

# Modeling Biomass Gasification Using Thermodynamic Equilibrium Approach

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Received: 21 May 2008 / Accepted: 8 December 2008 /  
Published online: 27 January 2009  
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**Abstract** In this paper, the thermodynamic equilibrium models for biomass gasification applicable to various gasifier types have been developed, with and without considering char. The equilibrium models were then modified closely matching the CH<sub>4</sub> only or both CH<sub>4</sub> and CO compositions from experimental data. It is shown that the modified model presented here based on thermodynamic equilibrium and taking into account local heat and mass considerations can be used to simulate the performance of a downdraft gasifier. The model can also be used to estimate the equilibrium composition of the syngas. Depending on the gasifier type and internal fluid flow, heat and mass transfer characteristics, with proper modification of the equilibrium model, a simple tool to simulate the operation and performance of varying types of biomass gasifier can be developed.

**Keywords** Biomass · Gasification · Chemical equilibrium · Modeling · Downdraft gasifier · Syngas

## Nomenclature

<i>a</i>	number of atom H in the biomass formula CH <sub><i>a</i></sub> O <sub><i>b</i></sub> N <sub><i>c</i></sub> S <sub><i>d</i></sub> based on 1 mol of carbon
<i>A</i>	coefficients of the heat capacity formula
$\Delta A$	change in coefficient <i>A</i> of a reaction, see formula 17
<i>b</i>	number of atom O in the biomass formula CH <sub><i>a</i></sub> O <sub><i>b</i></sub> N <sub><i>c</i></sub> S <sub><i>d</i></sub>
<i>B</i>	coefficients of the heat capacity formula
$\Delta B$	change in coefficient <i>B</i> of a reaction, similar to formula 17
<i>c</i>	number of atom N in the biomass formula CH <sub><i>a</i></sub> O <sub><i>b</i></sub> N <sub><i>c</i></sub> S <sub><i>d</i></sub>
<i>C</i>	coefficients of the heat capacity formula
<i>C<sub>P</sub></i>	heat capacity, J/mol·K
$\Delta C$	change in coefficient <i>C</i> of a reaction, similar to formula 17
<i>d</i>	number of atom S in the biomass formula CH <sub><i>a</i></sub> O <sub><i>b</i></sub> N <sub><i>c</i></sub> S <sub><i>d</i></sub>
<i>D</i>	coefficients of the heat capacity formula

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$\Delta D$	change in coefficient $D$ of a reaction, similar to formula 17
$e$	stoichiometric coefficient of $\text{H}_2\text{O}$ (liquid) in the overall gasification reaction 1
$E$	coefficients of the heat capacity formula
$f$	stoichiometric coefficient $\text{O}_2$ in the overall gasification reaction 1
$g$	stoichiometric coefficient $\text{N}_2$ in the overall gasification reaction 1
$\Delta G^0$	standard Gibbs free-energy change of a reaction at 298.15 K, J/kmol
$\Delta G_f^0$	Gibbs energy of formation of component $i$ at 298.15 K, J/mol
$\Delta H_{T_0}^0$	standard heat of reaction at temperature of $T_0$ ( $=298.15$ K), J/mol
$n_i$	represents the mole numbers of $\text{H}_2$ , $\text{CO}$ , $\text{CH}_4$ , $\text{CO}_2$ , $\text{H}_2\text{O}(\text{g})$ and $\text{C}(\text{s})$ , $i=1,2,\dots,6$
$K_0$	equilibrium constant at 298.15 K
$K_i$	equilibrium constants of the three equilibrium reactions 5–7
$P_t$	the total pressure in the reaction system, Pa
$R$	ideal gas constant
$T_0$	reference temperature, $T_0=298.15$ K
$T$	reaction temperature, K

