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# Conceptual Synthesis of Gasification-Based Biorefineries Using Thermodynamic Equilibrium Optimization Models

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**ABSTRACT:** An integrated biorefinery is a processing facility that converts biomass into a wide range of biochemical products and also provides a sustainable supply of biofuels and energy. One of its critical features is the ability to handle a wide variety of biomass feedstocks and the capacity to produce a portfolio of products through multiple conversion technologies. The gasification process is recognized as a promising option for initial processing of biomass, as it is a robust thermal conversion process. The composition of syngas, especially the ratio of H<sub>2</sub> to CO, is crucial when the syngas is further converted to liquid fuels and chemicals. To optimize the production of syngas for application in an integrated biorefinery, a systematic approach is needed to design the system and predict its performance. In this work, a modular optimization approach to link a stoichiometric equilibrium model of biomass gasification and structural models of synthesis processes is developed. In this approach, all model components are solved simultaneously. The approach is used to evaluate the equilibrium composition of syngas, the optimum operating temperature, and the required types and amounts of oxidants. Two case studies are used to illustrate the approach. A sensitivity analysis is then performed to assess the most significant factors affecting the process economics in these examples.

## 1. INTRODUCTION

Driven by the growing need for a sustainable and secure supply of energy and chemicals, as well as increasing attention to the environmental consequences of utilizing fossil fuels, there is much interest in the development of cost-effective biorefineries.<sup>1,2</sup> Biorefineries are processing facilities that convert biomass to generate a sustainable supply of biofuels, energy, and bulk and fine chemicals. These facilities are gaining attention because of their potential to reduce greenhouse emissions and improving energy security, trade balance, and domestic job opportunities. To convert biomass into value-added products, various technologies can be used; for example, biorefinery concepts have been proposed for systems based on first-generation (i.e., conventional crops) and second-generation (i.e., algal or lignocellulosic) biomass.<sup>3–5</sup> This work focuses on integrated biorefineries that use lignocellulosic biomass (e.g., algae, forestry waste, municipal solid waste, agriculture waste) as feedstocks.

Because of the numerous types of biomass feedstocks, products, and available technologies, there is a critical need for the development of systematic procedures for the synthesis of integrated biorefineries. As shown in the literature, process systems engineering has the potential to support the conceptual design of an integrated biorefinery.<sup>7</sup> It covers aspects of biomass logistics, biomass conversion kinetics, and process energetics.<sup>6</sup> Furthermore, established processing pathways available at the commercial scale have also been analyzed and optimized using process simulation and integration. Such processes cover power and heat generation,<sup>8,9</sup> biodiesel production and scheduling,<sup>10–14</sup> and bioethanol production.<sup>15–17</sup> Life-cycle

approaches have also been integrated with process design and integration of biorefineries.<sup>18</sup> Nevertheless, these types of stand-alone plants with limited product portfolios exhibit poor energy efficiency.<sup>2</sup> Thus, the concept of an integrated biorefinery that utilizes biomass as the feedstock in producing multiple products, analogous to the approach used for petroleum refineries, has been proposed.<sup>19</sup> However, regardless of the intended biomass input, the common feature is that an integrated biorefinery consists of multiple conversion platforms/technologies with different levels of material and heat integration to improve its environmental and economic performance.<sup>6</sup> To be cost-effective, an integrated biorefinery has to achieve a high degree of efficiency through multiple levels of integration.<sup>1,2,20–25</sup>

Current research and development efforts in the synthesis of integrated biorefineries focus on integrating the wide spectrum of biomass conversion technologies (thermal, biological, and physical conversion processes) to generate multiple biomass-based value-added products.<sup>20,26–33</sup> Mansoornejad et al.<sup>34</sup> further optimized the solution of the product allocation problem by integrating supply chain design with product allocation in the conceptual design of a forest biorefinery. Research in the area of process design and process integration has begun to explore additional aspects of biorefineries, focusing on material and energy integration between various processing and synthesis

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facilities within an integrated biorefinery.<sup>17,21–23</sup> Most recently, Tay et al.<sup>35</sup> presented a novel graphical approach based on the CHO ternary diagram to synthesize an integrated biorefinery. In addition, the proposed approach is also able to evaluate the gas-phase equilibrium composition of biomass gasification.

As shown in previous works,<sup>6,19</sup> another key feature of an integrated biorefinery is to have a flexible upstream processing platform to convert the feedstock (biomass) into a range of desired intermediates such as syngas, sugars, alcohols, succinic acid, and glycerol. Gasification is an attractive technology for the initial processing of biomass through robust thermal conversion that can handle a wide range of feedstocks.<sup>36,37</sup> Gasification typically operates in the temperature range of 600–1400 °C to convert biomass into a gaseous mixture of carbon dioxide (CO<sub>2</sub>), steam (H<sub>2</sub>O), methane (CH<sub>4</sub>), carbon monoxide (CO), and hydrogen (H<sub>2</sub>).<sup>38</sup> Such a gaseous product is commonly known as synthesis gas or syngas. Syngas can be used for the generation of heat and power, as well as feedstock for the production of chemicals and liquid fuels.<sup>39–42</sup>

It is noted that the composition of syngas, especially the ratio of H<sub>2</sub> to CO, is crucial when the syngas is to be further converted to liquid fuels and biochemicals.<sup>40,43</sup> Note also that the composition of syngas is strongly affected by the type of biomass, the type and amount of oxidants (e.g., steam and O<sub>2</sub>), and the gasification temperature. Thus, selecting the optimum parameters is crucial in the initial stage of conceptual design of an integrated biorefinery and is the focus of the study reported in this article.

The detailed modeling of biomass gasification has been extensively studied in the past few decades. As found in the literature,<sup>44–48</sup> gasification modeling efforts are divided into two categories: kinetic modeling and thermodynamic equilibrium modeling. Kinetic modeling is used for specific reactors and provides essential information on mechanisms and rates.<sup>44,45</sup> Meanwhile, equilibrium models determine the state based on thermodynamic limits.<sup>46–48</sup> According to Li et al.,<sup>47</sup> equilibrium models are more suitable for process design, evaluation, and improvement, as they determine the maximum potential conversion of reactants (biomass) based on equilibrium limit. Therefore, an equilibrium model of gasification is applied for the conceptual design of an integrated biorefinery in this work.

## 2. MODULAR OPTIMIZATION STRATEGY

In general, mathematical models can be classified as white-box, black-box, and gray-box models. A white-box model is the most detailed type, consisting of a detailed mechanistic description of real physical processes (e.g., reactions, operations). Because white-box models are very detailed, the process parameters modeled can be changed to optimize the process realistically. However, such models are normally complex and computationally intensive. On the other extreme, process modeling through a black-box model is very simple. Such models are mainly derived from first principles and consist of scale-invariant sets of linear energy and material balances. Therefore, such models can be solved easily to obtain the global optimal solution without much difficulty. However, black-box models do not provide detailed information of the process. Therefore, fine-tuning of the model cannot be performed. Gray-box models lie between detailed white-box models and simplistic black-box models. Gray-box models provide a computationally efficient alternative to detailed models, through the use of simplified relationships. For example, material and energy balances are functions of operating parameters

such as temperature and pressure. These relationships are expressed in algebraic form and can be derived empirically or semiempirically (e.g., through linear or polynomial curve-fitting of data from experiments or off-line simulations). Such an intermediate approach can be particularly useful for processes whose underlying mechanisms are not fully understood and, hence, not amenable to modeling using a white-box approach. This approach was demonstrated in polygeneration plants.<sup>49</sup>

In this work, a modular optimization strategy that breaks a large optimization problem into small parts is proposed. In this strategy, a “master” model consisting of black boxes is first constructed. Next, some of the black boxes are replaced by gray- or white-box models that enable the designer to “zoom in” on specific process units that happen to be of key interest. Meanwhile, the rest of the model still consists of black boxes. Such a strategy reduces the computational effort significantly as compared to pure white-box modeling. In addition, the overall formulation can be simplified without losing the insights of interest for the effective design of the processes.

