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Upgrading of syngas derived from biomass gasification: A thermodynamic analysis

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ABSTRACT

Hydrogen yields in the syngas produced from non-catalytic biomass gasification are generally low. The hydrogen fraction, however, can be increased by converting CO, CH₄, higher hydrocarbons, and tar in a secondary reactor downstream. This paper discusses thermodynamic limits of the synthesis gas upgrading process. The method used in this process is minimization of Gibbs free energy function. The analysis is performed for temperature ranges from 400 to 1300 K, pressure of 1–10 atm (0.1–1 MPa), and different carbon to steam ratios. The study concludes that to get optimum H₂ yields, with negligible CH₄ and coke formation, upgrading syngas is best practiced at a temperature range of 900–1100 K. At these temperatures, H₂ could be possibly increased by 43–124% of its generally observed values at the gasifier exit. The analysis revealed that increasing steam resulted in a positive effect. The study also concluded that increasing pressure from 1 to 3 atm can be applied at a temperature >1000 K to further increase H₂ yields.

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1. Introduction

Hydrogen (H₂) is an attractive alternative fuel for the future owing to its important role in reducing pollutants and greenhouse gases. Combustion of H₂ in an engine or electrochemical conversion in a fuel cell produces only energy and pure water. The rapid developments in the fuel cell technology and the concerns on environmental pollution from fossil fuels are two important factors that support H₂ as a potential future energy carrier. In fact, the necessity of minimizing environmental impacts from energy use is one of the greatest challenges we face today [1].

The adverse impacts that will be imparted to the environment will only be mitigated only if the H₂ is produced from renewable resources. In contrast, currently, about 96% of the H₂ is produced from steam reforming of fossil fuels at high temperatures with natural gas as the main feedstock (48%) followed by heavy oils and naphtha (30%) and coal (18%) [2]. Therefore, even in a hydrogen-based economy, if the hydrogen is produced from fossil fuels, the greenhouse gases emission to the environment is inevitable.

Currently, biomass has received much interest as an alternate energy source because it is renewable. Maniatis [3] showed that even though the reliability of the overall

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technology is low, employing biomass gasification to produce H_2 has high market potential. Hydrogen production from biomass is environmentally friendly because carbon dioxide (CO_2) released from the process will be reconsumed during the plant growth through photosynthesis, resulting in zero net CO_2 emissions. Renewability and abundant availability are key features of biomass as a feedstock for hydrogen production.

Gasification is the most mature thermochemical conversion technology available. Compared to steam reforming of natural gas or water electrolysis to produce hydrogen, biomass gasification showed the lowest dependency on the feedstock cost [4]. In addition, gasification of biomass feedstock is environmentally friendly because it produces net zero CO_2 emission, the most important greenhouse gas. Carbon dioxide produced during biomass gasification is eventually recycled for plant photosynthesis.

The inert-free synthesis gas (syngas) produced from biomass gasification consists of H_2 , CO_2 , carbon monoxide (CO), methane (CH_4), water (H_2O), and traces of tar and higher hydrocarbons such as ethane (C_2H_6), ethylene (C_2H_4), and acetylene (C_2H_2). Although the syngas composition is dependent on many factors such as gasifier type, operating conditions, gasifying agents, and feedstock properties, H_2 fraction is low for most uncatalyzed gasification processes. Hydrogen yield, however, can be improved by employing a separate catalytic reactor downstream to reform hydrocarbons and tar and to shift CO to produce additional H_2 .

The aim of this study is to analyze the thermodynamic limits of syngas upgrading as an effort to increase H_2 fraction in the syngas. The analysis is performed by employing minimization of Gibbs free energy function. The analysis is performed at different process variables (temperature, pressure, carbon to steam ratio, and reaction path). The equilibrium concentrations of different compounds were calculated by direct minimization of the Gibbs free energy function. This analysis was performed considering the following variable ranges: pressure 0.1–1 MPa (1–10 atm), temperature 400–1300 K, and actual carbon to steam (C/S) ratio from the literature and 1:1.

2. Method

Thermodynamic equilibrium compositions of a reaction can be estimated using minimization Gibbs energy function, G . The derivation of Gibbs energy function has been performed in earlier work [5] and the function is expressed as follows.

$$G = \sum_{i=1}^K x_i \Delta G_i^0 + RT \sum_{i=1}^K x_i \ln y_i + RT \sum_{i=1}^K x_i \ln P \quad (1)$$

where G_i^0 is Gibbs free energy formation for species i at standard conditions, x_i is number of moles of species i , y_i is mole fraction of species i , R is universal gas constant ($8.3144 \text{ J mol}^{-1} \text{ K}^{-1}$), T is absolute temperature, and P is total pressure (atm).