### Superscript

° standard state for property values

### Introduction

Biomass gasification is gaining increasing attention as one of the prominent thermochemical conversion methods to produce renewable fuels, energy and other products. In addition to producing energy for heat and power, synthesis gas from biomass gasification can be subsequently converted into liquid transportation fuels such as diesel and gasoline, alternative fuels such as methanol and dimethyl ether (DME), ethanol, and other chemicals. This route is referred as the “syngas platform”, or “one carbon platform” for conversion of biomass to biofuels and chemicals, differentiating it from the “sugar platform” where biomass is subjected to hydrolysis and saccharification and then the resulting sugars including glucose, xylose, mannose, etc. are converted into ethanol and sugar-derived building blocks such as 3-hydroxypropionic acid (3-HP), levulinic acid and xylitol, etc., which can later be used to produce various chemicals and materials [1]. The well-known Fischer–Tropsch (FT) synthesis is one of the most important gas-to-liquids (GTL) conversion technologies, which converts natural gas or syngas ( $\text{CO}+\text{H}_2$ ) to high-quality liquid transportation fuels (e.g., diesel and gasoline) containing less or no sulfur in a fixed bed or slurry reactor by using iron or cobalt-based or hybrid (composite) catalysts [2–4]. Methanol, a liquid transportation fuel or material for fuel cell, can be synthesized from syngas over the  $\text{Cu}/\text{ZnO}$  catalyst. DME is produced by a two-step process, i.e., synthesis of methanol from syngas and then dehydration of methanol to DME. It can also be directly synthesized from syngas in a single-step process [5] by use of the hybrid catalyst composed of  $\text{CuO}$ ,  $\text{ZnO}$ ,  $\text{Al}_2\text{O}_3$ , and/or  $\text{Cr}_2\text{O}_3$ ) for methanol synthesis and an acid function component (such as  $\gamma\text{-Al}_2\text{O}_3$ , H-ZSM-5 or HY zeolites) for conversion of methanol into DME [6]. In addition, ethanol and other higher alcohols can be produced from syngas with Co–Mo–K catalysts [7].

Coal or oil gasification has been practiced for many years, for example, Sasol’s gasification application in South Africa. There are more pilot scale or demonstration and commercial plants of gasification than those of pyrolysis and liquefaction, using coal or oil as feedstock [8]. In addition, most components for processing of clean syngas are

commercial or nearly commercial [9]. The research and development that has been underway in the coal or oil gasification can certainly benefit the future development of biomass gasification [8].

However, there are still apparent differences between biomass gasification and coal and other materials gasification, mostly related to the high level of volatiles (70–75%) in biomass compared to coal (20–25%), the different physical and structural characteristics of the feedstock, and the different char reactivity and particle mechanical properties. Hence, the vast experience with coal and other materials is not directly applicable [8]. Considering this and the fact that biomass gasification is a key process of the future biorefinery, a large number of researchers have been studying it [8, 10–15].

Biomass gasification is rather complex and many researchers have focused on modeling in order to better understand the gasification process and carry out design, simulation, and optimization of gasifiers and perform process analysis. There are many types of biomass gasifiers: fluidized bed (circulating fluidized bed [16], bubbling fluidized bed reactor [17]), fixed bed (downdraft [11, 18–20] and updraft [21–23]), cyclone [24], entrained flow [25, 26], moving-bed gasifiers [27, 28], etc. In terms of spatial dimensions, models of gasifiers can be divided into 0-D, 1-D, 2-D, and 3-D models, where D represents dimension. Among these, 1-D, 2-D, and 3-D models contains space variables considering local heat/mass transfer and possibly also fluid flow within the gasifiers. Among these dimensional models, 1-D models were most commonly used, for example, downdraft 1-D models [19, 20, 29, 30] and 1-D bubbling fluidized bed reactor 1-D models [17, 31]. There were a few of 2-D models published, for instances, downdraft 2-D models [32, 33]. Such approaches are more close to the commercial gasification processes than the 0-D (space-independent) model, also referred as thermodynamic equilibrium model. However, the thermodynamic equilibrium model is also imperative due to its ability to predict the maximum possible conversion of biomass during gasification and the theoretical efficiency. It is also important in the optimization of the operating conditions at the equilibrium state and also being a simple tool to estimate the gasification performance for preliminary techno-economic analysis of the whole process.