A systematic synthesis approach based on a modular optimization strategy for the conceptual design of an integrated biorefinery is proposed in this work. A large integrated biorefinery model is broken down into smaller models, each with a different level of modeling detail (i.e., white, gray, or black box) based on the sensitivity of the overall result to the process parameters. In this work, first, a detailed equilibrium model of biomass gasification (i.e., white box) is developed and validated. Then, it is extended to connect the mechanistic equilibrium biomass gasification (white-box) model to an empirical (black-box) downstream synthesis model to give a complete superstructural representation of an integrated biorefinery. Such a modular modeling and optimization strategy is employed to reduce the complexity of the overall model by focusing on just the key variables (i.e., gasification parameters) that affect the syngas compositions. As the synthesis process focuses only on the syngas specification requirements and conversion, a black-box model can be used without compromising the accuracy and practicality of the model.

In this article, an equilibrium model for biomass gasification is first introduced. Then, the model is validated with literature experiment and modeling results. Next, the application of modular optimization for the synthesis of a gasification-based integrated biorefinery is presented. To illustrate the proposed approach, two illustrative case studies are solved. In addition, to determine the effects of cost and price fluctuation toward the optimum solution, sensitivity analyses of key parameters are conducted.

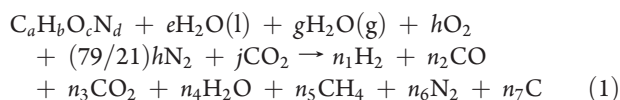
## 3. EQUILIBRIUM MODEL OF BIOMASS GASIFICATION

In general, thermodynamic equilibrium models are also further divided into two categories: stoichiometric and nonstoichiometric models.<sup>46,47</sup> Stoichiometric models are formulated based on stoichiometric chemical equations, whereas nonstoichiometric models are mainly based on minimization of the Gibbs free energy for the gasification process. As stated by Huang and Ramaswamy,<sup>46</sup> stoichiometric equilibrium models for gasification are being widely used because they provide a simple tool for estimating the performance of gasification for preliminary technical-economic analysis. In addition, optimizing a nonstoichiometric model can require a multiple-objective mathematical program, which is inherently difficult to solve. Multiple-objective optimization problems can be solved in the absence of weighting

factors to generate a Pareto optimal solution set. However, it does not provide a unique solution, which complicates the decision-making process. A unique solution in multiple-objective optimization problems can only be found by supplying additional information regarding the relative importance of each objective. Thus, to simplify the problem, a stoichiometric model was used in this work for the synthesis of an integrated biorefinery with maximum production/revenue and minimum waste generation.

As mentioned previously, lignocellulosic biomass (e.g., forestry waste, agricultural waste, energy crops) is the feedstock of interest in this work. Its chemical composition will vary depending on the source. However, the major components of lignocellulosic biomass are cellulose and other polysaccharides (collectively represented as  $C_6H_{10}O_5$ ) and lignin (represented as  $CH_{1.12}O_{0.377}$ ).<sup>50</sup> Therefore, lignocellulosic biomass can be generally expressed as  $C_aH_bO_cN_d$ , where  $a-d$  represent the numbers of atoms of carbon (C), hydrogen (H), oxygen (O), and nitrogen (N), respectively, which are determined from the ultimate analysis of the biomass.

As mentioned previously, there are five main gaseous species (i.e.,  $H_2$ , CO,  $CO_2$ ,  $H_2O$ , and  $CH_4$ ) involved in gasification. Because  $N_2$  is considered as inert gas, and char (solid carbon, C) is assumed to be in equilibrium with the gas phase in gasification,  $N_2$  and char are not taken into consideration in the gasification reaction. A general gasification reaction with air (79%  $N_2$  and 21%  $O_2$ ), steam ( $H_2O$ ), and  $CO_2$  can be represented by the equation



where  $e$ ,  $g$ ,  $h$ , and  $j$  are the stoichiometric coefficients (per mole of biomass) of biomass moisture, steam, air, and carbon dioxide, respectively, and  $n_1-n_7$  are the stoichiometric coefficients of  $H_2$ , CO,  $CO_2$ ,  $H_2O$ ,  $CH_4$ ,  $N_2$ , and solid carbon (C), respectively. The generic gasification equation indicates the possibility to use steam ( $g$ ), air or oxygen ( $h$ ), or  $CO_2$  ( $j$ ) as the gasification agent to produce syngas (mixture of  $H_2$ , CO,  $CO_2$ ,  $H_2O$ ,  $CH_4$ ,  $N_2$ ) with or without carbon deposition (C). The equilibrium mixture of syngas and the deposited carbon are determined by the equilibrium equations to be considered in this model.

The overall gasification reaction is governed by the overall mass balance, enthalpy balance, and equilibrium reaction equations. As gasification processes normally operate at high temperature and moderate pressure, it is reasonable to assume that syngas behaves as an ideal gas, whereas ash and  $N_2$  are assumed to be inert.<sup>47,51</sup> In addition, it is also assumed that reaction kinetics and transfer processes do not impede the achievement of equilibrium and that the carbon conversion is determined only by thermodynamic and material-balance constraints; similar assumptions have been used in previous works.<sup>47,51</sup> These assumptions could lead to over- or underprediction of the production of certain syngas components as compared to actual experiment. However, as shown in the results discussed in section 4, the proposed model is able to provide reasonably good predictions for the syngas composition and insight into the conceptual design of a gasification-based integrated biorefinery. In addition, equilibrium models are very useful for establishing preliminary benchmarks for conceptual design without excessive computational burdens and can thus be used as the basis for more detailed models once attractive solutions have been identified.

**3.1. Mass Balance.** For a given biomass with moisture content, based on eq 1, there are nine unknowns ( $n_1-n_5$ ,  $n_7$ ,  $g$ ,  $h$ , and/or  $j$ ) to be computed. The atomic balances of biomass gasification are expressed in the equations

C atomic balance

$$w(a) + j = n_2 + n_3 + n_5 + n_7 \quad (2)$$

H atomic balance

$$w(b) + w(2e) + 2g = 2n_1 + 2n_4 + 4n_5 \quad (3)$$

O atomic balance

$$w(c) + w(e) + g + 2h + 2j = n_1 + 2n_3 + n_4 \quad (4)$$

N atomic balance

$$w(d) + (79/21)h = n_6 \quad (5)$$

where  $w$  is the molar flow rate of the biomass.

Equations 2–5 are the atomic balances of C, H, O, and N, respectively. If pure  $O_2$  is used as the oxidant, then the second term on the left-hand side in eq 5 can be removed.

**3.2. Energy Balance.** Based on the first law of thermodynamics, the energy balance of a steady-state open system can be represented by

$$H^{RMs} + Q^T = H^{PG} + H^{Cr} \quad (6)$$

where  $H^{RMs}$  is the total enthalpy of raw materials at standard conditions (1 atm and 298 K) and  $Q^T$  is the amount of additional heat required to maintain the optimum gasification temperature.  $H^{PG}$  and  $H^{Cr}$  are the total enthalpies of product gases and char, respectively, at gasification conditions.

