

Feasibility of Hydrogen Production from Cellulose and Prediction of the Product Distribution: Thermodynamics Analysis

(Kebolehlaksanaan Pengeluaran Hidrogen daripada Selulosa dan Ramalan Pendedaran Produk: Analisis Termodinamik)

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ABSTRACT

High carbon emissions, depleting fossil energy reserves have become a global problem. It is necessary to develop renewable energy sources that are environmentally friendly. Hydrogen (H_2) is one of the energy sources and carriers that can be developed. This gas can be produced from renewable, sustainable, and economical resource such as biomass that contains cellulose as the main ingredient. This thermodynamic analysis of H_2 production from cellulose is necessary as a theoretical study to determine the feasibility of the reaction. The computational thermodynamic was analyzed using Microsoft Excel 2019 and Matlab Program R2013a. Prediction of the equilibrium composition of the substances involved in the reaction was attempted by minimization Gibbs free energy change with Lagrange undetermined multipliers methods. As a result, the value of ΔH_r^0 ; ΔS_r^0 and ΔG_r^0 are +624,7500 kJ/mol; +2,1491 kJ/mol.K and; -26,1540 kJ/mol, respectively. Analysis of equilibrium constant of this conversion has a large $\ln K$ value (> 1). A negative ΔG_r^0 value and large $\ln K$ indicates that the formation of H_2 from $(C_6H_{10}O_5)_n$ is plausible and feasible and reaction product formation is strongly favored at equilibrium. The composition of the substances involved at 298 K from the largest to the smallest is CH_4 (4.5 mol), H_2O (3 mol), CO_2 (1.5 mol), H_2 (1.28×10^{-5} mol), $HCOOH$ (5.85×10^{-10} mol), $C_6H_{12}O_6$ (3.72×10^{-10} mol) and $C_6H_{12}O_5$ (1.35×10^{-10} mol). Interestingly, H_2 yield will rise significantly with the increase of reaction temperature. This preliminary study provides an overview of reaction conditions so that H_2 production from biomass can be produced maximally.

Keywords: Biomass; hydrogen; Lagrange multiplier; thermodynamic

ABSTRAK

Pelepasan karbon yang tinggi dan penurunan simpanan tenaga fosil telah menjadi masalah global. Oleh kerana itu, sumber tenaga boleh diperbaharui yang mesra alam perlu dibangunkan. Hidrogen (H_2) adalah salah satu sumber tenaga dan pembawa tenaga yang dapat dikembangkan. Gas diatomik ini dapat dihasilkan daripada sumber yang boleh diperbaharui, lestari dan murah seperti biojisim yang mengandungi selulosa sebagai bahan utama. Analisis termodinamik bagi penghasilan H_2 daripada selulosa diperlukan sebagai kajian teori untuk menentukan kebarangkalian tindak balas menggunakan kaedah perkiraan. Termodinamik komputasi dianalisis menggunakan Microsoft Excel 2016 dan Matlab Program R2013a. Ramalan komposisi keseimbangan bahan yang terlibat dalam percubaan tindak balas dengan meminimumkan perubahan tenaga bebas Gibbs dengan kaedah pengganda tidak ditentukan Lagrange. Hasilnya, nilai ΔH_r^0 ; ΔS_r^0 dan ΔG_r^0 masing-masing adalah +624,7500 kJ/mol; +2,1491 kJ/mol.K dan -26,1540 kJ/mol. Analisis pemalar keseimbangan penukaran ini mempunyai nilai $\ln K$ yang besar (> 1). Nilai ΔG_r^0 negatif dan $\ln K$ besar menunjukkan bahawa pembentukan H_2 daripada $(C_6H_{10}O_5)_n$ munasabah dan boleh dilaksanakan dan pembentukan produk reaksi cenderung terhasil pada titik keseimbangan. Komposisi produk yang terlibat pada suhu 298 K dari yang terbesar hingga yang terkecil adalah CH_4 (4.5 mol), H_2O (3 mol), CO_2 (1.5 mol), H_2 (1.28×10^{-5} mol), $HCOOH$ (5.85×10^{-10} mol), $C_6H_{12}O_6$

(3.72×10^{-10} mol) dan $C_6H_{12}O_5$ (1.35×10^{-10} mol). Menariknya, pembentukan H_2 meningkat dengan ketara seiring dengan peningkatan suhu tindak balas. Kajian teoritis awal ini memberikan gambaran umum dan pertimbangan keadaan reaksi sehingga produksi H_2 daripada biojisim dapat dihasilkan secara maksimum.