The idea is to find the set of x_i s which minimize the value of Gibbs energy function. This can be solved in two ways [6]: (i) stoichiometric or (ii) non-stoichiometric thermodynamic approaches. In the stoichiometric approach, the system is

described by a set of stoichiometrically independent reactions, and they are typically chosen arbitrarily from a set of possible reactions [7]. On the other hand, in a non-stoichiometric approach, the equilibrium composition is found by the direct minimization of the Gibbs free energy for a given set of species [8]. The advantages of the latter approach are [9]: (a) selection of a possible set of reactions is not necessary, (b) no divergence occurs during the computation, and (c) an accurate estimation of the initial equilibrium composition is not necessary. The non-stoichiometric approach is used in this study.

The nonlinear objective function as seen in Eq. (1) is minimized using non-linear programming (nlp) procedure of SAS version 11. The equivalent Gibbs energy function, $f(x)$, used in SAS is as follows:

$$f(x) = \sum_{i=1}^n x_i \left[c_i + \ln \left(\frac{x_i}{s} \right) \right] \quad (2)$$

with

$$c_i = \left(\frac{G^0}{RT} \right)_i + \ln P \quad (3)$$

and

$$s = \sum_{i=1}^n x_i \quad (4)$$

Standard Gibbs free energy of formation (G^0) for each species at atmospheric pressure and different temperatures of the involved species was obtained from Yaws [10] and Rossini [11]. For solid and liquid phases, the change in Gibbs energy formation with pressure is very small and can be ignored. For gas, however, the change in the Gibbs energy with pressure is presented as follows:

$$\Delta G = G^P - G^0 = \int_{P^0}^P RT \ln(P/P^0) \quad (5)$$

where P^0 is standard pressure (1 atm) and P is operating pressure.

In order to find the x_j that minimize the value of G , it is necessary that the values of x_j satisfy the elemental mass balances, i.e.,

$$\sum_{i=1}^m a_{li} x_i = b_l \quad (6)$$

where a_{li} is the atomic number of element i in a molecule of species l ; b_l is atomic number of element l in the products side for $l = 1-m$; and m is number of chemical elements involved in the mixture.

2.1. Approach

In most upgrading processes the output of gas stream is mainly composed of five major compounds, namely H_2 , CO, CO_2 , CH_4 , and H_2O . For this reason, we consider these five compounds as constituents of the model. Carbon (C), hydrogen (H) and oxygen (O) atoms are involved in all the products considered in this study, and, therefore, only these three atoms are used for the elemental mass balance (Eq. (6)).

The initial composition of the input gas is based on the syngas composition from experimental studies found in the

literature. Six studies [12–17] have been consulted to get different initial composition of syngas derived from biomass gasification process, and they are presented in Table 1. Most of them used circulating fluidized bed (CFB) gasifiers with air or steam as gasifying agent. It can be revealed that steam gasification system produced more moist syngas with minute quantities of N₂, while air gasification system produced N₂-rich syngas. To estimate the atomic contribution of tar, naphthalene (C₁₀H₈) is used as a model compound to represent tar [18]. Most the literature, however, do not have tar data.

Excess of steam is useful to reform hydrocarbons and to shift CO. To investigate the effect of steam, the analysis is performed at two levels of C/S ratios. The first C/S ratio level is based on the original ratio found in the syngas exited from the gasification unit. The second level is conducted by adding extra steam to achieve a C/S ratio of 1:1.

In this study, nitrogen (N₂) is assumed to be inert and will not affect the composition of the upgraded syngas.

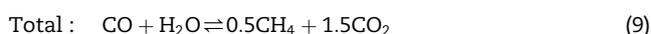
3. Results and discussion

3.1. Effect of temperature on equilibrium composition

Fig. 1 depicts the typical equilibrium compositions of products resulted from the Gibbs free energy minimization analysis at the temperature window between 400 and 1300 K. The initial syngas composition for this case was obtained from Albertazzi et al [12]. At the initial water content of 37.7% (Table 1), the C/S ratio was 1.36. In Fig. 1, the initial values of four main

species in the syngas exited from the gasifier, namely H₂, CO, CO₂, and CH₄, are also depicted with empty symbols.