Assuming that there is no heat loss in the system, the left-hand side of eq 6 signifies the total rate of internal energy transported by the reactants plus the additional heat transferred into the gasifier, whereas the right-hand side of eq 6 refers to the total rate of internal energy transport by the gasification products at the elevated temperature. Based on eq 6, the detailed energy balance of biomass gasification is

$$\begin{aligned} & H_{f, \text{biomass}}^\circ + eH_{f, H_2O(l)}^\circ + gH_{f, H_2O(g)}^\circ + hH_{f, O_2}^\circ \\ & + \left(\frac{79}{21}\right)hH_{f, N_2}^\circ + jH_{f, CO_2}^\circ + Q^T \\ & = n_1H_{f, H_2}^\circ + n_2H_{f, CO}^\circ + n_3H_{f, CO_2}^\circ + n_4H_{f, H_2O(g)}^\circ \\ & + n_5H_{f, CH_4}^\circ + n_6H_{f, N_2}^\circ + n_7H_{f, C}^\circ + \int_{T^\circ}^T \bar{n}\bar{C}_p dT \quad (7) \end{aligned}$$

where  $T^\circ$  and  $T$  are the temperatures of standard conditions (298 K) and gasification, respectively.  $H_{f, \text{biomass}}^\circ$ ,  $H_{f, H_2O(l)}^\circ$ ,  $H_{f, H_2O(g)}^\circ$ ,  $H_{f, O_2}^\circ$ ,  $H_{f, N_2}^\circ$ ,  $H_{f, CO_2}^\circ$ ,  $H_{f, H_2}^\circ$ ,  $H_{f, CO}^\circ$ ,  $H_{f, CH_4}^\circ$ , and  $H_{f, C}^\circ$  are the standard heats of formation of biomass, water, steam,  $O_2$ ,  $N_2$ ,  $CO_2$ ,  $H_2$ , CO and  $CH_4$ , respectively.  $H_{f, H_2O(g)}^\circ$  refers the heat of formation of steam at its supply temperature ( $T^{\text{supply}}$ ).

As shown in eq 7, to determine the enthalpy of gaseous products at elevated temperature, the mean heat capacity flow



**Table 1.** Heats of Formation at 25 °C ( $H_f^\circ$ ) of Various Chemical Species<sup>52</sup>

species	kcal/mol	kJ/mol
H <sub>2</sub> O(l)	−68.3174	−285.84
H <sub>2</sub> O(g)	−57.7979	−241.83
CO	−26.416	−110.52
CO <sub>2</sub>	−94.052	−393.51
CH <sub>4</sub>	−74.52	−311.79
O <sub>2</sub>	0	0
N <sub>2</sub>	0	0
H <sub>2</sub>	0	0
C	0	0

rate of gaseous products ( $\bar{n}\bar{C}_p$ ) is included. This term is formulated in the model as

$$\int_{T^o}^T \bar{n}\bar{C}_p dt = \int_{T^o}^T (n_1 C_{p,H_2} + n_2 C_{p,CO} + n_3 C_{p,CO_2} + n_4 C_{p,H_2O(g)} + n_5 C_{p,CH_4} + n_6 C_{p,N_2} + n_7 C_{p,C}) dt \quad (8)$$

where  $C_{p,H_2}$ ,  $C_{p,CO}$ ,  $C_{p,CO_2}$ ,  $C_{p,H_2O(g)}$ ,  $C_{p,CH_4}$ ,  $C_{p,N_2}$ , and  $C_{p,C}$  are the specific heat capacities of H<sub>2</sub>, CO, CO<sub>2</sub>, steam, CH<sub>4</sub>, N<sub>2</sub>, and solid carbon, respectively. In this work, the specific heat capacities [measured in cal/(mol·K)] of all gaseous products are considered as functions of temperature as follows<sup>52</sup>

$$C_{p,H_2} = 6.62 + 0.00081T \quad (9)$$

$$C_{p,CO} = 6.60 + 0.00120T \quad (10)$$

$$C_{p,CO_2} = 10.34 + 0.00274T - 195500/T^2 \quad (11)$$

$$C_{p,H_2O(g)} = 8.22 + 0.00015T + 0.00000134T^2 \quad (12)$$

$$C_{p,CH_4} = 5.34 + 0.0115T \quad (13)$$

$$C_{p,N_2} = 6.50 + 0.00100T \quad (14)$$

$$C_{p,C} = 2.673 + 0.002617T - 116900/T^2 \quad (15)$$

Because the biomass can be derived from a variety of feedstocks, the standard heat of formation is not a constant. However, according to Schuster et al.<sup>53</sup> and De Kam et al.,<sup>54</sup> the standard heat of formation can be derived from the higher heating value (HHV) of biomass and the enthalpy of the combustion products (CO<sub>2</sub> and H<sub>2</sub>O) as

$$H_{f,biomass}^\circ = \alpha H_{f,CO_2}^\circ + \beta H_{f,H_2O}^\circ - (HHV \times MW_i) \quad (16)$$

where  $\alpha$  and  $\beta$  are the stoichiometric coefficients of the complete combustion of biomass and  $MW_i$  is the molecular weight of biomass  $i$ . Note that, in eq 16,  $H_{f,biomass}^\circ$  is expressed in units of kJ/mol, and HHV is expressed in units of kJ/g. According to Sheng and Azevedo,<sup>55</sup> the HHV of biomass can be estimated as

$$HHV = -1.3675 + 0.3137C\% + 0.7009H\% + 0.0318O\% \quad (17)$$

where C% and H% are the weight percentages of carbon and hydrogen, respectively, in the biomass and O\*% is the sum of the weight percentages of oxygen and other elements, that is,  $O^*\% = 100 - C\% - H\% - \text{ash}\%$ .

Table 1 lists the standard heats of formation of various chemical species involved in gasification. To determine the heat of formation of steam at  $T^{\text{supply}}$ , one can use the equation

$$H_{f,H_2O(g)} = H_{f,H_2O(g)}^\circ + \int_{T^o}^{T^{\text{supply}}} C_{p,H_2O(g)} dt \quad (18)$$

**3.3. Equilibrium Reactions.** In general, a gasifier can be divided into four zones, namely, the drying, combustion, reaction, and pyrolysis zones.<sup>46,56,57</sup> In this modeling work, only reactions in the reaction zone are taken into consideration. This is because these reactions have the most influence on the syngas composition for most gasifiers.<sup>48,53,59,60</sup> To simplify the modeling of reaction zone in a gasifier, five reactions (eqs 19–23) that involve all chemical species are considered<sup>46,53,56</sup>

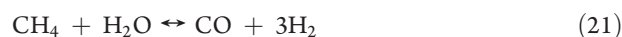
Boudouard equilibrium



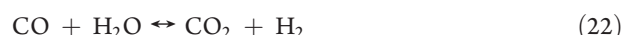
Hydrogenating gasification/methanation



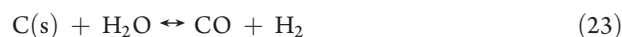
Methane decomposition



Water–gas shift reaction



Heterogeneous water–gas shift reaction



As shown in previous works,<sup>60,61</sup> in the case where no solid carbon remains in the equilibrium state (i.e., excess oxidants are supplied), only two independent reactions of eqs 19–23 need to be considered for the equilibrium equations. On the other hand, in the case where solid carbon (i.e., char) remains as a gasification product because of an oxidant deficit, three independent reactions are needed for the equilibrium calculations. However, it is noted that all sets of independent reactions used to represent the equilibrium mixture and its corresponding species provide the same equilibrium composition as predicted by the thermodynamic theory of independent reaction selection.<sup>60,61</sup> In this work, methane decomposition (eq 21), the water–gas shift reaction (eq 22), and the heterogeneous water–gas shift reaction (eq 23) are selected to represent the interactions of all components.