There are two methods for thermodynamic equilibrium modeling: stoichiometric method based on stoichiometric reactions and non-stoichiometric method based on minimizing the total Gibbs free energy in the system. Up till now, stoichiometric thermodynamic equilibrium models for biomass gasification have been widely applied [34–39]. Most of these have not considered char production in their models. A few of researchers [35, 37] considered the char in their models, but did not establish the modified models for use. Li et al. [40, 41] accounted for char in their model and established the modified models for coal gasification, but, to our knowledge, similar work for biomass gasification considering char and at the same time establishing the modified models has not been reported. The purpose of this paper is to develop a stoichiometric thermodynamic equilibrium model for biomass gasification with and without char, and then develop a modified model to simulate the performance of a downdraft gasifier.

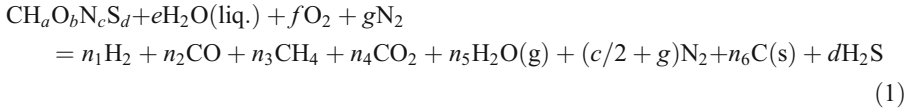
## Thermodynamic Equilibrium Model

### Overall Reaction and Elemental Balance Equations

The general chemical formula of lignocellulosic biomass, based on 1 atom of carbon, can be expressed in the form of  $\text{CH}_a\text{O}_b\text{N}_c\text{S}_d$ , omitting the other elements such as Cl and traces of metal elements and where  $a$ ,  $b$ ,  $c$ ,  $d$ , representing the numbers of atoms of H, O, N, and

S, respectively. The composition of individual elements can be determined from the ultimate analysis of the biomass.

Assuming that the gasification reactions are at thermodynamic equilibrium, and the gasification products contain the gas species of  $H_2$ ,  $CO$ ,  $CH_4$ ,  $CO_2$ ,  $H_2O$ ,  $N_2$ , and  $H_2S$ , and the solid species of solid carbon only, i.e., char only contains solid carbon here (ash is assumed to be inert in the gasification and not considered in the simulation), the overall gasification reaction with steam and air can be written as:



From Eq. (1), the elemental balances for C, H and O are easily obtained:

C:

If not considering char ( $n_6=0$ ),

$$1 = n_2 + n_3 + n_4 \quad (2a)$$

If considering char,

$$1 = n_2 + n_3 + n_4 + n_6 \quad (2b)$$

$$\text{H:} \quad a + 2e = 2n_1 + 4n_3 + 2n_5 + 2d \quad (3)$$

$$\text{O:} \quad b + e + 2f = n_2 + 2n_4 + n_5 \quad (4)$$

### Equilibrium Equations

In the downdraft gasifier, there are four zones: drying for removal of moisture, pyrolysis of biomass into oil, char, and volatiles, oxidation of the volatile products of pyrolysis, and gasification of char from pyrolysis [11]. In this paper, only the reaction zone is considered and simulated by the thermodynamic equilibrium model.

There are three main independent equilibrium reactions, which can be used for equilibrium calculations [37]:

Steam methane reforming reaction



Water–gas shift reaction



Primary water–gas reaction



The three equilibrium constants for the three reactions (5), (6), and (7) are described in Eqs. (8a), (9a), and (10), respectively.

$$K_1 = \frac{n_2 \times n_3^3 \times P_t^2}{n_3 \times n_5} \quad (8a)$$

$$K_2 = \frac{n_4 \times n_1}{n_2 \times n_5} \quad (9a)$$

$$K_3 = \frac{n_2 \times n_1 \times P_t}{n_5} \quad (10)$$

Where  $K_1$ ,  $K_2$  and  $K_3$  are the equilibrium constants for the reactions (5), (6), and (7), respectively.  $P_t$  is the total pressure in the system. According to  $\frac{d \ln K}{dT} = \frac{\Delta H_f^0}{RT^2}$ , the equilibrium constants can be derived:

$$\begin{aligned} \ln K &= \ln K_0 + \left[ \frac{\Delta A}{R} \ln T + \frac{\Delta B}{2R} T + \frac{\Delta C}{6R} T^2 + \frac{\Delta D}{12R} T^3 + \frac{\Delta E}{20R} T^4 - \frac{F}{RT} \right]_{T_0}^T \\ &= \ln K_0 + \frac{\Delta A}{R} \ln \frac{T}{T_0} + \frac{\Delta B}{2R} (T - T_0) + \frac{\Delta C}{6R} (T^2 - T_0^2) \\ &\quad + \frac{\Delta D}{12R} (T^3 - T_0^3) + \frac{\Delta E}{20R} (T^4 - T_0^4) - \frac{F}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \end{aligned} \quad (11)$$