Kata kunci: Biojisim; hidrogen; pengganda Lagrange; termodinamik

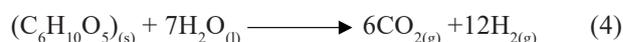
INTRODUCTION

The decline in environmental quality due to carbon emission has become a global problem. Based on the Statistical Review of Energy released by BP in 2020, the trend of carbon emission is showed where the average annual growth in carbon emissions during 2018 and 2019 is greater than the 10-year average. The industrial and transportation sectors are the largest energy consumers and contribute to the increase in greenhouse gases. This is because the primary energy source currently used is fossil energy (petroleum, natural gas, and coal) (BP 2020). The use of renewable energy sources that are environmentally friendly is absolutely necessary not only because of high carbon emissions but also depleting fossil energy reserves. Hydrogen (H_2) is one of the energy sources and carriers that can be developed. H_2 has high chemical energy per mass (122 kJ/g) (Dincer & Zamfirescu 2016), superior to that of many fossil fuels, and its combustion only results in water and zero carbon (Singh & Dutta 2018). This diatomic gas can be produced from renewable, sustainable, and economical resources such as plant crops, agricultural residues, and woody biomass (Lan et al. 2020). Biomass contains lignocellulose that mainly consists of three polymers which are cellulose (>40%), hemicellulose (20%-40%), and lignin (5%) (Kuehnel & Reisner 2018; Megashah et al. 2018).

Hydrogen can be produced from cellulose ($C_6H_{10}O_5$)_n in several thermochemical processes such as steam gasification (>1000K), fast pyrolysis (450-650K), thermo-catalytic reforming which is associated with the problems of catalyst deactivation and by-product (e.g. CO) production and hydrolysis by acids or enzymes (Nikolaidis & Poullikkas 2017; Takise & Sekine 2019). Due to high energy intensity and difficulties in H_2 separation and purification from mixture yields, nowadays, preferred H_2 production is from photocatalytic reforming process (photoreforming) (Hao et al. 2018; Lan et al. 2020). This process offers more sustainable and environmentally friendly technology since it employs solar as energy source and photocatalyst to accelerate the reaction. Cellulose can be convert to H_2 according to the following reactions (Hao et al. 2018):



Therefore, the net reaction will be



Some researchers doubt this process can be used for effective H_2 production. This is maybe because of the rigid intra and inter-molecular hydrogen bonds in cellulose, it is difficult to hydrolyze cellulose to platform organic molecules and then converting it to H_2 . Hence, thermodynamic analysis of H_2 production from cellulose is necessary to determine the feasibility of the reaction. Some of the existing thermodynamic studies generally use platform organic compounds (Huang et al. 2020) such as methanol, ethanol, glycerol, and monosaccharides such as glucose. Thermodynamic studies of polysaccharides have not been carried out and existing studies use the glucose molecule as a model because it is a major derivative of cellulose.

This paper discusses the thermodynamic analysis of cellulose reforming to H_2 in the absence of a photocatalyst. This analysis will be a preliminary study to assess the feasibility of this reaction. Using the computational method, this theoretical study can be used to predict the conditions of the cellulose reforming reaction and the distribution of the products obtained.

MATERIALS AND METHODS

COMPUTATIONAL THERMODYNAMIC ANALYSIS

This thermodynamic study was attempted by means of a computational procedure using Microsoft Excel 2019 and Matlab Program R2013a. The analysis consists of several steps, namely: (1) calculating changes in reaction for both standard enthalpy (ΔH_r°) and entropy (ΔS_r°),

and then the change in free energy of reaction Gibbs (ΔG_r°); (2) determine the reaction equilibrium constant (K) at various temperatures (3) determine the change in total Gibbs free energy (ΔG^t); (4) minimization of Gibbs energy and prediction of the equilibrium composition of the substances involved in the reaction at the specified temperature and pressure. This minimization introduces Lagrange undetermined multipliers methods and computed using MatLab R2013a program.