As mentioned previously, all gaseous components are assumed to be ideal gases, and the activity coefficient of carbon is also assumed to be equal to 1. Therefore, the equilibrium constants

**Table 2.** Comparison of Results for Air Gasification for Wood Waste ( $\text{CH}_{1.44}\text{O}_{0.66}$ ) with a Moisture Content of 20 wt %<sup>a</sup>

species	amounts of gaseous products (% v/v, % mol equiv)			
	current work	equilibrium model <sup>60</sup>	equilibrium model <sup>58</sup>	experimental result <sup>58</sup>
H <sub>2</sub>	23.52	18.44	21.06	15.23
CO	21.70	17.46	19.61	23.04
CO <sub>2</sub>	11.45	13.13	12.01	16.42
CH <sub>4</sub>	0.01	0.00	0.64	1.58
N <sub>2</sub>	43.32	50.96	46.68	42.31

<sup>a</sup> Temperature = 1073 K, pressure = 1 atm.

corresponding to eqs 21–23 ( $K_{21}$ ,  $K_{22}$ , and  $K_{23}$ , respectively) are given by

$$K_{21} = \frac{x_1^3 x_2 P^2}{x_4 x_5} \quad (24)$$

$$K_{22} = \frac{x_1 x_3}{x_2 x_4} \quad (25)$$

$$K_{23} = \frac{x_1 x_3 P}{x_2 x_4} \quad (26)$$

where  $x_u$  is the molar fraction of component  $u$  and  $P$  is the operating pressure of the gasifier.

To determine the equilibrium constants, one can use the standard free energy of formation and the thermodynamic relation<sup>62</sup>

$$K_{\text{eqn}} = \exp \left( \sum_{y=1}^q \nu_y \ln k_{\text{prod}} - \sum_{z=1}^r \nu_z \ln k_{\text{reac}} \right) \quad (27)$$

where  $K_{\text{eqn}}$  is the equilibrium constant for the gasification reaction;  $\nu_y$  and  $\nu_z$  are the stoichiometric coefficients of components  $y$  and  $z$ , respectively; and  $k_{\text{prod}}$  and  $k_{\text{reac}}$  are the thermodynamic equilibrium constants for the formation reactions of product and reactant, respectively, involved in the reaction at temperature  $T$ . Based on the work of Baron et al.,<sup>62</sup> the thermodynamic equilibrium constants of H<sub>2</sub>O ( $k_{\text{H}_2\text{O}}$ ), CH<sub>4</sub> ( $k_{\text{CH}_4}$ ), CO ( $k_{\text{CO}}$ ), and CO<sub>2</sub> ( $k_{\text{CO}_2}$ ) can be expressed by the equations

$$\ln k_{\text{H}_2\text{O}} = 28780T^{-1} - 0.69477 \ln T - 1.4283 \times 10^{-3}T + 0.74925 \times 10^{-6}T^2 - 1.3785 \times 10^{-10}T^3 \quad (28)$$

$$\ln k_{\text{CH}_4} = 8372.2T^{-1} - 1.0769 \ln T - 5.6435 \times 10^{-3}T + 2.9046 \times 10^{-6}T^2 - 5.2351 \times 10^{-10}T^3 \quad (29)$$

$$\ln k_{\text{CO}} = 13612T^{-1} + 1.8317 \ln T - 2.7584 \times 10^{-3}T + 0.6536 \times 10^{-6}T^2 - 0.78772 \times 10^{-10}T^3 \quad (30)$$

$$\ln k_{\text{CO}_2} = 47280T^{-1} + 0.1322 \ln T - 0.94025 \times 10^{-3}T + 0.45112 \times 10^{-6}T^2 - 0.91901 \times 10^{-10}T^3 \quad (31)$$

Thus, given the biomass gasification temperature ( $T$ ),  $K_{21}$ – $K_{23}$  can be determined using eqs 24–31. Note that, based on the calculated  $K_{21}$ – $K_{23}$  values, the composition of all components ( $x_1$ – $x_5$ ) present in the gasification product can also be determined.

As presented in Cairns and Tevebaugh<sup>63</sup> and Duff and Bauer,<sup>64</sup> trace amounts of atomic hydrogen, methyl radicals, and acetylene ( $\text{C}_2\text{H}_2$ ) are produced at high temperature ( $>1500$  K). Thus, a maximum gasification temperature,  $T^{\text{max}}$ , of 1500 K is included in this model

$$T \leq T^{\text{max}} \quad (32)$$

To validate the proposed model, the generated results were compared with the existing modeling results and experimental data in the literature. Next, the proposed model was converted to an optimization model to target the maximum syngas production based on a given biomass and the requirement of an integrated biorefinery.

#### 4. MODEL VALIDATION

As discussed in the previous section, biomass gasification (eq 1) is modeled in this work using three independent reactions when formation of solid carbon is taken into consideration. According to Cairns and Tevebaugh<sup>63</sup> and Li et al.,<sup>47</sup> all carbon will appear in the gas phase in the form of CO, CO<sub>2</sub>, and CH<sub>4</sub> when excess oxidant is supplied and the equilibrium point is located on or below the carbon deposition boundaries. Therefore, in the case where sufficient or excess oxidant is supplied to the gasifier, no solid carbon is deposited at equilibrium, so  $n_7$  is omitted from eq 2, and eq 26 is not included in the model.<sup>46,48,58,60</sup>

To validate the accuracy of the model, the results generated in this work were compared with the previously reported experimental and modeling results for biomass gasification with air<sup>58,60</sup> and steam.<sup>53,65</sup> Note that biomass gasification with CO<sub>2</sub> as the oxidant is newly proposed and is not yet widely tested, so no valid experimental results were available for comparison.

For biomass gasification with air, two reported results taken from Zainal et al.<sup>58</sup> and Mountouris et al.<sup>60</sup> were used to validate the results generated in this work. Zainal et al.<sup>58</sup> conducted both experimental and thermodynamic equilibrium modeling for an air-blown downdraft gasifier, whereas Mountouris et al.<sup>60</sup> developed the GasifEq model, which is based on thermodynamic equilibrium model for a plasma gasifier. The results reported in Zainal et al.<sup>58</sup> and Mountouris et al.<sup>60</sup> are summarized in Table 2. To validate the model, the same feedstock, operating conditions (temperature and pressure), and type of oxidant were specified based on the previous works.<sup>58,60</sup>

As shown in previous works,<sup>58,60</sup> wood waste ( $\text{CH}_{1.44}\text{O}_{0.66}$ ) with a moisture content of 20% can be gasified with air at 1073 K and 1 atm. Based on the given biomass, the molecular weight ( $\text{MW}_i$ ) and stoichiometric coefficient of the moisture content ( $e$ ) are specified as 24 g/mol and 0.3333, respectively. The stoichiometric coefficients of the products from complete combustion of the biomass ( $\alpha$  and  $\beta$ ) are given as 1 and 0.72, respectively. Because the amount of air used in gasification was not specified in previous works,<sup>58,60</sup> it is assumed here that all of the nitrogen found in the product gas comes from air. According to Zainal et al.,<sup>58</sup> the total amount of nitrogen in the product gas determined from equilibrium model and actual experimental result are given at a mole fraction of 0.4668 and 0.4231. Thus, to determine the amount of air to be supplied to attained a gasification temperature of 1073 K, an additional constraint is included in the current model

$$n_6 / (n_1 + n_2 + n_3 + n_4 + n_5 + n_6) < 4.668 \quad (33)$$

It is further assumed that no carbon deposition occurs at the given gasification temperature.<sup>58,60</sup> Hence, following the previous

Table 3. Comparison of Results for Steam Gasification

species	amounts of gaseous products (% v/v, % mol equiv)			
	pine wood waste ( $\text{CH}_{1.6}\text{O}_{0.64}$ ) with a moisture content of 5.01 wt % <sup>a</sup>		beech wood chips ( $\text{CH}_{1.45}\text{O}_{0.71}\text{N}_{0.002}$ ) with a moisture content of 25 wt % <sup>b</sup>	
	current work	experimental result <sup>65</sup>	current work	equilibrium model <sup>53</sup>
H <sub>2</sub>	60.15	37	54.60	56.20
CO	25.82	33	35.95	31.20
CO <sub>2</sub>	13.96	20	9.23	12.50
CH <sub>4</sub>	0.07	9	0.21	0.10