Where

$$F = \Delta H_{T_0}^0 - \left( \Delta A T_0 + \frac{\Delta B}{2} T_0^2 + \frac{\Delta C}{3} T_0^3 + \frac{\Delta D}{4} T_0^4 + \frac{\Delta E}{5} T_0^5 \right) \quad (12)$$

$$\ln K_0 = -\frac{\Delta G^0}{RT} \quad (13)$$

$$\Delta G^0 = \sum v_i G_{fi}^0 \quad (14)$$

$$C_p^0 = A + BT + CT^2 + DT^3 + ET^4 \quad (15)$$

$$\Delta C_p^0 = \Delta A + \Delta BT + \Delta CT^2 + \Delta DT^3 + \Delta ET^4 \quad (16)$$

$$\Delta A = \sum_{\text{products}} nA - \sum_{\text{reactants}} nA \quad (17)$$

With similar definitions for  $\Delta B$ ,  $\Delta C$ ,  $\Delta D$ , and  $\Delta E$ .

#### Thermodynamic Equilibrium Models

Two thermodynamic equilibrium models are taken into account, i.e., Model 1 (not including char) consisting of Eqs. (2a), (3), (4), (8a), (9a), and Model 2 (considering char) consisting of Eqs. (2b), (3), (4), (8a), (9a), (10).

For Model 2, under the given gasification temperature  $T$  and pressure  $P_t$ ,  $K_1$ ,  $K_2$ , and  $K_3$  can be determined by Eqs. (11), (12), (13), (14), (15), (16). Then  $n_i$  ( $i=1-6$ ) are obtained by solving the nonlinear Eqs. (2b), (3), (4), (8a), (9a) and (10), for a specific biomass ( $a$ ,  $b$ ,  $c$ ,  $d$ , and  $e$  are known) under the given amount of air ( $f$  and  $g$  are known). Model 1 was solved similarly.

### Modified Model—Based on Experimental Compositions

In an actual gasification system, it is always the case that the chemical reactions are not exactly at equilibrium due to the kinetic (including mass/heat transfer) limitations [16]. Therefore, it is necessary to establish the modified model considering the fractional achievement of equilibrium, i.e., the modified models are made by multiplying the coefficient  $\beta_1$  to  $K_1$  in Eq. (8a), and  $\beta_2$  to  $K_2$  in Eq. (9a), as seen in Eqs. (8b) and (9b), respectively.

$$\beta_1 K_1 = \frac{n_2 \times n_1^3 \times P_t^2}{n_3 \times n_5} \quad (8b)$$

$$\beta_2 K_2 = \frac{n_4 \times n_1}{n_2 \times n_5} \quad (9b)$$

Where  $\beta_1$  can be determined by fixing the fraction of  $\text{CH}_4$  in the dry syngas at its average value of the experimental data, and  $\beta_2$  estimated by fixing the fraction of  $\text{CO}$  in the dry syngas at its average value of the experimental data.

Specifically, modification of Model 1 (not including char) by fixing the fraction of  $\text{CH}_4$  only, i.e.,  $y_{\text{CH}_4}$  is mainly described by Eqs. (2a), (3), (4), (8b), (9a). This is called M1F1 model. The modification of Model 1 by fixing both  $y_{\text{CH}_4}$  and  $y_{\text{CO}}$  (fraction of  $\text{CO}$ ) is mainly described by Eqs. (2a), (3), (4), (8b), (9b). This is called M1F2 model. Similarly, the modification of Model 2 (including char) by fixing  $y_{\text{CH}_4}$  only is called M2F1, consisting of Eqs. (2b), (3), (4), (8b), (9a), (10), and the modification of Model 2 by fixing both  $y_{\text{CH}_4}$  and  $y_{\text{CO}}$  is called M2F2, consisting of Eqs. (2b), (3), (4), (8b), (9b), (10). The resulting nonlinear equations were solved in a similar way as described earlier.