From the figure, it can be observed that temperature considerably influenced the equilibrium compositions. Methane and CO₂ gradually decreased at temperatures <600 K and >1000 K. Between 600 and 1000 K, however, both species declined drastically with increasing temperature. The high composition of CO₂ and CH₄ at low temperatures could be attributed to simultaneous reactions of water gas shift (WGS) and methanation (Eqs. (7)–(9)) as well as reforming of higher hydrocarbons and tar.



The absence of CO and H₂ and the decrease of water in this region confirm the occurrence of aforementioned simultaneous reactions.

Carbon monoxide and H₂, on the other hand, increased with increasing temperature. The increase in CO and H₂ is most likely as a result of the reforming of CH₄ as depicted by Eqs. (10) and (11).



It could be inferred that above reaction schemes are predominant at temperatures below 900 K. In this region, the

Table 1 – The original syngas composition from different cases.

Reference →	Albertazzi [12] et al	Gabra et al [13]	Chen et al [14]	Corella et al [15]	Kersten et al [16]	Wang et al [17]
Gasifier type	CFB, Varnamo	Cyclone	CFB	CFB	CFB	Indirectly heated FB
Oxidant	O ₂ -Steam	Steam	Air	Air	Air	Air
Temperature, K	1223	1066	1026	1073	1023	1073
Syngas composition exited gasifier (vol.%, wet, N ₂ -free):						
H ₂	11.90	10.03	11.49	11.33	19.16	26.11
CO	11.97	17.40	24.10	22.48	22.86	30.91
CO ₂	28.19	22.01	30.70	21.59	26.40	15.39
CH ₄	8.25	3.37	4.69	5.31	6.44	6.53
C ₂ H ₆	0.08	0.07	0.00	0.00	0.13	0.37
C ₂ H ₄	1.54	1.35	1.43	2.48	2.21	2.96
C ₂ H ₂	0.00	0.84	0.00	0.00	0.00	0.25
H ₂ O	38.06	44.95	27.60	36.81	22.81	17.49
Total	100.00	100.00	100.00	100.00	100.00	100.00
N ₂	0.95	0.11	54.38	43.40	45.02	33.7
C ₁₀ H ₈ (Tar)	0.27	na	na	na	na	0.19
C/S ratio (Original)	1.36	1.08	2.26	1.48	2.66	3.56
Atomic Composition (b _i) at original C/S ratio						
C	0.5387	0.2668	0.2843	0.3070	0.3302	0.5059
H	1.4040	0.7281	0.4682	0.7200	0.6508	1.0530
Orang-orang	1.0540	0.5868	0.5158	0.5790	0.5353	0.6430
C/S ratio	1	1	1	1	1	1
Atomic Composition (b _i) at C/S ratio 1:1						
C	0.5387	0.2668	0.2843	0.3070	0.3302	0.5059
Hampir	1.7270	0.7657	0.7850	0.9180	1.0630	1.7810
Orang-orang	1.2160	0.6056	0.6742	0.6780	0.7416	1.0070

Note: na = not available.

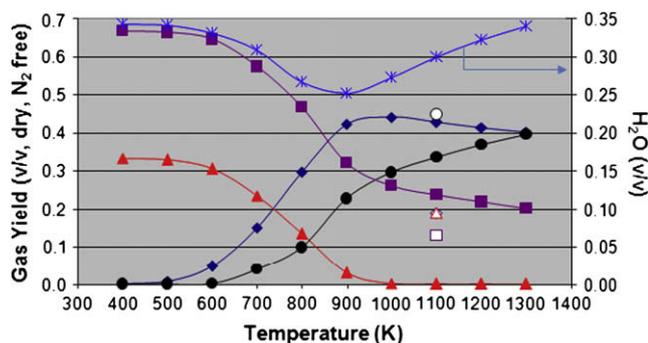


Fig. 1 – Typical gas yields resulted from the Gibbs free energy minimization analysis at temperatures 400–1300 K and S/C of 1.36 (initial gas composition taken from Albertazzi et al [12]). Legend: ◆ H₂ ▲ CH₄ ● CO ■ CO₂ * H₂O (Empty symbols are initial values for corresponding species).

increase in temperature results in decreased amounts of CO₂, CH₄, and H₂O (in the left hand side of the equations), and an increase in CO and H₂ (on the right hand side). In addition, the increase of H₂ could be attributed to the water gas shift reaction (Eq. (7)).

Above 900 K, however, the amount of H₂O produced increased with increasing temperatures. This is as a consequence of the reverse WGS reaction. It is well known that at high temperature the WGS reaction (Eq. (7)) is reversed to the promotion of the backward reaction. The reverse WGS reaction is also attributed to a decrease of H₂ after reaching a maximum point at 1000 K.