For the first step, we calculate ΔH_r° ; ΔS_r° and ΔG_r° according to (5), (6) and (7)

$$\Delta H_r^0 = \Delta H_f^0 \text{ product} - \Delta H_f^0 \text{ reactant} \quad (5)$$

$$\Delta S_r^0 = \Delta S^0 \text{ product} - \Delta S^0 \text{ reactant} \quad (6)$$

$$\Delta G_r^0 = \Delta G_f^0 \text{ product} - \Delta G_f^0 \text{ reactant} \quad (7)$$

The equilibrium constant (K) determined based on (8):

$$K' = \exp(-\Delta G_r^0/RT) \quad (8)$$

Or by Van't Hoff equation:

$$\ln \frac{K}{K'} = -\frac{\Delta H_r^0}{R} \left(\frac{1}{T} - \frac{1}{T'} \right) \quad (9)$$

that can be rewrite as

$$\ln K = -\frac{\Delta H_r^0}{R} \left(\frac{1}{T} - \frac{1}{T'} \right) + \ln K' \quad (10)$$

$$y = -ax + b$$

with ΔH_r^0 is standard enthalpy; T is reference temperature of reaction (298 K); and T' is determined temperature of the reaction (This thermodynamic analysis take place at T=303-353 K). K' is reference of equilibrium constant. The value of ln K can be plotted to T.

Further thermodynamic analysis step aims to calculate the equilibrium composition by minimizing the free energy of Gibbs. The Gibbs energy minimization is limited or constrained by the number of moles of the substance (atoms) involved in the reaction (atomic balance constraints) (Khonde et al. 2021; Tsanas et al. 2017).

The total Gibbs free energy change can be calculated by (11).

$$G^t = \sum_{i=1}^N n_i \cdot \mu_i \quad (11)$$

$$\text{where } \mu_i = G_i^0 + RT \ln \frac{f_i}{f_i^0} \quad (12)$$

and for gases compounds

$$f_i = y_i \Phi_i P \quad (13)$$

Hence, the total Gibbs free energy change from the mixture can be written as

$$G^t = \sum_{i=1}^N n_i \cdot G_i^0 + RT \sum_{i=1}^N n_i \ln \frac{y_i \Phi_i P}{p^0} \quad (14)$$

Subsequently, (14) is the *objective function* that will be minimized.

In a closed system, the number of moles of each atom is fixed during a chemical reaction. The total number of moles of a particular atom present in all chemical species in each chemical reaction must equal the initial mole number of that atom.

$$\sum_{i=1}^N n_i a_{i,k} = A_k \quad \text{which } k = 1, 2, 3, \dots \quad (15)$$

Or

$$\sum_{i=1}^N n_i a_{i,k} - A_k = 0 \quad \text{which } k = 1, 2, 3, \dots \quad (16)$$

Minimization was done by substituting boundary conditions in the objective function. The boundary condition is the number of atoms involved in the reaction based on the proposed mechanism, namely three atoms including C, H, and O. The number of moles of the three atoms is entered in the objective function using the Lagrange Multiplier: λ_1 , λ_2 and λ_3 .

Therefore (14) will be:

$$\sum_{i=1}^{N-1} n_i \left(\Delta G_i^0 + RT \ln \frac{y_i \Phi_i P}{p^0} + \sum \lambda_k a_{ik} \right) = 0 \quad (17)$$

which $i = 1, 2, \dots, N$

where G_t is the total Gibbs free energy; G_i^0 is standard Gibbs free energy of species (i); R is the molar gas constant; T is the temperature of the system; f_i is fugacity of species (i) in the system, f_i^0 is standard state fugacity of species (i) and n_i is the number of moles of species (i).

RESULTS AND DISCUSSION

STANDARD ENTHALPY (ΔH°), ENTROPY (ΔS°) AND GIBBS FREE ENERGY CHANGE (ΔG°) OF REACTION
Conversion of cellulose to hydrogen involves the

formation, destruction and rearrangement of chemical bonds of compound involve in the reaction, so there will be a change in energy of the system. The change of energy can be observed from ΔH_r° ; ΔS_r° ; and ΔG_r° . Standard enthalpy change can be useful for determining the temperature effect on the equilibrium constant of H_2 production and thus on H_2 yield. In addition, Gibbs free

energy changes can be useful for determining the existence of chemical equilibrium in the system and the influence of process variables on the H_2 yield (Hill & Root 2014). One of the important things in thermodynamics analysis is the availability of thermodynamics data sources. In this analysis, the data is tabulated in Table 1 and obtained from Smith et al. (2018) and Voitkevich et al. (2012).