### Determination of Deviation Temperature

Model 1 (not considering char) and Model 2 considering char can also be utilized to calculate the deviation temperature between the model and experiment at the same or close to product compositions. Specially, the model temperature was obtained by minimization of the sum of square of residues between the experimental compositions at a specific temperature and simulation compositions. Then the deviation temperature between the model and experiment was determined.

## Model Input and Physical Properties

### Feedstock Properties and Operating Conditions

The biomass properties and the gasification conditions are shown in Table 1.

**Table 1** Properties and the gasification conditions of biomass feedstock.

Biomass	Rubber wood [42]	Sawdust [39]	Biomass Solid waste [39]
Moisture	16	10	16
Ultimate elemental analysis (wt % on dry basis)			
C	50.6	52	51.034
H	6.5	6.07	6.776
O	42	41.55	39.178
N	0.2	0.28	2.642
S	0	0	0.37
Ash	0.7	0.1	0
Operation condition			
Reactor Temp. ( $T_R$ ), K	1,113	1,073.15	1,073.15
Reactor Pres. ( $P_R$ ), Pa	101,325	101,325	101,325
Oxidant (Air or O <sub>2</sub> and N <sub>2</sub> )			
O <sub>2</sub> flowrate, mol/hr	0.3781	0.3273	0.4647
N <sub>2</sub> flowrate, mol/hr	1.4224	1.2313	1.7482

### Physical Properties of Product Species

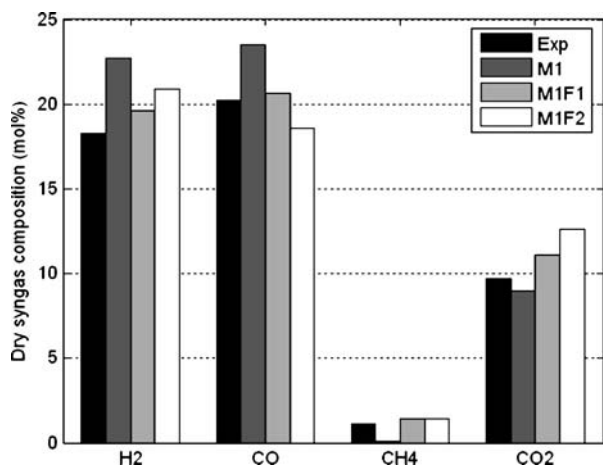
The coefficients in the heat capacity formula Eq. (15) for gas product species H<sub>2</sub>, CO, CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub>, H<sub>2</sub>S and solid char (C) were taken from a chemical properties handbook [43]. The standard enthalpy of formation, the standard Gibbs free energy of formation, and the standard enthalpy of combustion at 25°C were taken from the process simulator Aspen Plus.

## Results and Discussion

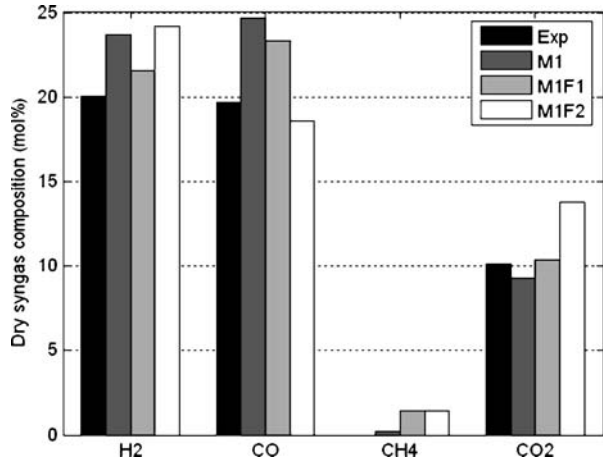
### Results of Model 1 and Its Modified Models

Figures 1, 2, and 3 show the comparison between Model 1 and its modified models and the experimental data.