<sup>a</sup> Temperature = 1073 K, pressure = 1 atm, S/B = 1.39. <sup>b</sup> Temperature = 1073 K, pressure = 1 atm, S/B = 0.31.

proposed approach,  $n_7$  and eq 26 are not included in the model. In addition, the gasification temperature is given as 1073 K, and no external heat is required to maintain the temperature in the gasification zone in both cases. Therefore, eq 32 is revised to eq 34, and the additional eq 35 is included in the model

$$T = 1073 \quad (34)$$

$$Q^T = 0 \quad (35)$$

The results obtained by solving the presented model (eqs 2–5, 7–18, 24, 25, 27–31, and 33–35) are summarized in Table 2 for comparison. As shown, the results generated from the model in this work closely match the results reported in previous works.<sup>58,60</sup> In addition, the equilibrium gasification model results are sufficiently close to the experimental values for process synthesis purposes. The discrepancy with the experimental values reported by Zainal et al.<sup>58</sup> is probably due to the fact that equilibrium is not attained in experiments or in an actual gasifier. The modeling results in this work agree closely with other modeling results reported in the literature.<sup>58,60</sup>

Next, experiment and modeling results taken from Wei et al.<sup>65</sup> and Schuster et al.,<sup>53</sup> respectively, were used for validation of the proposed model for biomass gasification with steam. Wei et al.<sup>65</sup> presented experimental results on the steam gasification of pine sawdust ( $\text{CH}_{1.6}\text{O}_{0.64}$ ) with a moisture content of 5.01 wt % ( $\text{MW}_i = 25.05$  g/mol,  $e = 0.07$ ,  $\alpha = 1$ ,  $\beta = 0.80225$ ) in a free-fall reactor. The gasification temperature and steam-to-biomass molar ratio (S/B) were set as 1073 K and 1.39 (1.0 g/g), respectively. In the previous work,<sup>65</sup> an electric heater was used to maintain the temperature in the gasifier. To determine the heat input from the electric heater, eq 36 is included in the model. Based on the given S/B molar ratio, the stoichiometric coefficient of steam per mole of biomass ( $g$ ) is specified by eq 37.

$$Q^T > 0 \quad (36)$$

$$g = 1.39 \quad (37)$$

The model (eqs 2–5, 7–18, 24, 25, 27–31, 34, 36, and 37) was solved, and the results are summarized in Table 3, along with the results reported by Wei et al.<sup>65</sup>

On the other hand, Schuster et al.<sup>53</sup> presented a thermodynamic equilibrium model for steam gasification of beech wood chips ( $\text{CH}_{1.44}\text{O}_{0.71}\text{N}_{0.002}$ ) in a circulating bed gasifier. This biomass consists of 25%wt of moisture and other parameters of biomass are given as follows:  $\text{MW}_i = 33.08$ ,  $e = 0.46$ ,  $\alpha = 1$ ,  $\beta = 0.72355$ . In this case, the gasification temperature and S/B molar ratio were 1073 K and 0.31 (0.17 g/g), respectively. It is

noted that the circulating bed materials were heated in a separate combustor and circulated between the gasification zone and the combustor to maintain the operating temperature at 1073 K. In addition, based on the S/B molar ratio, the stoichiometric coefficient of steam ( $g$ ) is specified as

$$g = 0.31 \quad (38)$$

Equations 2–5, 7–18, 24, 25, 27–31, 34, 36, and 38 were solved simultaneously, and the results are again summarized in Table 3.

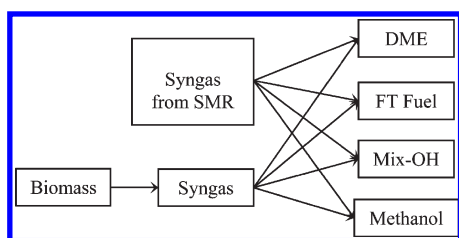
As shown in Table 3, noticeable differences are observed between the current results and those of Wei et al.,<sup>65</sup> especially in the overprediction of the H<sub>2</sub> content and the underprediction of the CH<sub>4</sub> content in the syngas. However, it is interesting to note that the results of the current model are comparable to the results reported by Schuster et al.<sup>53</sup> According to Schuster et al.,<sup>53</sup> the trend of over- and underprediction of H<sub>2</sub> and CH<sub>4</sub> contents, respectively, occurs because of the slow kinetics of the methane decomposition reaction (eq 21). Thus, during the experiments, the equilibrium composition of the mixture is not attained. It is worth noting that equilibrium models are very useful in establishing benchmarks for conceptual design and can be used as the basis for more detailed models once attractive solutions have been identified.

## 5. MODULAR OPTIMIZATION FOR GASIFICATION-BASED INTEGRATED BIOREFINERY

In this work, the thermodynamic gasification equilibrium white-box model previously described is linked to the subsequent synthesis process black-box models through the total flow rate of syngas produced through biomass gasification in the equation

$$n_T = n_1 + n_2 + n_3 + n_4 + n_5 + n_6 \quad (39)$$

In the case where syngas from biomass gasification is not sufficient to fulfill the required volume or composition specification of the synthesis processes, it is assumed that fresh syngas can be supplied from external sources. In this model, fresh syngas from steam methane reforming (SMR) with a higher H<sub>2</sub>/CO ratio, in the range of 3–10, is available to increase the syngas volume or to improve the quality of syngas from biomass gasification before further synthesis of value-added products through various synthesis processes (Figure 1). Syngas from SMR is preferred over a pure hydrogen supply because, in most of the relevant processes, CO is the limiting reactant. Therefore, using syngas from SMR not only can improve the syngas quality, but can also supply additional CO for the synthesis processes. The following equations represent the distribution of syngas



**Figure 1.** Superstructural representation of a gasification-based integrated biorefinery.

from biomass and SMR to various synthesis processes to produce products  $p$

$$n_T = \sum_p n_{\text{Bio}}^p \quad (40)$$

$$n_{\text{SMR}} = \sum_p n_{\text{SMR}}^p \quad (41)$$

$$n_T^p = n_{\text{Bio}}^p + n_{\text{SMR}}^p \quad \forall p \quad (42)$$

where  $n_T$  and  $n_{\text{SMR}}$  are the flow rates of syngas from biomass gasification and SMR (if required), respectively;  $n_{\text{Bio}}^p$  and  $n_{\text{SMR}}^p$  are the splitting flow rates for syngas from biomass gasification and SMR to downstream processes. Meanwhile,  $n_T^p$  is the total molar flow rate of final products  $p$ .

As each synthesis processes has a specified range or minimum  $\text{H}_2/\text{CO}$  ratio syngas requirement, the following equations are included in the model to determine the product portfolios and link the  $\text{H}_2/\text{CO}$  requirement of the syngas to the gasification model

$$\begin{aligned} X_{\text{lower}}^p \left( n_{\text{Bio}}^p \times \varphi_{\text{Bio}}^{\text{CO}} + n_{\text{SMR}}^p \times \varphi_{\text{SMR}}^{\text{CO}} \right) &\leq n_{\text{Bio}}^p \times \varphi_{\text{Bio}}^{\text{H}_2} + n_{\text{SMR}}^p \\ &\times \varphi_{\text{SMR}}^{\text{H}_2} \leq X_{\text{upper}}^p \left( n_{\text{Bio}}^p \times \varphi_{\text{Bio}}^{\text{CO}} + n_{\text{SMR}}^p \times \varphi_{\text{SMR}}^{\text{CO}} \right) \end{aligned} \quad (43)$$

where  $\varphi_{\text{Bio}}^{\text{CO}}$  and  $\varphi_{\text{Bio}}^{\text{H}_2}$  are the molar fractions of CO and  $\text{H}_2$ , respectively, in the syngas from biomass gasification;  $\varphi_{\text{SMR}}^{\text{CO}}$  and  $\varphi_{\text{SMR}}^{\text{H}_2}$  are the molar fractions of CO and  $\text{H}_2$ , respectively, in the syngas from SMR; and  $X_{\text{upper}}^p$  and  $X_{\text{lower}}^p$  are the upper and lower limits, respectively, of the  $\text{H}_2/\text{CO}$  specification required for the different synthesis processes to produce products  $p$ .

