of OBR can also reduce the amount of carbon monoxide content.

In addition to synthesis gas production, methane may also be generated from n-butanol decomposition (R-3), hydrogenations of carbon monoxide, carbon dioxide, and coke (R-7, R-8, R-9, and R-10), and butyric aldehyde decomposition (R-18). Methane however, can be consumed during methane decomposition (R-4), steam reforming of methane (R-11), and dry reforming of methane (R-12).

Fig. 3 shows methane yield as a function of SBR and OBR at temperatures ranging from 300 to 1000 °C. Methane yield is predicted to decrease with increasing temperatures, SBR, and/or OBR. At low temperatures, methane was predicted to be the main product since it is produced via hydrogenation of carbon monoxide, carbon dioxide and coke. Methane production is predicted to be inhibited at high temperatures since it can be reformed by steam and dry

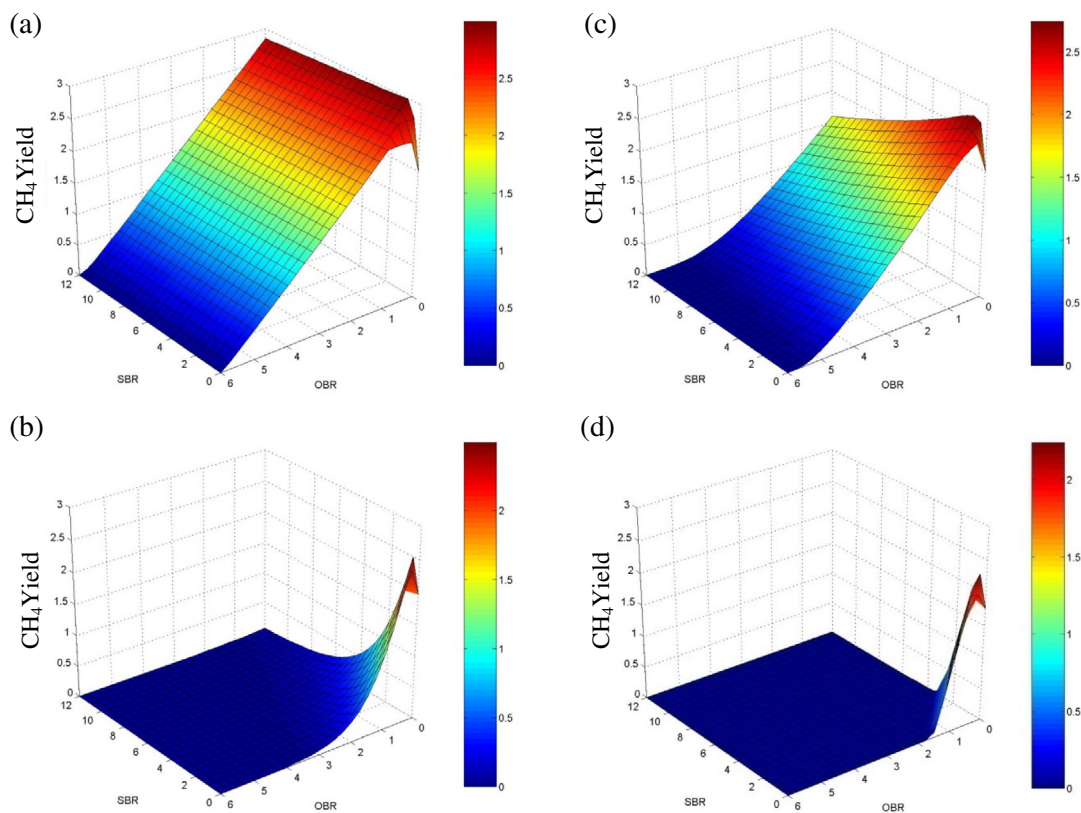


Fig. 3. Methane yield as a function of SBR and OBR at 1 bar and temperatures: (a) 300 °C, (b) 500 °C, (c) 700 °C and (d) 900 °C.