Fig. 1 also reveals that between 900 and 1100 K is an effective temperature range for syngas upgrading. This is because at this temperature range, thermodynamics favor the highest H₂ yield while CH₄ production is practically inhibited. This implies that gas upgrading can be performed without any extra cooling or heating because syngas resulting from typical gasification systems is already at this temperature range. Compared to initial values, it was observed that, at this temperature range, H₂ content enhanced from 19 to 44 (vol.%, dry, inert free), while CO₂ content increased from 13 to 22%. Methane and CO content reduced from 19% to 0 and from 44 to 30%, respectively. The equilibrium gas compositions for all cases are discussed below.

3.2. Effect of initial syngas composition

Fig. 2 shows the effect of different initial syngas compositions on the equilibrium composition at atmospheric pressure and temperatures from 400 to 1300 K. The initial syngas composition (as shown in Table 1) is represented by the lead author of the sources referred. It can be observed that the initial syngas composition of different gases influences the equilibrium composition. It could be noted that the trends were analogous between compounds. The effect of initial syngas composition on H₂ and CO yields were more pronounced at temperatures above 900 K whereas the effect on CH₄ yield was more pronounced at temperatures below 800 K.

The four cases involving initial syngas compositions from Albertazzi et al [12], Corella et al [15], Gabra et al [13], and Kersten et al [16] resulted in close H₂ yields. From Table 1, it can be observed that the initial values of H₂ were close for the cases of Albertazzi et al [12], Gabra et al [13], and Corella et al

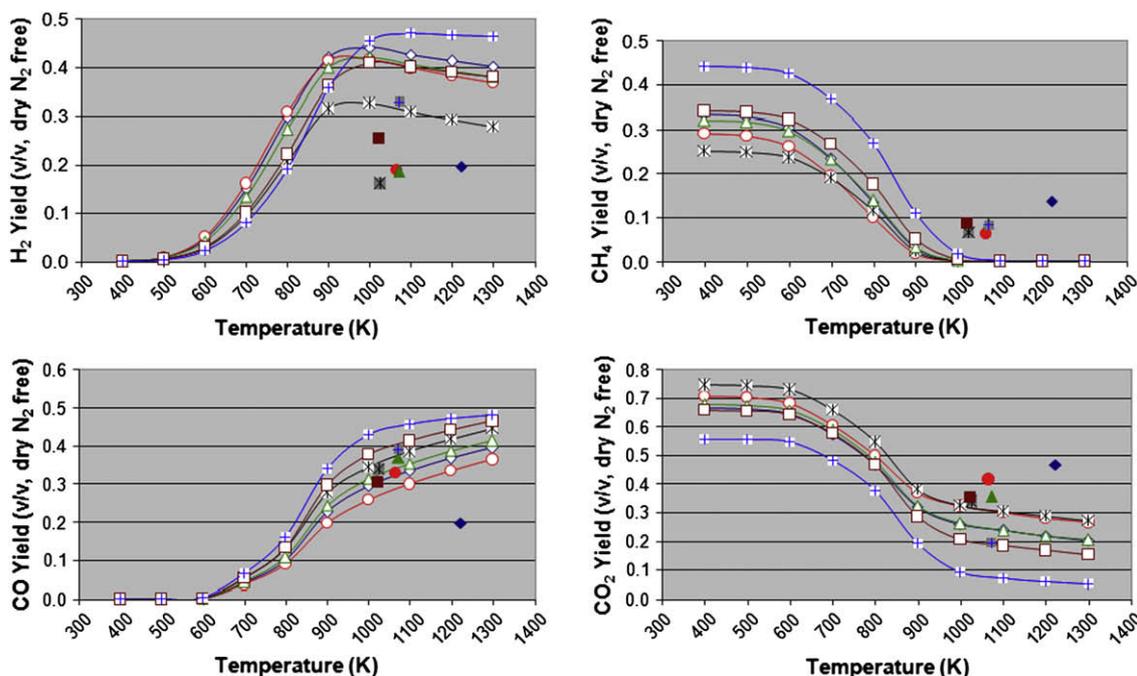


Fig. 2 – Equilibrium gas compositions at temperatures between 400 and 1300 K resultant from different initial syngas compositions. (Legend: ◇ Albertazzi; ▲ Gabra; × Chen; □ Corella; ○ Kersten; + Wang, solid symbols are initial values of respective species and cases as given in Table 1).