TABLE 1. Thermodynamic value of component involves in reaction

No	Component	ΔH_r° (kJ/mol)	ΔS_r° (J/mol.T)	ΔG_r° ((kJ/mol)
1	$(C_6H_{10}O_5)_n^*$	-985	212.1	-681
2	H_2O^{**}	-285.83	70	-237
3	CO_2^{**}	-393.51	213.8	-394.359
4	H_2^{**}	0	130.7	0

*Based on (Voitkevich et al. 2012), **Based on (Smith et al. 2018)

From (5), (6) and (7), the value of ΔH_r° ; ΔS_r° and ΔG_r° are +624,7500 kJ/mol; +2,1491 kJ/mol.K and -26,1540 kJ/mol, respectively. Even though the value of ΔH_r° is positive, the value is too small compared to the positive value of ΔS_r° . This resulted in the negative value of ΔG_r° . With a negative ΔG_r° value, the reaction to form H_2 from $(C_6H_{10}O_5)_n$ can take place spontaneously under standard conditions (298 K, 1 atm). The reaction takes place

exothermically (Hua et al. 2020; Smith et al. 2018). This negative value of ΔG_r° also indicate that the conversion of cellulose can be accelerated using a catalyst.

DETERMINE THE REACTION EQUILIBRIUM CONSTANT (K) AT VARIOUS TEMPERATURES

Equilibrium constants are very sensitive to temperature. The equilibrium constants of reactions are exhibited as a function of temperature in Table 2 and Figure 1.

TABLE 2. Equilibrium constant K and K' value

T (x)	K'	Ln K'	K	(y)
303	32276.87	10.38	2.00×10^6	14.54
308	27270.63	10.21	1.00×10^8	18.40
313	23165.27	10.05	4.00×10^9	22.13
318	19779.16	9.89	1.53×10^{11}	25.75
323	16970.83	9.74	5.08×10^{12}	29.26
328	14629.38	9.59	1.52×10^{14}	32.65
333	12667.32	9.45	4.10×10^{15}	35.95
338	11015.25	9.31	1.00×10^{17}	39.15
343	9617.74	9.17	2.24×10^{18}	42.25
348	8430.34	9.04	4.57×10^{19}	45.27
353	7417.17	8.91	8.57×10^{20}	48.20