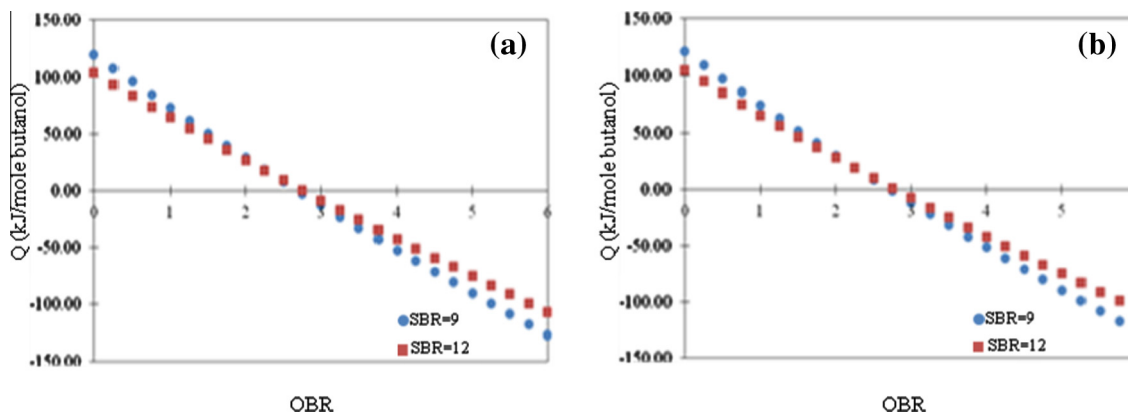


Fig. 4. Overall heat of reaction as a function of SBR and OBR at temperatures: (a) 700 °C and (b) 800 °C.

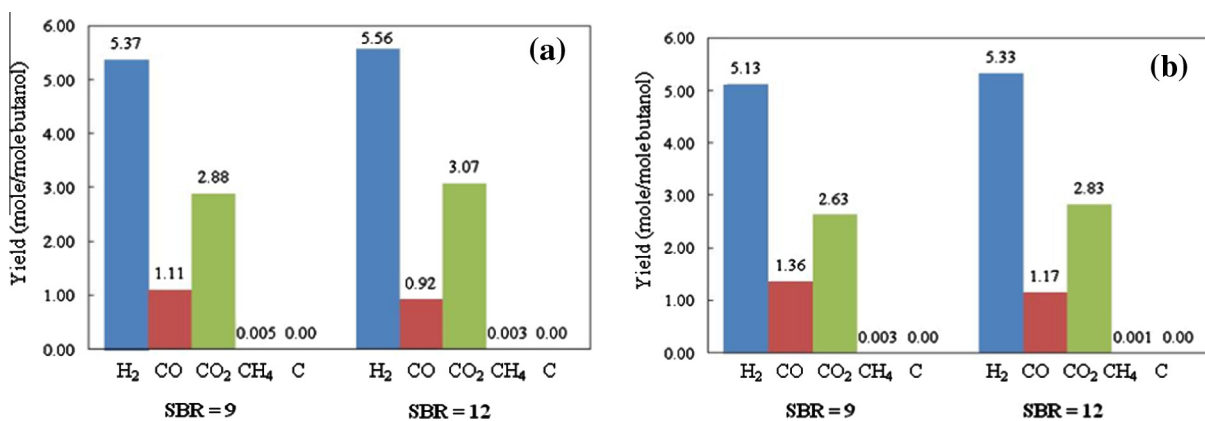


Fig. 5. Product distribution at thermoneutral operation condition: (a) 700 °C and (b) 800 °C.

reforming. At SBR of 9–12, methane is predicted to be completely inhibited at temperatures greater than 700 °C for all OBR.

3.1.3. Thermoneutral condition

According to the thermodynamic investigations, temperatures of between 700 and 800 °C and SBR ranging from 9 to 12 can produce hydrogen by n-butanol reforming at industrially acceptable yields. Fig. 4 shows the overall heats of reaction as a function of SBR and OBR at 700 and 800 °C. The optimal OBR was determined to achieve the thermoneutral condition. It was found that an OBR of 2.70 was suitable for SBR of 9 at 700 °C and OBR of 2.65 at 800 °C. For SBR of 12, OBR of 2.80 and 2.75 were suitable at 700 and 800 °C, respectively.

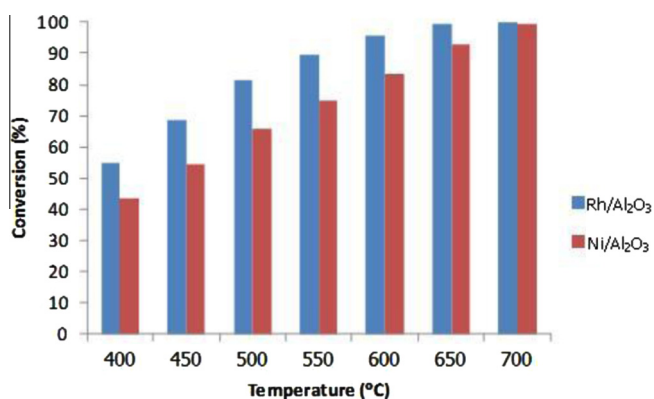


Fig. 6. Conversion of steam reforming of butanol in the presence of Rh/Al₂O₃ and Ni/Al₂O₃ from 400 to 700 °C.