**Fig. 1** Dry syngas composition (mol%) of Rubber wood (SSR values of M1, M1F1 and M1F2 are 0.0067, 0.0016, and 0.0035, respectively) Note that M1 is Model 1 (without considering char), and SSR the sum of squares of the residual error between the model predictions and the experiment. SSR represents the model performance. Smaller SSR value indicates a better model performance



**Fig. 2** Dry syngas composition (mol%) of sawdust (SSR values of M1, M1F1 and M1F2 are 0.0102, 0.0063, and 0.0099)



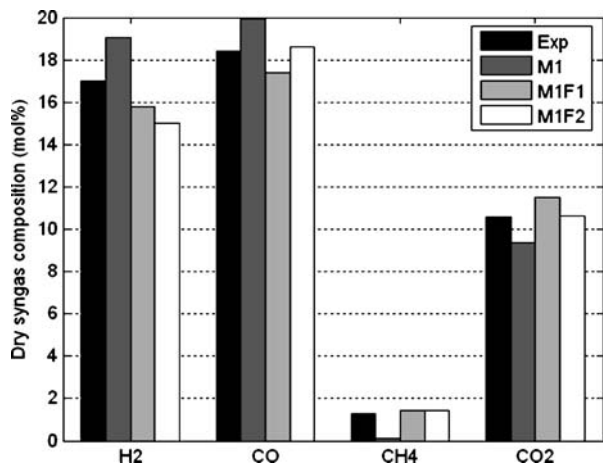
It can be seen from Figs. 1, 2, and 3 that the results of Model 1 (not considering char) are close to experimental data. In addition, the modification of Model 1 by fixing  $y_{\text{CH}_4}$  only, i.e., M1F1 can improve the predictive capability. Whereas the modification of Model 1 by fixing both  $y_{\text{CH}_4}$  and  $y_{\text{CO}}$ , i.e., M1F2 lead to poorer predictive capability. This is probably because Model 1 has one unknown variables less than the Model considering char, and thus fixing both  $y_{\text{CH}_4}$  and  $y_{\text{CO}}$  may become over-estimation.

#### Results of Model 2 and Its Modified Models

Figures 4, 5, and 6 show the comparison between model 2 (considering char) and its modified models and the experimental data.

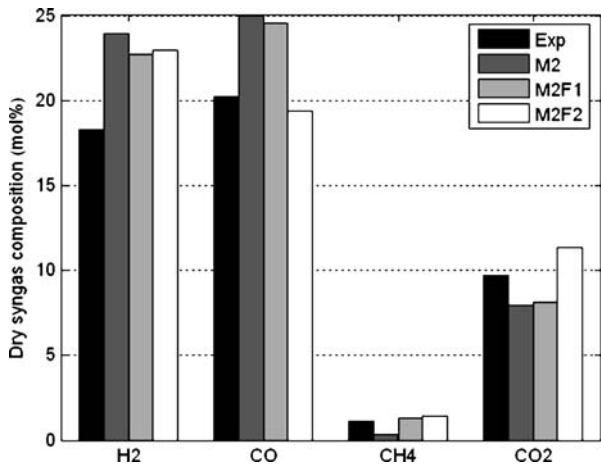
From Figs. 4, 5, and 6 it is found that the results of the Model 2 (M2) considering char, are far removed from the experimental data, specifically, the simulation value of  $y_{\text{CO}}$  is much higher than that of the experimental data, while the model value of CO<sub>2</sub> is much

**Fig. 3** Dry syngas composition (mol%) of biomass solid waste (SSR values of M1, M1F1, and M1F2 are 0.011, 0.004, and 0.007)