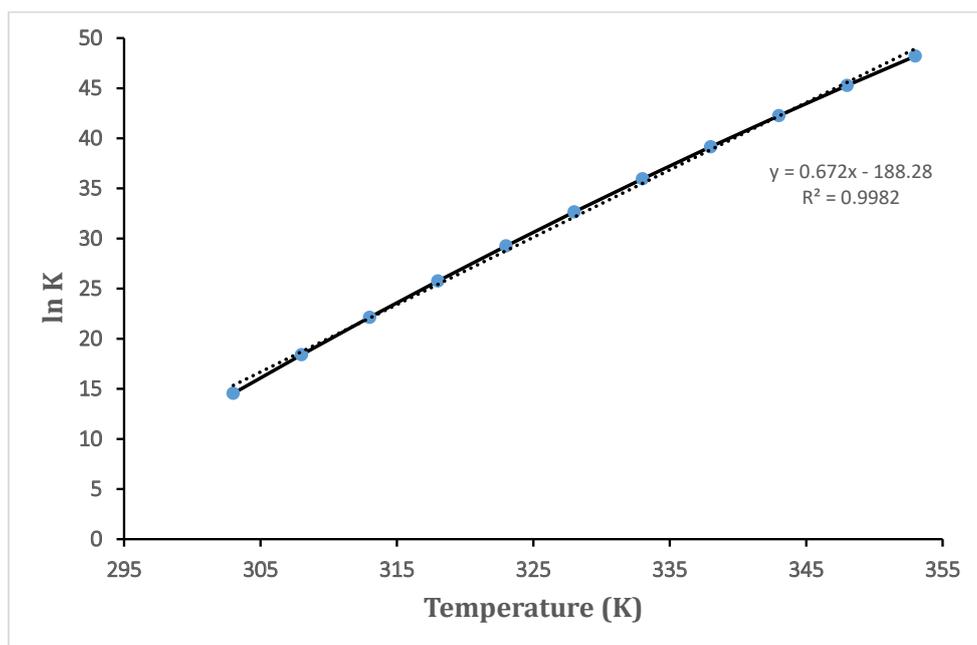


FIGURE 1. Plot of ln K vs T reaction

A large ln K value (> 1) indicates that the reaction, the formation of H_2 from $(C_6H_{10}O_5)_n$ can be plausible and feasible. With a negative ΔG_r^0 value and large ln K, the product formation at equilibrium is strongly favored at equilibrium (Cheng et al. 2019; Muhammad et al. 2017). The higher the temperature, the greater the value of ln K, which indicates an infinite equilibrium.

PRODUCT DISTRIBUTION ANALYSIS

Based on the possible reaction mechanisms as stated by Hao et al. (2018) and Zou et al. (2018), the substances involved in the reaction is served in Table 3 that consists of cellulose $((C_6H_{10}O_5)_n)$, water (H_2O), glucose ($C_6H_{12}O_6$), formic acid ($HCOOH$), carbon dioxide (CO_2), hydrogen (H_2) and methane (CH_4).

TABLE 3. Reaction components and several quantities for analysis product*

No	Component	ΔG_r^0 (kJ/mol)	Mol (initial feed)	Initial guess (mol)**
1	$(C_6H_{10}O_5)_n$	-681.0	1	0.23×10^{-3}
2	H_2O	-237.0	7	1.00×10^{-3}
3	$C_6H_{12}O_6$	-910.4	0	0.70×10^{-3}
4	$HCOOH$	-278.8	0	1.10×10^{-3}
5	CO_2	-394.4	0	85.3×10^{-3}
6	H_2	0	0	195.2×10^{-3}
7	CH_4	-50.5	0	0.11×10^{-3}

*based on Zhang et al. (2016), **assumption: total pressure 1 atm, temperature 298 K

The value of number of atomic mass k in the system (A_k) that is required can be determined from the initial mole numbers, and the number of atom k per molecule

$i(a_{ik})$ values that comes directly from the chemical formulas of each species in the reaction (as shown in Table 4).

TABLE 4. The number of atom C, O and H that entered in the objective function using the Lagrange Multiplier

	Atom k		
	Carbon(C)	Oxygen (O)	Hydrogen (H)
	A_k = number of atomic mass k in the system (1mol $C_6H_{10}O_5$ and 7 mol H_2O)		
	$A_C=6$	$A_O=6$	$A_H=24$
Component i	a_{ik} = number of atom k per molecule i		
$C_6H_{10}O_5$	$a_{C_6H_{10}O_5,C}=6$	$a_{C_6H_{10}O_5,O}=5$	$a_{C_6H_{10}O_5,H}=10$
H_2O	$a_{H_2O,C}=0$	$a_{H_2O,O}=1$	$a_{H_2O,H}=2$
$C_6H_{12}O_6$	$a_{C_6H_{12}O_6,C}=6$	$a_{C_6H_{12}O_6,O}=6$	$a_{C_6H_{12}O_6,H}=12$
HCOOH	$a_{HCOOH,C}=1$	$a_{HCOOH,O}=2$	$a_{HCOOH,H}=2$
CO_2	$a_{CO_2,C}=1$	$a_{CO_2,O}=2$	$a_{CO_2,H}=0$
H_2	$a_{H_2,C}=0$	$a_{H_2,O}=0$	$a_{H_2,H}=2$
CH_4	$a_{CH_4,C}=1$	$a_{CH_4,O}=0$	$a_{CH_4,H}=4$

Based on computational analysis, the composition of the substances involved in (reaction temperature 298 K from the largest to the smallest are CH_4 (4.5 mol), H_2O (3 mol), CO_2 (1.5 mol), H_2 (1.28×10^{-5} mol), HCOOH (5.85×10^{-10} mol), $C_6H_{12}O_6$ (3.72×10^{-10} mol) and $C_6H_{10}O_5$ (1.35×10^{-10} mol). The corresponding product distributions at temperatures between 298-398 K are illustrated in Figures 2 and 3. Figure 2 shows the cellulose, glucose, formic acid and hydrogen distribution as a function of temperature whereas Figure 3 shows methane, water and carbon dioxide as a function of temperature.