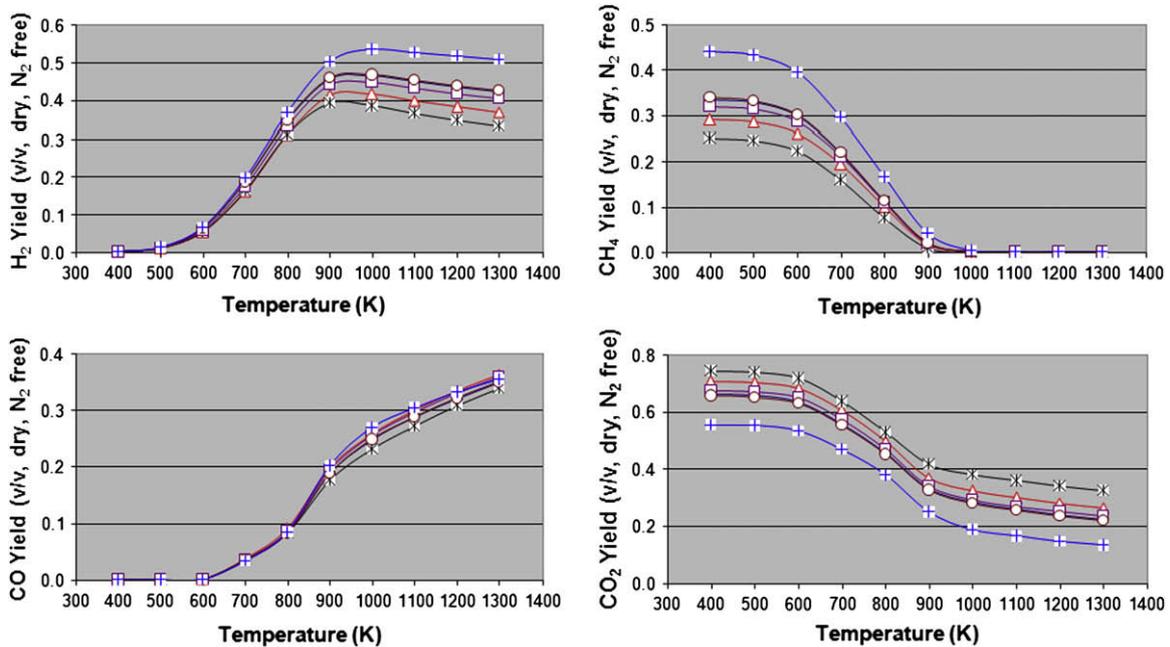


Fig. 3 – Equilibrium composition at 400–1300 K, C/S ratio 1:1, and different initial syngas composition. Legend: \diamond Abertazi; \triangle Gabra; \times Chen; \square Corella; \circ Kersten; $+$ Wang.

[15]. For the case of Kersten et al [16], the initial H_2 value was relatively higher than the other three. However, the maximum point of H_2 at equilibrium state was close to that of the other three cases. This might have resulted from the high C/S ratio of 2.66.

At temperatures >1000 K, the highest H_2 yield was observed for the case of Wang. This could have resulted from the simultaneous effects of high H_2 (26.11%) and low CO_2

(15.39%) in the initial syngas composition. Conversely, the case of Chen et al [14], which had a low initial H_2 value (11.49%) but a high initial CO_2 value (30.70%), produced the lowest H_2 yield at the same temperature.

On examination, the optimum point of H_2 varied from 32.8 for the case of Chen to 47.1% for the case of Wang. The improvement of H_2 yield for all the cases examined spanned from 43 to 126% from its initial value. At the same time, CH_4