According to a previous work,<sup>38</sup> the molar production of product  $p$  ( $F^p$ ) is normally calculated based on CO conversion ( $Y^p$ ). To determine the mass production of product  $p$  ( $F_m^p$ ), conversion factors ( $Y_m^p$ ) are also included in the model (as shown in eq 45). In addition,  $F_m^p$  is often bounded by predefined lower ( $F_m^{\text{lower}}$ ) and upper ( $F_m^{\text{upper}}$ ) limits as shown in eq 46.

$$F^p = \left( \varphi_{\text{Bio}}^{\text{CO}} \sum_p n_{\text{Bio}}^p + \varphi_{\text{SMR}}^{\text{CO}} \sum_p n_{\text{SMR}}^p \right) Y^p \quad (44)$$

$$F_m^p = F^p Y_m^p \quad (45)$$

$$F_m^{\text{lower}} < F_m^p < F_m^{\text{upper}} \quad (46)$$

For the preliminary conceptual design, economic potential (EP, i.e., the profit excluding the capital costs and operating

and maintenance costs) is normally computed to determine the economic feasibility of product portfolios and the corresponding process pathways.<sup>66,67</sup> Thus, in this work, the optimization objective is to maximize the economic potential (EP)

$$\begin{aligned} \text{EP} = \sum_p F_m^p P^p - \left[ \sum_i (w_i \text{MW}_i) P^i + (g \text{MW}_{\text{H}_2\text{O}}) P^{\text{H}_2\text{O}} \right. \\ \left. + (h \text{MW}_{\text{O}_2}) P^{\text{O}_2} + (j \text{MW}_{\text{CO}_2}) P^{\text{CO}_2} \right. \\ \left. + (n_{\text{SMR}} \varphi_{\text{SMR}}^{\text{CO}}) P^{\text{SMR}} + Q^T P^Q \right] \end{aligned} \quad (47)$$

where  $P^p$ ,  $P^i$ ,  $P^{\text{H}_2\text{O}}$ ,  $P^{\text{O}_2}$ ,  $P^{\text{CO}_2}$ , and  $P^Q$  are the prices per unit mass of product  $p$ , biomass  $i$ , steam,  $\text{O}_2$ ,  $\text{CO}_2$ , and heat, respectively.  $P^{\text{SMR}}$  is the price per unit molar flow rate of syngas measured at the corresponding CO molar flow rate, and  $w_i$  is the molar flow rate of biomass  $i$ .  $\text{MW}_i$ ,  $\text{MW}_{\text{H}_2\text{O}}$ ,  $\text{MW}_{\text{O}_2}$ , and  $\text{MW}_{\text{CO}_2}$  are the molecular weight of biomass  $i$ , steam,  $\text{O}_2$  and  $\text{CO}_2$ , respectively.  $F_m^p$  is the mass production rate of product  $p$ , and  $Q^T$  is the minimum heat required to maintain the gasification temperature at  $T$  without supplying excess oxidants.  $g$ ,  $h$ , and  $j$  are the numbers of moles of steam,  $\text{O}_2$ , and  $\text{CO}_2$ , respectively, per mole of biomass required for the gasification process.

Note that annualized capital and operating costs are omitted from eq 47. In this work, the proposed model was optimized based on the objective function in eq 47 using commercial optimization software (LINGO, version 10.0, with Global Solver) to evaluate the equilibrium composition of syngas, optimum operating temperature, and type and amount of oxidants required, based on the syngas requirements of processes to convert syngas into final products (e.g., biofuel, methanol). The thermodynamic equilibrium model and the process synthesis model were solved simultaneously as a single, unified superstructure model, instead of sequentially. As a result, the syngas allocated to each synthesis process meets the  $\text{H}_2/\text{CO}$  requirement of syngas, which sets as constraints in the model. The generic nonlinear program described here can have up to 70 variables and 70 constraints, based on the specific case study. Two case studies were solved to illustrate the proposed approach.

## 6. CASE STUDIES

Biomass gasification is recognized as a potential option for the initial processing of biomass in an integrated biorefinery that produces value-added products (e.g., biofuels, biochemicals), as well as heat and power. As mentioned previously, the syngas composition is crucial for its further use in an integrated biorefinery to produce various products through synthesis processes (Table 4). Figure 1 shows the superstructure representation of a gasification-based integrated biorefinery. As shown, syngas can be converted into various products, such as dimethyl ether (DME), Fischer–Tropsch fuel (FT fuel), mixed alcohol (Mix-OH), and methanol. With the proposed optimization model, a conceptual design for an integrated biorefinery that uses syngas as an intermediate can be synthesized. In addition, with the modular modeling and optimization approach using white- and black-box process models, the proposed model is able to determine the optimum operating parameters (e.g., temperature, type and amount of oxidant) of the biomass gasification to produce syngas that fulfills the requirements of the downstream processes.

**6.1. Case Study 1: Synthesis of Gasification-Based Integrated Biorefinery with Optimum Product Portfolio.** In this



Table 4. Conversion and Cost Data for Integrated Biorefinery Products

biorefinery conversion technology	H <sub>2</sub> /CO requirement		conversion		product <i>p</i>	price (\$US/kg)
	$X_{\text{lower}}^p$	$X_{\text{upper}}^p$	$Y^p$	$Y_m^p$		
methanol synthesis	3	3	0.99	32	methanol	0.1000
mixed-alcohol synthesis	1	3	0.30	18.5	mixed-alcohol fuel	0.6235
FT fuel synthesis	1.7 (iron catalyst)	1.7	0.80	14.14	FT crude oil	0.5086
	2.4 (cobalt catalyst)	2.4				
DME synthesis	2	2	0.90	23	DME fuel	0.3904

Table 5. Prices of Raw Materials

raw material	price
O <sub>2</sub> ( <i>h</i> )	0.210 \$US/kg
steam ( <i>g</i> )	0.008 \$US/kg
CO <sub>2</sub> ( <i>j</i> )	0.010 \$US/kg
biomass (wood waste)	0.005 \$US/kg
syngas from SMR	1.485 \$US/kg of CO <sup>a</sup>
heat ( $H^{\text{heat}}$ )	0.01668 \$US/MJ

<sup>a</sup> 41.58 \$US/kmol of corresponding CO.

case study, the feedstock to an integrated biorefinery is given as 1 t/h of wood waste (CH<sub>1.44</sub>O<sub>0.66</sub>) with 7% moisture (MW<sub>wood waste</sub> = 24,  $e = 0.10$ ,  $\alpha = 1$ ,  $\beta = 0.72$ ). The equivalent molar flow rate (kmol/h) of wood waste is

$$w_{\text{wood waste}} = 38.75 \quad (48)$$

First, the wood waste is gasified under pressurized conditions. According to Larson et al.,<sup>68</sup> pressurized biomass gasification can be performed at a pressure of up to 36 bar to minimize the additional compression requirement to transfer the produced syngas to the downstream synthesis processes, where methanol synthesis, FT crude synthesis, DME synthesis, and mixed-alcohol synthesis are performed at approximately 40, 30, 66, and 110 bar, respectively.<sup>68</sup> Another advantage of a pressurized gasification system is to produce useful power through gas expansion when excess or unconverted syngas is available. Thus, in this case study, the gasifier is set to operate at a pressure of 36 atm in the white-box biomass gasification model (eq 49), and the gasification temperature is set in the conventional range of 1200–1500 K (eq 50)

$$P = 36 \text{ atm} \quad (49)$$

$$1200 \text{ K} < T < 1500 \text{ K} \quad (50)$$

As carbon deposition ( $n_7$ ) is not desired in an efficient gasification process, the proposed model ensures that wood waste is fully gasified through the condition

$$n_7 = 0 \quad (51)$$

The proposed model (eqs 2–5, 7–18, 24–31, and 39–51) was solved with the optimization objective given by eq 52 using the data presented in Tables 4 and 5.