The product distribution at the thermoneutral condition is presented in Fig. 5. At 700 °C, the yield of hydrogen, carbon monoxide and carbon dioxide were 5.37, 1.11 and 2.88 respectively for SBR of 9, while at the same temperatures the yields were 5.56, 0.92 and 3.07 for SBR of 12. The yields of hydrogen, carbon monoxide and carbon dioxide at 800 °C were 5.13, 1.36 and 2.63 respectively for SBR of 9 whereas at SBR 12, they were 5.33, 1.17 and 2.83. The estimated efficiency of the n-butanol oxidative reforming was 0.68 approximately. However, the energetic efficiency in a real process could be very different due to the energy required for producing oxygen from the air. Importantly, it was predicted that carbon formation and methane generation are relatively low at this high temperature.

3.2. Catalytic activities toward steam and oxidative steam reforming of n-butanol

3.2.1. Effect of temperature on conversion

Conversion of n-butanol over Ni/Al₂O₃ and Rh/Al₂O₃ towards the steam reforming at temperature range from 400 to 700 °C was studied, to differentiate catalytic activities between both catalysts. Fig. 6 shows that hydrogen production increases with increasing temperature for both catalysts. Rh/Al₂O₃ is more active, to compare with Ni/Al₂O₃ for all temperatures. The conversion of butanol for both catalysts approached 100 at around 700 °C.

3.2.2. Activity toward steam reforming

Ni/Al₂O₃ and Rh/Al₂O₃ were firstly studied in the steam reforming of n-butanol at 700 °C using SBR of 9.0. The variations in n-butanol conversion and product distribution with time over different catalysts are shown in Fig. 7. It can be seen that the conversion of

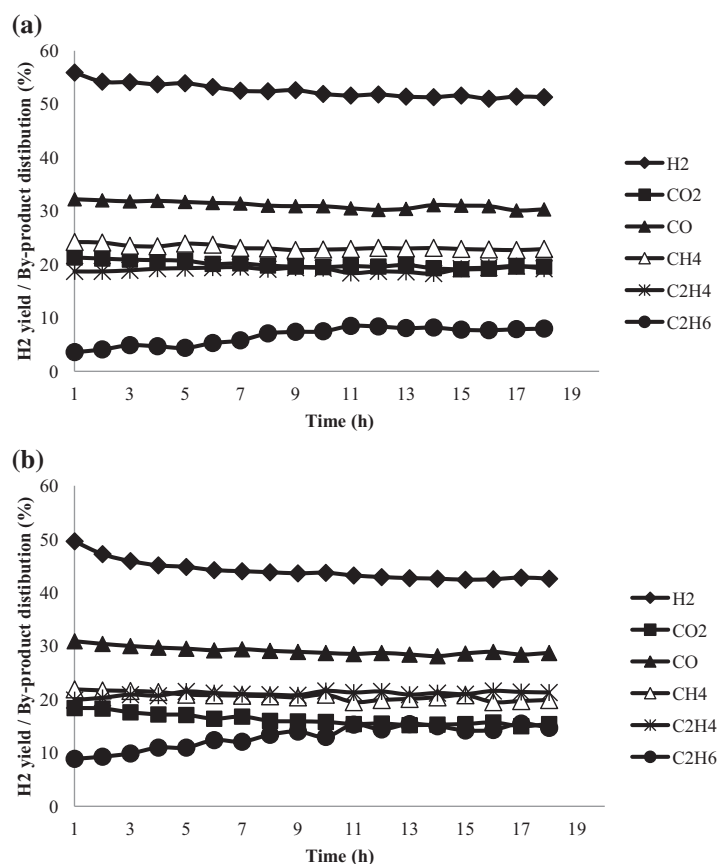


Fig. 7. Steam reforming of butanol in the presence of Rh/Al₂O₃ (a) and Ni/Al₂O₃ (b) at 700 °C using SBR of 9.0.