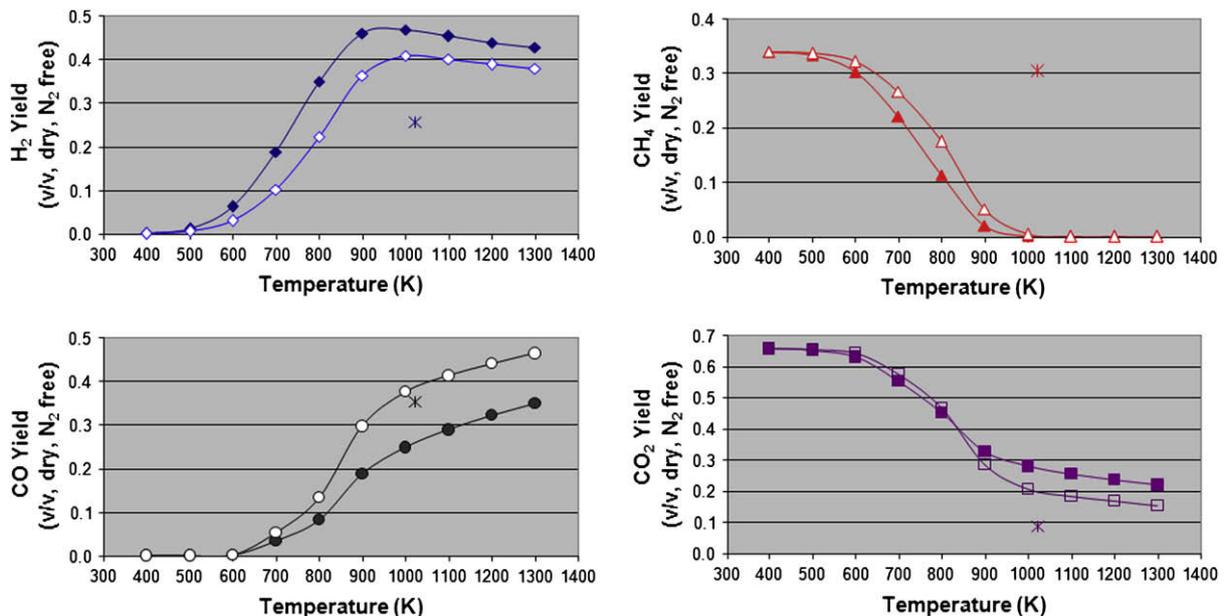


Fig. 4 – Effect of C/S ratio on the equilibrium gas composition at temperatures 400–1300 K: empty symbol for C/S 2.66:1 and solid symbol for C/S 1:1. Initial gas composition is taken from Kersten et al [16] and initial values of respective species are symbolized with star (*).

was reduced by almost 100% from its initial value for all cases. The equilibrium value of CO_2 at that point varied from 7 to 35%. The reduction of CO_2 from its initial values ranged from 17 to 64%. In comparison to its initial value, the equilibrium of CO at that point greatly varied among all cases: three cases showed decreasing values in CO ranging from 8 to 31%, three others showed increasing values in CO from 17 to 49. At the point when equilibrium H_2 reached a maximum, the syngas has a variation of H_2/CO ratio from 1.0 to 1.8 for all cases.

The variation in the equilibrium gas composition, in part, may have resulted from different C/S ratios, which varied from 1.08 to 3.56 in the original syngas (Table 1). Therefore, in order to investigate the contribution of C/S to the equilibrium composition, the thermodynamic analysis at C/S of 1:1 was also performed for all cases. In actual practice, this can be achieved by adding extra steam to the syngas. The results are depicted in Fig. 3.

For all cases, it can be observed that the addition of steam positively influenced the upgraded syngas: H_2 yield increases, while CO and CH_4 decrease. In addition, the equilibrium gas composition had H_2 to CO ratio around 2:1 for most cases. This ratio is a particularly advantageous. Fischer–Tropsch synthesis, for instance, requires the H_2 to CO ratio of feed gas to be 2:1. The same ratio is also essential for alcohol synthesis from syngas through thermochemical (catalytic) process. This result suggests that there is greater success in upgrading syngas produced from steam gasification rather than from air gasification. The reason is that syngas produced from steam gasification is more humid, thus, there is no need for additional steam.

Fig. 4 depicts the effects of C/S ratio on the equilibrium gas composition with initial syngas condition taken from Kersten et al [16]. Upgrading this syngas at original C/S ratio (2.66) did not effectively reduce CO (in fact, it increased CO from 35% to

around 40%). By adding steam to a C/S ratio 1:1, the CO can be reduced significantly to 25%.

3.3. Effect of pressure

Fig. 5 depicts the effect of pressure on the upgraded gas yield at a temperature range of 400–1300 K. It can be observed that there was no considerable effect of increasing pressure at low temperatures (<600 K). At temperatures >600 K, CO can be suppressed by increasing reaction pressure. However, no significant change in H_2 yield was observed until 900 K. At temperatures >900 K, increasing pressure from one to three atmospheres increased H_2 yield significantly. The effect of increasing pressure from 1 to 3 atm was also observed on the increase in CO_2 and CH_4 . Further increase in pressure, however, resulted in a less significant change in H_2 , CH_4 , and CO_2 yields.

3.4. Carbon formation

Because a catalyst is required for upgrading syngas, the knowledge of conditions promoting carbon or coke formation is essential. Carbon formation in the catalyst surface is detrimental because it poisons the catalyst and results in an irreversible deactivation of the catalyst. The loss of catalyst activity due to carbon formation may occur through blockage of active sites of the catalyst, catalyst breakdown due to the accumulation of whisker carbon, encapsulation of the metal crystals, or physical blockage of the reactor tube [18]. Formation of carbon also causes the loss of effective surface area, lowers the heat transfer rate from catalyst to gas, and plugs the void space within the catalyst [19]. Carbon formation may arise due to the decomposition of CO or CH_4 or the reaction of CO_2 or CO with H_2 [9].