The most significant finding from Figure 2 is that hydrogen increased exponentially as temperature increase within the stipulated temperature boundary. At temperature 298 K, 1.28×10^{-5} moles of H_2 is produced and when the temperature reached 398 K, H_2 of 3.50×10^{-4} moles is produced that is an increase of 27 times. In the other hand, the composition of cellulose, glucose and formic acid decreased insignificantly with increasing temperature. At 298 K, the composition of cellulose,

glucose and formic acid are 1.35×10^{-10} mol; 3.72×10^{-10} mol and 5.85×10^{-10} mol, respectively. Meanwhile, at T 398 K the amount was reduced to 1.98×10^{-22} mol; 6.37×10^{-22} mol and 22×10^{-22} mol. It is assumed that decrease in cellulose, glucose, and formic acid take place because that substance was converted to H_2 . According to the insight on the reaction mechanism, hydrogen can be produced from cellulose by forming intermediate products including glucose, formic acid or other oxygenate products (Hao et al. 2018; Lan et al. 2020; Zhang et al. 2016). The more cellulose converted into organic compounds, the easier it is to for H_2 to be produced and this is the reason H_2 formation increased rapidly (Syaahidah et al. 2020). The conversion of cellulose into organic products begins with the dissociation of β -(1,4)- the glycosidic bonds in these polysaccharides into saccharides as their monomers. Such process of attaining hydrogen from biomass is complicated (Ahorsu et al. 2018). This dissociation stage is the rate limiting step for the formation of H_2 from cellulose. Furthermore, these saccharides can be transformed into other intermediate products such as

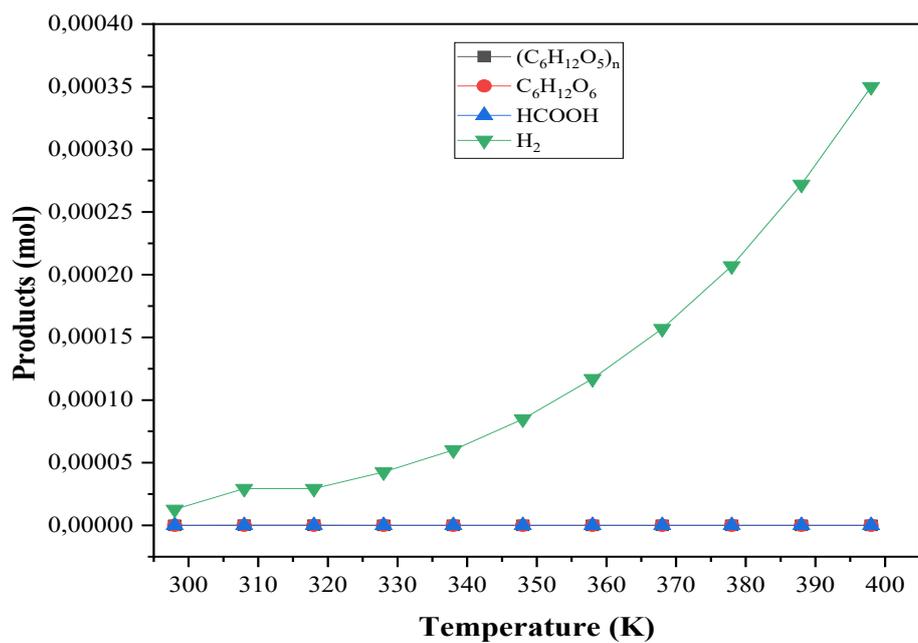


FIGURE 2. Product distribution (cellulose, glucose, formic acid and hydrogen) as a function of temperature