**Fig. 4** Dry syngas composition (mol%) of rubber wood (SSR values of M2, M2F1, and M2F2 are 0.012, 0.010, and 0.006)

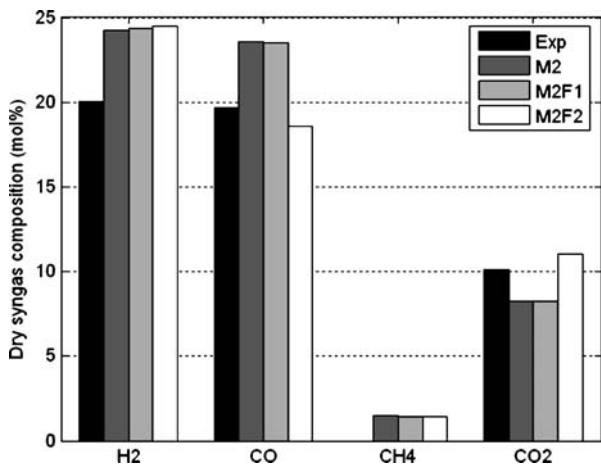


lower than those of experiments. Therefore, the prediction of syngas composition cannot be improved by the modification of M2 by fixing  $\gamma_{CH_4}$  only, i.e., M2F1. Instead, the prediction performance can be improved by the modified model M2F2, which fixes both  $\gamma_{CH_4}$  and  $\gamma_{CO}$ . This is possibly due to the increase number of unknown variables for Model 2 considering char compared to the Model without considering char, and thus fixing both  $\gamma_{CH_4}$  and  $\gamma_{CO}$  may become more accurate than fixing  $\gamma_{CH_4}$  only.

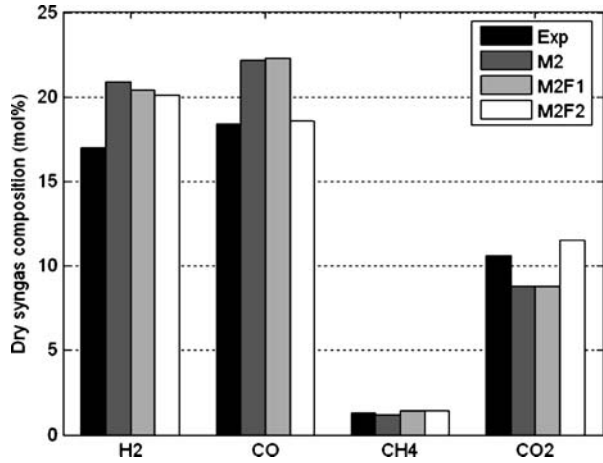
Deviation Temperature between the Model and Experiment

Table 2 shows that when the model gasification temperature is 125 °C lower than the actual gasification temperature the model results are close to the real data. This temperature deviation also proves that the modified models based on the equilibrium model as described above are significantly necessary.

**Fig. 5** Dry syngas composition (mol%) of sawdust (SSR values of M2, M2F1 and M2F2 are 0.010, 0.010, and 0.006)



**Fig. 6** Dry syngas composition (mol%) of biomass solid waste (SSR values of M2, M2F1, and M2F2 are 0.007, 0.006, and 0.003)



## Conclusions

Thermodynamic equilibrium model without considering char, Model 1, reported here can well describe the downdraft biomass gasifier at high temperature when there is no formation of char. Modified equilibrium model matching the  $y_{\text{CH}_4}$  in the product gas closer to its average experimentally determined value fits the experimental data very well after a proper choice of beta.

Thermodynamic equilibrium model considering char, Model 2, is obviously more general and widely applicable than Model 1. However, due to the complexities of including char, the equilibrium model predictions do not match well with experimental results. Modified equilibrium model considering char closely matching both  $y_{\text{CH}_4}$  and  $y_{\text{CO}}$  in the product gas can better describe the commercial downdraft gasifier. In addition to equilibrium considerations, local complex fluid flow, heat and mass transfer characteristics and their influence on local equilibrium of an actual gasifier, can be simulated and lumped into the model, as a first approximation, by modifying the model gasification temperature to help improve the model accuracy in prediction of syngas compositions. This provides a viable tool for process simulation such as mass and energy balances and optimization and further development.

**Table 2** Dry syngas comp. (mol %) of biomass solid waste ( $\Delta T_{\text{R}}=125$  °C).

	Rubber wood		Sawdust		Biomass solid waste	
	Exp [42]	M2	Exp [39]	M2	Exp [19]	M2
H <sub>2</sub>	18.3	20.7	20.06	20.46	17	16.39
CO	20.2	24.3	19.7	19.29	18.4	16.88
CH <sub>4</sub>	1.1	2.3	0	2.79	1.3	2.18
CO <sub>2</sub>	9.7	9.7	10.15	13.37	10.6	12.47
N <sub>2</sub>	50.7	43	50.1	44.1	52.7	51.99
SSR	0.008		0.005		0.001	

Where  $\Delta T_{\text{R}} = (\text{Experimental or actual gasification temperature}) - (\text{Model gasification temperature})$

**Acknowledgment** The University of Minnesota Initiative for Renewable Energy and the Environment (IREE) is gratefully acknowledged for its financial support.

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