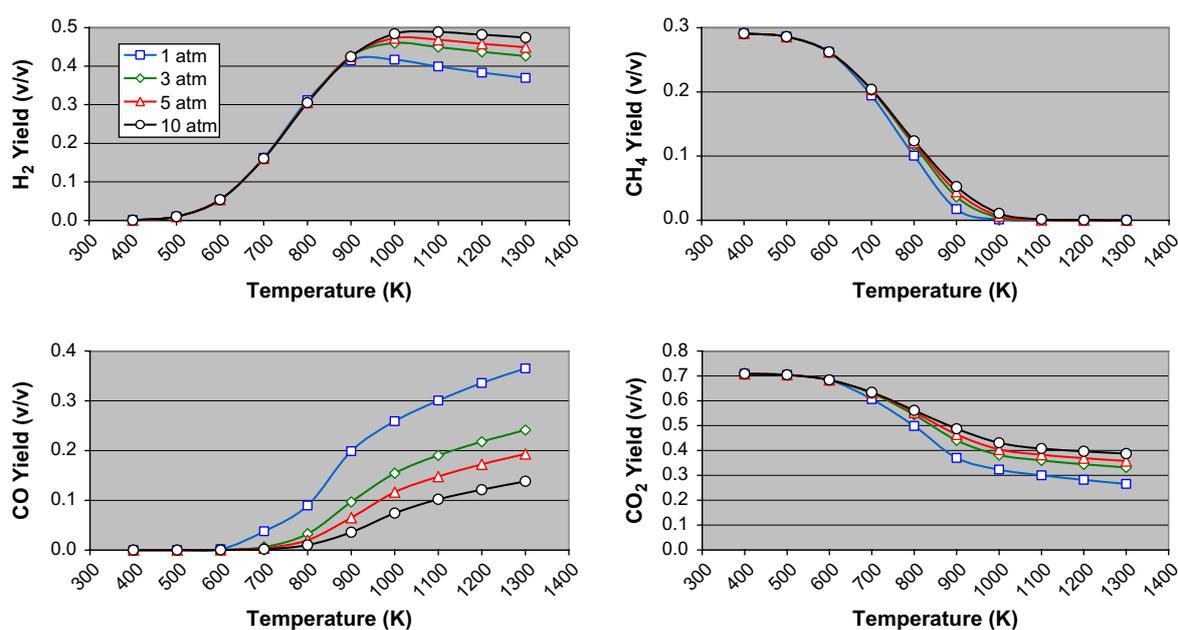


Fig. 5 – Effect of pressure on the gas yield (dry, N_2 free) at temperatures 400–1300 K (initial gas composition is taken from Gabra et al [13] with C/S of 1.36).

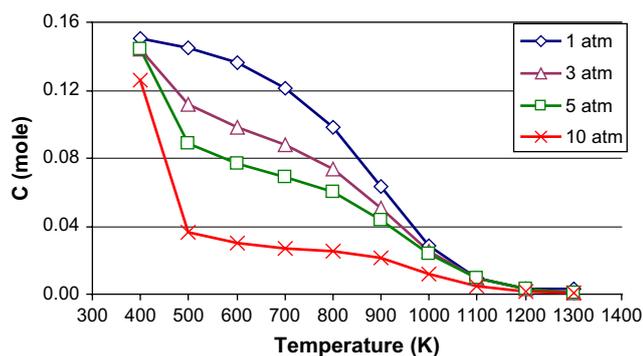
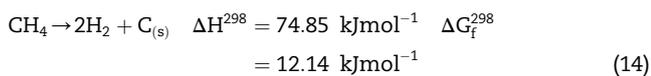
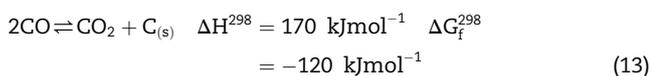


Fig. 6 – Effect of temperature and pressure towards carbon formation (initial syngas composition from Gabra et al [13] with C/S ratio 1.1).

Coke formation happens through several routes including disproportionation of CO into CO₂ known as Boudouard reaction (Eq. (13)) and decomposition of CH₄ (Eq. (14)).