n-butanol was closed to 100% for all catalysts. Regarding the product composition, apart from the productions of H₂, CO, and CO₂, significant amounts of CH₄ and C₂H₄ (with some formations of C₂H₆, and C₃H₆) were also detected from the reaction. Among these two catalysts, considerable higher H₂ yields were detected for Rh/Al₂O₃. The generations of saturated and unsaturated C₂₊ hydrocarbons (e.g. ethylene and ethane) are the major difficulties for the catalytic steam reforming, as these components act as very strong promoters for carbon formation:



According to the range of temperature in this study, carbon formation would be formed via the decomposition of hydrocarbons and Boudouard reactions (Eq. (12)). In order to determine the amount of carbon formation occurred in the system, the post-reaction oxidation experiments were carried out after a helium purge by introducing of 10% O₂ in He. The amounts of carbon formations on the surface of these catalysts were determined by measuring CO₂ yield (using Microcal Origin Software). It was found that high amount of carbon formation was observed at this operating condition (6.4 mmol g_{cat}⁻¹ for Ni/Al₂O₃ and 4.8 mmol g_{cat}⁻¹ for Rh/Al₂O₃).

As the next step, SBR was varied from 9.0 to 10.0 and 12.0; in addition, the operating temperature was increased from 700 °C to 800 °C and 900 °C. Tables 4 and 5 present the effect of SBR on H₂ yield and other product distributions at 700–900 °C. The degree of carbon deposition observed from the post-reaction oxidation measurements over spent catalysts from various conditions are also given in those tables. It can be seen that H₂ and CO₂ slightly increase with increasing H₂O content, whereas CO decreases; this could be mainly due to the contribution of the water gas shift reaction. In addition, the increase of CH₄ and decreases of C₂H₄, C₂H₆, and C₃H₆ with increasing inlet H₂O content could be due to the decomposition of high hydrocarbons to CH₄. As shown in Table 4, although the amount of carbon deposition was found to decrease with increasing H₂O content, significant amounts of carbon deposition remain observed. Regarding the effect of temperature, it can be seen that the activities of the catalyst significantly increased with increasing temperature, particularly for Rh/Al₂O₃. At 900 °C, the main products from the steam reforming over Rh/Al₂O₃ were H₂, CO, CO₂, and CH₄, with insignificant amounts of C₂H₄. The post-reaction oxidation experiments also indicated the greater resistance toward carbon deposition at high temperature.

3.2.3. Activity toward oxidative reforming

Further studies were carried out by adding O₂ together with n-butanol and H₂O as an oxidative reforming operation. The SBR was kept constant at 9.0, while the OBR were varied from 2.5, 2.7, 3.0, and 3.2. The effect of O₂ concentration on the product composition at 700 °C is shown in Fig. 8. It can be seen that the main products are similar to these of the steam reforming (e.g., H₂, CO, CO₂, and CH₄); nevertheless, at suitable O₂/carbon molar ratios, higher H₂, CO, and CO₂ were observed from the oxidative reforming, whereas less CH₄, C₂H₆, C₂H₄, and C₃H₆ were found compared to the steam reforming at the same operating conditions particularly for Rh/Al₂O₃. Importantly, the dependences of O₂ on H₂ yield are non-monotonic. H₂ increased with increasing O₂/carbon molar ratio until the OBR reached 2.7; then, oxygen presented a negative effect on H₂ production at higher OBR values. The post-reaction oxidation measurements were then carried out to determine the degree of carbon formation on catalyst surfaces. The TPO results in Table 6 show that significantly lower qualities of carbon deposited were observed at high O₂/carbon molar ratios.

By addition of O₂ along with n-butanol and H₂O, the partial oxidation of n-butanol takes place and n-butanol are converted to H₂ and CO. Thus, the rate of n-butanol decomposition reduces and less C₂H₆, C₂H₄, and C₃H₆ are generated, which consequently results in the lower degree of carbon deposition on the surface of catalyst. In addition, O₂ also prevents the formation of carbon species via the hydrocarbon depositions by oxidizing these hydrocarbons to gaseous elements that are unfavored to form carbon species. The decrease of H₂ yield at OBR above 2.7 could also be due to the metal oxidation (as indicated in Table 6) as well as the combustion of H₂ with excess O₂ to form H₂O.

Fig. 9 shows the main products from the reaction in the presence of Ni/Al₂O₃ catalyst were H₂, CO, CH₄, C₂H₄ and C₂H₆. Additionally, a significant buildup of carbon was observed on the surface of the catalyst after the reaction was completed. The presence of carbon indicates the incomplete reforming of n-butanol over this catalyst. It is important to note that, formation of C₂H₄ and C₂H₆ are major obstacles for the catalytic n-butanol oxidative reforming, since these components act as strong promoters of carbon formation.