$$\text{maximize EP} \quad (52)$$

The optimized results are summarized in Table 6. Figure 2 shows the simplified flowsheet of an integrated biorefinery. As

Table 6. Optimized Results for Case Study 1

Optimized Integrated Biorefinery		
biomass	1000 kg/h wood waste at 7 wt % moisture	
product(s)	dimethyl ether (DME)	
H <sub>2</sub> /CO requirement	2.0	
production rate	604.29 kg/h	
economic potential	43.77 \$US/h	
gasification parameter	optimized value	
<i>P</i> (atm)	36	
<i>T</i> (K)	1200	
optimum oxidant	steam	
steam-to-biomass ratio (w/w)	0.33	
additional external heating required (MJ/ton of wood waste)	4011.51	
dry syngas production rate (ton/ton of biomass)	1.17	
dry syngas composition	molar flow rate (kmol/h)	mol % (dry)
H <sub>2</sub>	28.90	42.72
CO	26.36	38.96
CO <sub>2</sub>	6.25	9.24
CH <sub>4</sub>	6.14	9.08
fresh syngas from SMR	molar flow rate (kmol/h)	mol %
H <sub>2</sub>	29.49	91.24
CO	2.83	8.76
overall syngas specification supplied to DME synthesis ratio (specification)		
H <sub>2</sub> /CO (mol/mol)	58.39/29.19 (~2)	

shown, wood waste is first gasified using ultra-high-temperature steam at 1200 K. The optimum steam-to-biomass ratio (w/w) is located at 0.33, which is within the reasonable range stated in the literature (e.g., Franco et al.<sup>69</sup>). In addition, the amount of additional energy needed for gasification at 1200 K is determined as 4011.51 MJ/h. Note that the EP of this case study is targeted as 43.77 \$US/h per tonne of wood waste, and 604.29 kg/h of DME is produced.

Wood waste is reported to have a heating value of approximately 15000 MJ/t, and the amount of energy required for the gasification process is approximately 27% of the total heat content in the feedstock.<sup>70</sup> Thus, it is noted that further optimization and energy integration during the detailed design

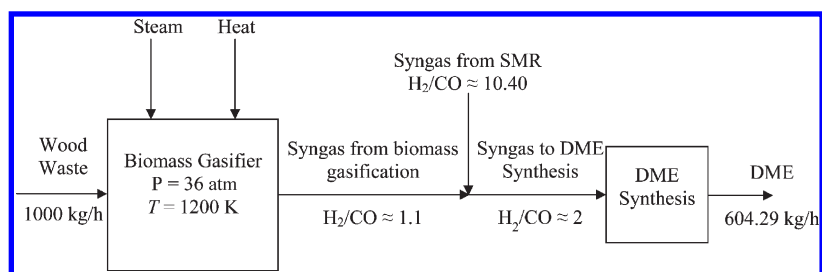


Figure 2. Simplified integrated biorefinery flowsheet for case study 1.

Table 7. Optimized Results for Case Study 2

Optimized Integrated Biorefinery			
biomass	600 kg/h wood waste at 7 wt % moisture, 400 kg/h EFB at 10 wt % moisture		
product(s)	methanol, dimethyl ether (DME)		
H <sub>2</sub> /CO requirement	3.0 and 2.0		
production rate	100 kg/h methanol, 564.10 kg/h DME		
economic potential	15.40 \$/US/h		
gasification parameter		optimized value	
P (atm)		36	
T (K)		1200	
optimum oxidant		steam	
steam-to-biomass ratio (w/w)		0.36	
additional external heating (MJ/ton of biomass)		3863.53	
dry syngas production rate (ton/ton of biomass)		1.19	
dry syngas composition	syngas to methanol synthesis (kmol/h)	syngas to DME synthesis (kmol/h)	mol % (dry)
H <sub>2</sub>	2.61	25.59	41.65
CO	2.50	24.47	39.86
CO <sub>2</sub>	0.61	5.95	9.69
CH <sub>4</sub>	0.54	5.31	8.64
fresh syngas from SMR	syngas to methanol synthesis (kmol/h)	syngas to DME synthesis (kmol/h)	mol %
H <sub>2</sub>	6.86	28.91	91.24
CO	0.66	2.78	8.76
ratio (specification)			
overall syngas specification	methanol synthesis	DME synthesis	
H <sub>2</sub> /CO (mol/mol)	9.47/3.16 (~3)	54.50/27.25 (~2)	

phase can be performed to minimize the net energy consumption of the overall integrated biorefinery. As shown in Table 6, the total syngas produced from wood waste gasification is at the rate of 1.17 t/t of biomass. Based on the syngas composition (in Table 6), the H<sub>2</sub>/CO ratio is approximately 1.10 (= 28.90/26.36). Following the requirements on the H<sub>2</sub>/CO ratio (Table 4), it is noted that the produced syngas does not meet the required ratio for DME. Thus, additional fresh syngas from steam methane reforming (SMR) with a high H<sub>2</sub>/CO ratio of 10.40 (CO and H<sub>2</sub> molar fractions,  $\phi$ , of 0.09 and 0.91, respectively) is required to be supplied to the syngas network. Based on the optimized results, 29.48 kmol/h of hydrogen, with

the corresponding CO flow rate of 2.83 kmol/h, from SMR is required to improve the overall syngas specification to a H<sub>2</sub>/CO ratio of 2. The model for case study 1 has a total of 60 variables and 58 constraints.

**6.2. Case Study 2: Synthesis of a Gasification-Based Integrated Biorefinery with Multiple Feedstocks and Products.** In this case study, the proposed model is revised for synthesis of gasification-based integrated biorefinery with multiple feedstocks and products. In the case with multiple feedstocks, eqs 2–5 are revised as follows

C atomic balance

$$\sum_i w_i a_i + j = n_2 + n_3 + n_5 + n_7 \quad (53)$$

H atomic balance

$$\sum_i w_i b_i + \sum_i w_i 2e_i + 2g = 2n_1 + 2n_4 + 4n_5 \quad (54)$$

O atomic balance

$$\sum_i w_i c_i + \sum_i w_i e_i + g + 2h + 2j = n_2 + 2n_3 + n_4 \quad (55)$$

N atomic balance

$$\sum_i w_i d_i + (79/21)h = n_6 \quad (56)$$

where  $i$  represents the types of biomass available as feedstocks in the integrated biorefinery.

For the enthalpy balance section of the biomass gasification model, the equations to determine the heat of formation of biomass (eqs 16 and 17) are also revised as follows

$$H_{f, \text{biomass}}^\circ = \alpha H_{f, \text{CO}_2}^\circ + \beta H_{f, \text{H}_2\text{O}}^\circ - \left( \text{HHV} \sum_i \gamma_i \text{MW}_i \right) \quad (57)$$

$$\begin{aligned} \text{HHV} = & -1.3675 + 0.3137 \sum_i \gamma_i (\text{C}\%)_i \\ & + 0.7009 \sum_i \gamma_i (\text{H}\%)_i + 0.0318 \sum_i \gamma_i (\text{O}\%)_i \end{aligned} \quad (58)$$

where  $\gamma_i$  is the mixing ratio of multiple types of biomass  $i$ .