The Boudouard reaction is exothermic and it is favorable at low temperatures. On the other hand, CH₄ decomposition is endothermic and favorable at high temperatures.

Fig. 6 shows the possibility of coke formation at temperatures 400–1300 K and pressures 1–10 atm. It appears that coke formation was favorable at low temperatures and low pressures. Increasing temperature resulted in decreasing coke formation. At temperatures >1000 K, coke formation was practically negligible. Implications of this result are that syngas upgrading can be performed without any concerns on coke formation because syngas exiting from biomass gasification is typically in this temperature range. The figure also shows that

increasing pressure resulted in decreasing of coke formation, especially at low to medium temperatures (<900 K).

3.5. Comparison: thermodynamic vs. experimental

Several efforts have been made for upgrading syngas derived from biomass gasification using catalytic reforming. Two cases are presented here for comparison between actual results and thermodynamic limits. First case is taken from the work of Corella et al [15] with commercial steam reforming catalysts based on nickel. The second is taken from Wang et al [17] with Ni–Mg oxides catalysts. Table 2 summarizes important parameters and compares initial, actual, and thermodynamic optimums of gas composition.

It can be observed that the H₂ yield of upgraded gas from the work of Wang et al [17] was close to the thermodynamic optimum resulted from our analysis. The work of Corella et al [15], which agreed closely with thermodynamic analysis results using ASPEN^{plus}, showed considerable differences, especially for H₂ which is much lower and CH₄ which is much higher from our analysis. This discrepancy of gas composition from ASPEN^{plus} and our analysis may be as a result of several factors such as temperature, rounding accuracy, differences of Gibbs free energy values used, and the number and type of final compounds expected. As a matter of fact, our analysis was conducted at 1063 K, identical to the temperature Corella et al used, while ASPEN^{plus} analysis was run at 1073 K. However, it can be observed from Fig. 2 that gas composition does not differ significantly due to increasing temperature from 1063 K to 1073 K. Similarly, the effect of accuracy due to rounding is expected to be insignificant. The last two factors (differences of Gibbs energy values and the number and type of final compounds) could be critical. As a matter of fact, Corella et al's simulation included ethylene (C₂H₄) as one of final compounds but our analysis did not. Based on the good agreement of our work with the work of Wang et al [17], however, it suggests that our simple method using commonly available software can be used to predict the equilibrium composition of upgraded syngas with high accuracy and repeatability.

Table 2 – Comparison of experimental results vs. thermodynamic equilibrium of upgrading syngas derived from biomass gasification (vol.%, dry, N₂-free).

Reference (Catalyst)	Comparison	Temp (K)	H ₂	CO	CH ₄	CO ₂
Corella et al (1998) [15] (Ni-based catalyst)	Exit Gasifier	1073	17.93	35.57	8.40	34.17
	Reformer	1063	33.58	32.57	5.46	27.51
	ASPEN ^{plus}	1073	34.18	33.33	4.06	27.56
	Current simulation	1063	41.22	34.02	0.00	24.69
Wang et al (2006) [17] (NiO–MgO ₂)	Exit Gasifier	1073	33.07	39.16	8.27	19.50
	Reformer ^a	1023	45.74	40.24	0.58	13.41
	Current simulation	1023	45.95	43.71	1.51	8.94
(NiO/MgO ₂)	Reformer ^a	1023	45.65	41.02	0.45	12.81
	Current simulation	1023	45.95	43.71	1.51	8.94
(Ni _{0.03} –Mg _{0.97} O)	Reformer ^a	1123	44.94	42.71	0.32	11.92
	Current simulation	1123	47.05	46.08	0.00	6.73

^a Wang et al [17] presented data in form of graphs. The values presented here were estimated from the graphs using DIGXY software.

4. Conclusions

A thermodynamic analysis for upgrading syngas derived from biomass gasification was performed. Calculating the minimization of the Gibbs free energy function was the basis of the analysis. The study concludes that upgrading syngas is best practiced at a temperature range between 900 and 1100 K. At these temperatures H₂ yield is maximized with negligible CH₄ yield and coke formation. The results also showed that at these temperatures, H₂ could be possibly increased by 43–124% of its initial values in the syngas exiting from the gasifier. Similarly, CO₂ decreased by 24–64% of the initial values, whereas CH₄ practically decreased by 100%. The equilibrium values of CO showed a discrepancy: some cases were lower than its initial values whereas some others were higher than its initial values. The analysis revealed that increasing steam resulted in a positive effect on the overall gas composition. The study also concluded that increasing pressure from 1 to 3 atm can be applied at temperatures >1000 K to increase H₂ yield.

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