The Boudouard reaction and the decomposition of hydrocarbons are the major pathways for carbon formation at high temperature since they produce the largest changes in Gibbs free

Table 4
Effect of inlet SBR on the product distribution and degree of carbon formation after exposure in steam reforming of butanol at 700 °C for 18 h.

Catalyst	SBR	Product distribution (%)						Carbon formation (mmol g _{cat} ⁻¹)
		YH ₂	SCO ₂	SCO	SCH ₄	SC ₂ H ₄	SC ₂ H ₆	
Rh/Al ₂ O ₃	9.0	51.3	19.6	30.3	22.9	19.2	8.0	4.8
	10.0	55.9	21.5	29.1	25.8	17.2	6.4	4.4
	12.0	58.3	24.7	28.7	28.0	15.1	3.5	3.7
Ni/Al ₂ O ₃	9.0	42.6	15.4	28.7	19.9	21.3	14.7	6.4
	10.0	44.9	17.8	26.4	23.5	18.9	13.4	6.2
	12.0	45.3	18.3	25.1	27.4	16.0	13.2	5.8

Table 5
Effect of temperature on the product distribution and degree of carbon formation after exposure in steam reforming of butanol at SBR of 9.0 for 18 h.

Catalyst	Temperature (°C)	Product distribution (%)						Carbon formation (mmol g _{cat} ⁻¹)
		YH ₂	SCO ₂	SCO	SCH ₄	SC ₂ H ₄	SC ₂ H ₆	
Rh/Al ₂ O ₃	700	51.3	19.6	30.3	22.9	19.2	8.0	4.8
	800	58.4	21.9	33.4	37.0	5.9	1.8	4.3
	900	62.9	24.8	36.1	39.1	0.0	0.0	3.6
Ni/Al ₂ O ₃	700	42.6	15.4	28.7	19.9	21.3	14.7	6.4
	800	49.3	18.4	30.3	38.0	7.7	5.6	6.1
	900	55.2	19.9	32.8	45.3	1.2	0.8	6.0

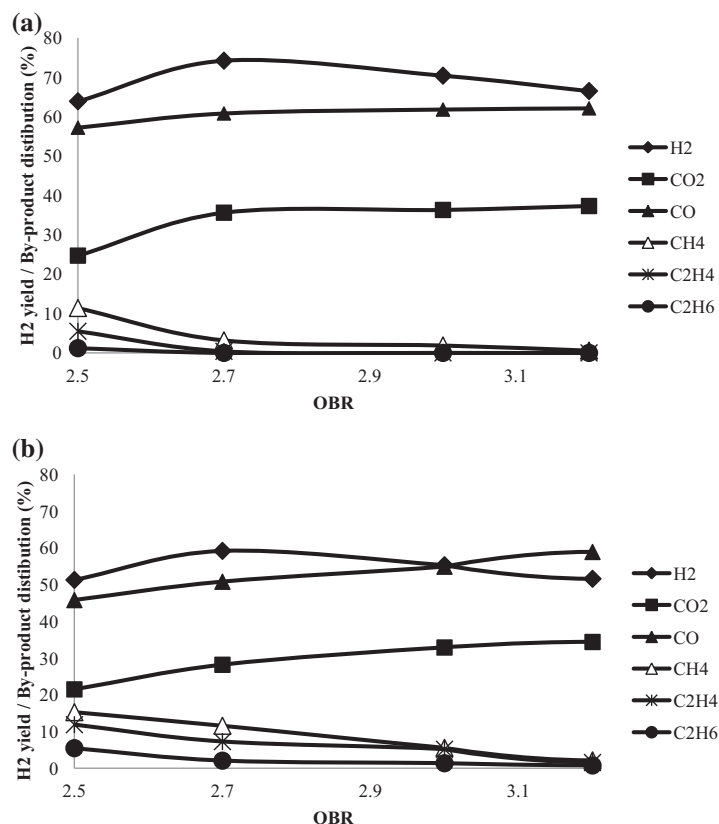


Fig. 8. Effect of OBR on the autothermal reforming of butanol in the presence of Rh/Al₂O₃ (a) and Ni/Al₂O₃ (b) at 700 °C using SBR of 9.0.