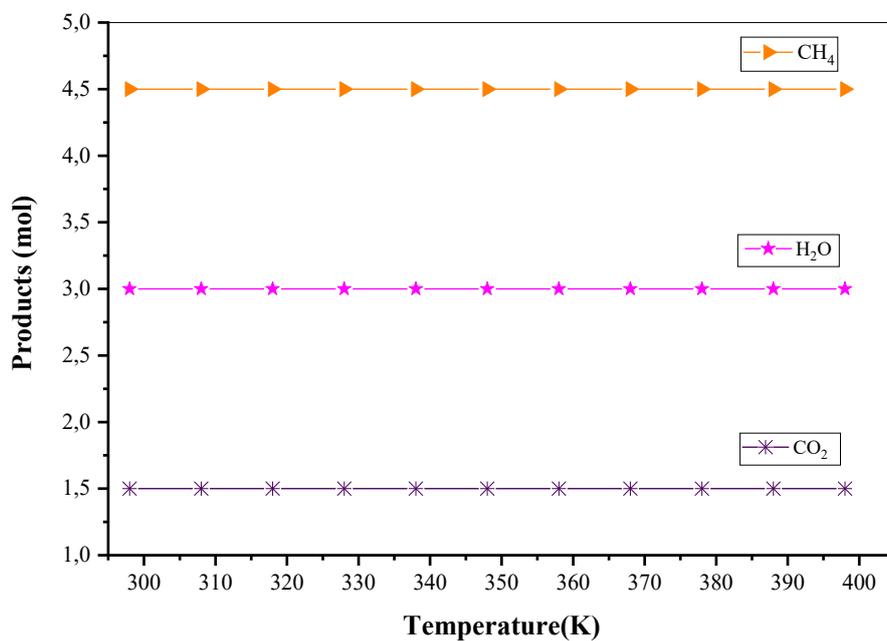
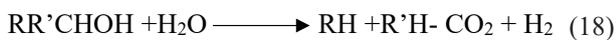


FIGURE 3. Product distribution (methane, water and carbon dioxide) as a function of temperature

alcohol or carboxylic acid or furfural and finally into hydrogen and other products within a complex reaction network (Lan et al. 2020; Puga 2016; Speltini et al. 2014; Syaahidah et al. 2020; Zou et al. 2018).

Other chemical compounds involved in the conversion of cellulose to hydrogen are methane, water, and carbon dioxide. From Figure 3, it is predicted that there is no change in their compositions. Methane is obtained as one of the main products in cellulose conversion to hydrogen. This gas may be produced from intermediate product that have alkyl group in their structure. Alkyl (CH_3 -) will react with proton (H^+) resulted CH_4 (Bahruji et al. 2011; Bowker et al. 2014; Hao et al. 2018) following reaction route:



From the thermodynamic equilibrium point of view, H_2 was dominantly resulted at high temperature, while

CH_4 was produced at low temperature. It is a challenge to eliminate this low hydrocarbon from this reaction. Researchers suggested to carry out methane steam reforming and successive water-gas shift reaction to obtain maximum yield of H_2 (Shimura & Yoshida 2011). The reformation of cellulose to hydrogen also produces large amount of CO_2 . CO_2 is produced by the oxidation of the alkyl groups of the intermediate products. However, CO_2 from biomass is considered more environmentally friendly than CO_2 produced from fossil fuels (Danish & Ulucak 2020; Koruba et al. 2017; Sher et al. 2020). Through photosynthesis, this CO_2 will be reversed reacted into cellulose (biomass) (Chen et al. 2019). In addition, CO_2 and CH_4 tend to produce if the intermediate product contains either glycerol or methanol (Tasleem et al. 2020). Furthermore, the produced CO_2 subsequently transformed to CH_4 and this is the plausible explanation of why CH_4 is largely produced. The proposed reaction mechanism of cellulose to hydrogen is illustrated in Figure 4.

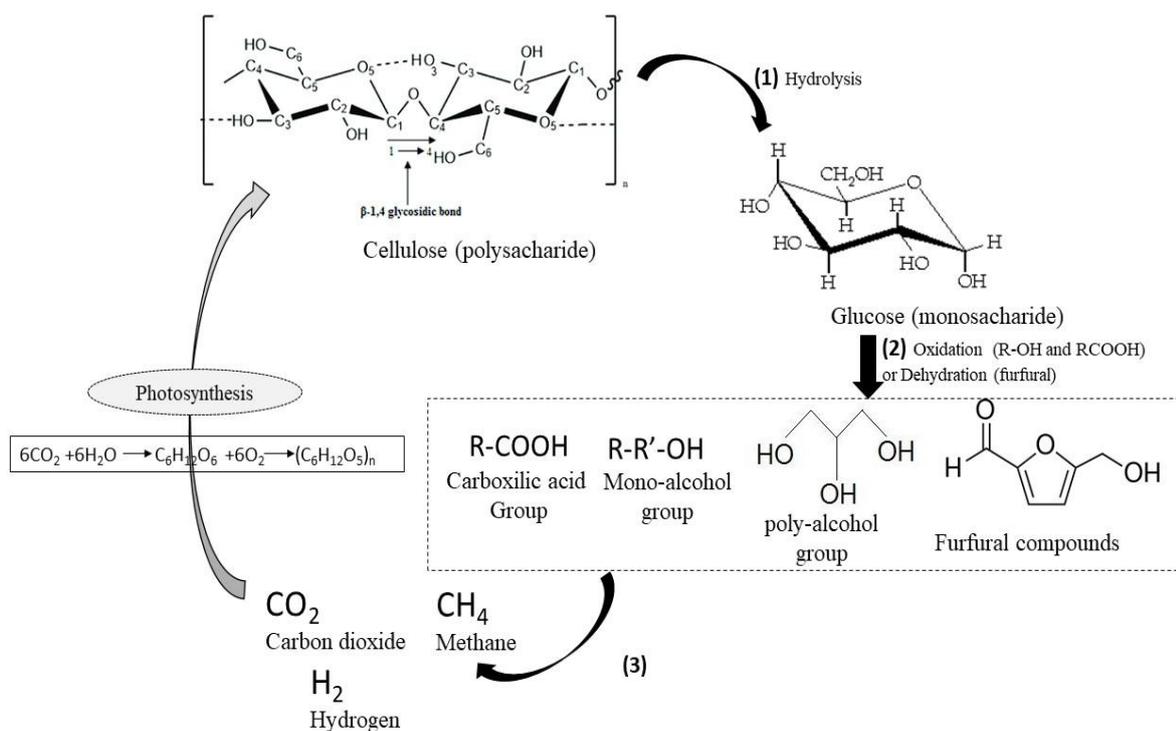


FIGURE 4. Proposed reaction mechanism of hydrogen evolution from cellulose

Prediction of product distribution in this study can be taken into consideration to increase the amount of hydrogen produced from the conversion of cellulose. Ideally, the reaction equilibriums can be adjusted by

manipulating temperature for some objectives: (1) maximize H_2 production, (2) reduce greenhouse gases (CH_4 and CO_2) production, and (3) minimize carbon release (Cheng et al. 2019). The manipulating reaction

also can be attempted by applying an appropriate catalyst to adjust H_2 production. The catalyst is expected to direct the reaction product so that the main product has a relatively high yield.

CONCLUSIONS

Hydrogen is feasible to be produced from biomass that contains cellulose. The value of ΔH_r^0 , ΔS_r^0 and ΔG_r^0 are +624,7500 kJ/mol; +2,1491 kJ/mol.K and -26,1540 kJ/mol, respectively. With a negative ΔG_r^0 value, the forward reaction to produce H_2 from $(C_6H_{10}O_5)_n$ will proceed spontaneously and exothermic under standard conditions. Analysis of equilibrium constant of this conversion has a large $\ln K$ value (> 1). It indicates that the formation of H_2 from $(C_6H_{10}O_5)_n$ can be plausible and feasible. With a negative ΔG_r^0 value and large $\ln K$, the product formation at equilibrium is strongly favored at equilibrium. The composition of the substances involved in (at 298K) from the largest to the smallest are CH_4 (4.5 mol), H_2O (3 mol), CO_2 (1.5 mol), H_2 (1.28×10^{-5} mol), $HCOOH$ (5.85×10^{-10} mol), $C_6H_{12}O_6$ (3.72×10^{-10} mol), and $C_6H_{12}O_5$ (1.35×10^{-10} mol). Interestingly, H_2 yield will increase significantly at elevated temperatures.

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