Table 6

Effect of inlet OBR on the degrees of carbon formation and metal reducibility after exposure in oxidative reforming of butanol at 700 °C with SBR of 9.0 for 18 h.

Catalyst	OBR	Carbon formation (mmol g _{cat} ⁻¹)	Metal reducibility (%)
Rh/Al ₂ O ₃	2.5	2.9	95.1
	2.7	1.4	95.0
	3.0	0.8	90.2
	3.2	0.2	87.5
Ni/Al ₂ O ₃	2.5	5.7	95.6
	2.7	2.2	94.3
	3.0	1.0	87.6
	3.2	0.2	84.1

energy. Carbon formation would occur by the decomposition of hydrocarbons as well as the Boudouard reaction under the range of temperatures used in this study.

In contrast to the reactions using Ni/Al₂O₃, for reaction over rhodium based catalyst (Rh/Al₂O₃), less carbon formation was observed. The main products produced were H₂, CO, and CO₂ with small amounts of CH₄. All product yields were close to the thermodynamic values predicted in the model when compared to those of Ni/Al₂O₃. It is common knowledge that the catalytic activity of Rh is relatively greater than that of Ni. Hence, these studies indicate that a highly active catalyst is required for the oxidative reforming of n-butanol. Further, the results indicate that both carbon

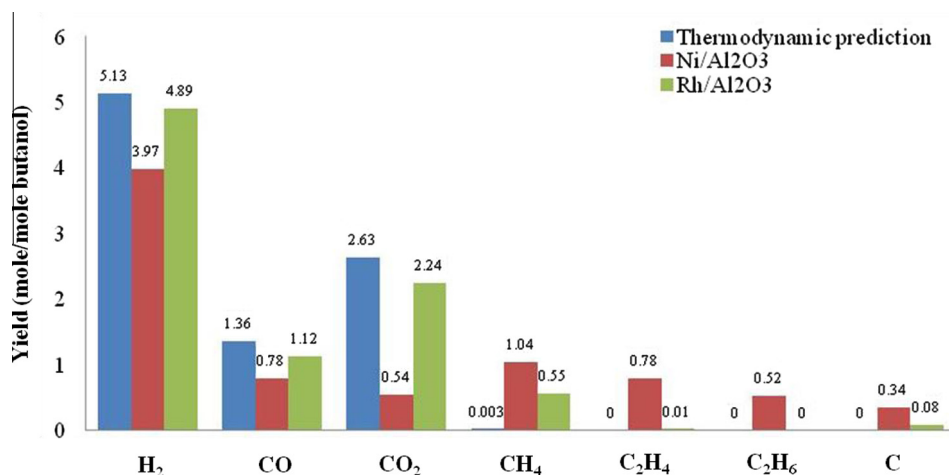


Fig. 9. Catalytic activity of Ni/Al₂O₃ and Rh/Al₂O₃ toward the oxidative reforming of n-butanol at 700 °C, OBR of 2.70 and SBR of 9.

deposition and the formation of higher hydrocarbons in the gaseous products are the main concerns. More research into the catalytic materials is required, from which judicious choice of catalyst should result in less coke formation, higher yield of hydrogen and longer durability of catalyst.

4. Conclusions

In this study, the thermodynamics of hydrogen production via n-butanol oxidative reforming was studied using a Gibbs free energy minimization method at temperatures between 300 and 1100 °C, SBR between 0 and 12 and OBR between 0 and 6. The main products from n-butanol oxidative reforming were predicted to be hydrogen, water, oxygen, carbon monoxide, carbon dioxide, and methane with small quantities of elemental carbon formation.

The results indicate that the most favorable conditions for hydrogen production were at temperatures ranging from 700 to 800 °C, SBR of 9–12, and OBR of 1.5–3. The thermoneutral operation conditions can be obtained at OBR of 2.70–2.80 at 700 °C and 2.65–2.75 at 800 °C. Under the thermoneutral operating conditions, the maximum hydrogen yield was predicted to be 5.56 mol/mol_{butanol} at 700 °C and 5.33 mol/mol_{butanol} at 800 °C. Additionally, carbon and methane formation were inhibited at these high temperatures. The thermodynamic results were tested and found to be in good agreement with the practical experimental results. The experimental set up performed was the oxidative reforming of n-butanol over Ni/Al₂O₃ and Rh/Al₂O₃ catalysts. The catalytic performance of rhodium based catalyst (Rh/Al₂O₃) towards the n-butanol oxidative reforming achieved results close to the thermodynamically predicted values.

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