In this hypothetical case study, two feedstocks [i.e., wood waste and empty fruit bunches (EFB) from palm oil processing] are available at different quantities to the integrated biorefinery. It is assumed that the available amounts of wood waste ( $w_{\text{wood waste}}$ )

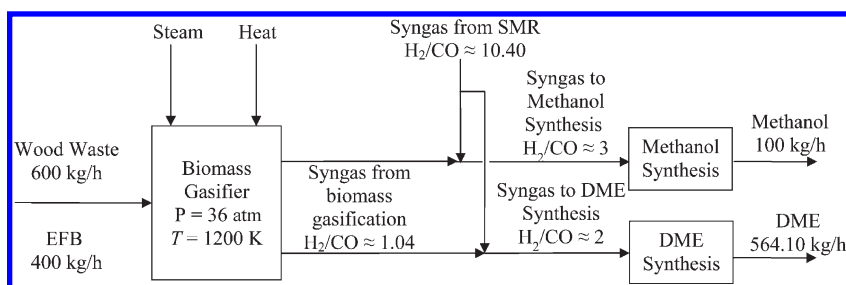


Figure 3. Simplified integrated biorefinery flowsheet for case study 2.

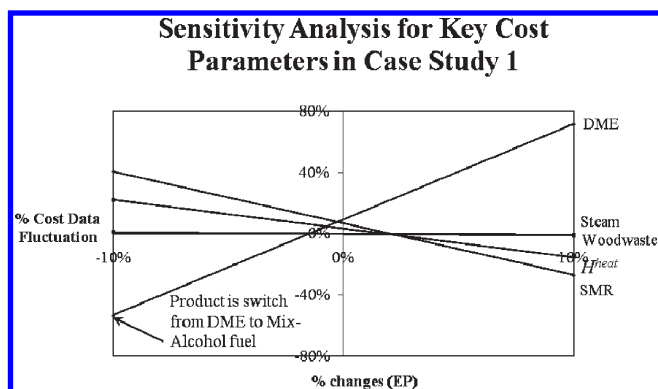


Figure 4. Sensitivity analysis of key cost parameters for case study 1.

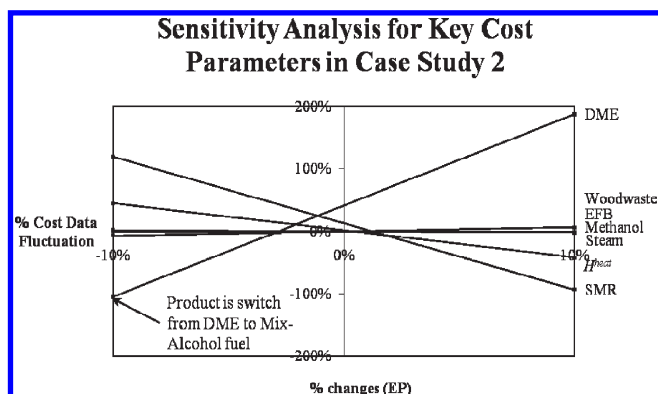


Figure 5. Sensitivity analysis of key cost parameters for case study 2.

and EFB ( $w_{\text{EFB}}$ ) are 600 kg/h (23.26 kmol/h) and 800 kg/h (32.31 kmol/h), respectively. In addition, the maximum capacity of the integrated biorefinery is 1000 kg of biomass per hour. It is further assumed that the minimum requirement of methanol is given as 100 kg/h (eq S9)

$$F_{\text{m}}^{\text{methanol}} \geq 100 \text{ kg/h} \quad (\text{S9})$$

Other than methanol, the other final products, such as DME, FT fuel and mixed alcohol, are also taken into consideration. In this case study, the optimization objective is to maximize EP. Therefore, the most beneficial product (high EP) is selected first to fulfill the minimum demand. The proposed model was solved subject to the additional constraint (eq S9), and the optimized results are summarized in Table 7 and shown in Figure 3.

Table 8. Sensitivity Analysis for Case Study 1

cost parameter	economic potential (EP)		
	−10%	base case	+10%
DME	−48.45%	43.77 \$US/h	+71.67%
$H^{\text{heat}}$	+22.15%		−15.29%
syngas from SMR	+40.67%		−26.93%
steam	0.62%		−0.62%
wood waste	+1.06%		−1.06%

Table 9. Sensitivity Analysis for Case Study 2

cost parameter	economic potential (EP)		
	−10%	base case	+10%
methanol	−6.50%	15.39 \$US/h	+6.50%
DME	−104.67%		187.78%
$H^{\text{heat}}$	+44.74%		−41.87%
syngas from SMR	+119.66%		−92.96%
steam	+1.88%		−1.88%
wood waste	+1.81%		−1.81%
EFB	+1.04%		−1.04%

The maximum EP of this case is targeted as 15.40 \$US/h. As shown in Figure 3, all available wood waste (600 kg/h) is selected as the feedstock of the synthesized integrated biorefinery. Meanwhile, an additional 400 kg/h of EFB is supplied to the gasification process to produce syngas. As shown in Table 7, the optimum steam-to-biomass ratio (w/w) is 0.36, 3863.53 MJ/h of additional heating is required to gasify the biomass at 1200 K, and 1.19 t of dry syngas is produced per tonne of the biomass. Moreover, based on the equilibrium model, the composition of the produced syngas was determined and is listed in Table 7. As shown, the  $\text{H}_2/\text{CO}$  ratio of the syngas is approximately 1.05 (= 41.65/39.86), which is a typical ratio for biomass gasification. Note that this quality of syngas does not meet the downstream requirements for methanol and DME synthesis, with  $\text{H}_2/\text{CO}$  requirements of 2 and 3, respectively. Therefore, additional fresh syngas from SMR with a  $\text{H}_2/\text{CO}$  ratio of 10.40 ( $\text{CO}$  and  $\text{H}_2$  molar fractions,  $\phi$ , of 0.09 and 0.91, respectively) is required to adjust the biomass syngas composition to meet the downstream requirements. Based on the optimized result, 9.3 mol % of the syngas produced from biomass gasification is allocated to methanol synthesis, and the remainder is allocated to DME synthesis. Note also that the syngas from biomass gasification that is allocated to both methanol and DME syntheses requires

**Table 10. Optimized Results for Case Study 1 with a 10% Drop in Price of DME**

Optimized Integrated Biorefinery		
biomass	1000 kg/h wood waste at 7 wt % moisture	
product(s)	mixed-alcohol fuel	
H <sub>2</sub> /CO requirement	1.0–3.0	
production rate	177.56 kg/h mixed-alcohol fuel	
economic potential	22.56 \$US/h	
gasification parameter	optimized value	
P (atm)	36	
T (K)	1293	
optimum oxidant	steam	
steam-to-biomass ratio (w/w)	0.25	
additional external heating required (MJ/ton of wood waste)	4894.08	
dry syngas production rate (ton/ton of biomass)	1.15	
dry syngas composition	molar flow rate (kmol/h)	mol % (dry)
H <sub>2</sub>	31.99	45.22
CO	31.99	45.22
CO <sub>2</sub>	4.81	3.95
CH <sub>4</sub>	3.96	5.60
fresh syngas from SMR	molar flow rate (kmol/h)	mol %
H <sub>2</sub>	—	91.24
CO	—	8.76
overall syngas specification supplied to DME synthesis	ratio (specification)	
H <sub>2</sub> /CO (mol/mol)	31.99/31.99 (~1)	

additional syngas from SMR to improve its H<sub>2</sub>/CO ratio. As shown in Table 7, 6.86 kmol/h of H<sub>2</sub> (with the corresponding CO flow rate of 0.66 kmol/h) from SMR is fed to methanol synthesis to achieve a H<sub>2</sub>/CO ratio of 3, and 28.91 kmol/h of H<sub>2</sub> (with the corresponding CO flow rate of 2.78 kmol/h) is fed to DME synthesis. Note that, in this process, two final products (i.e., methanol and DME) are generated from wood waste and EFB, where methanol and DME are the primary product and the byproduct, respectively. The model for case study 2 has a total of 71 variables and 71 constraints.

## 7. SENSITIVITY ANALYSIS OF KEY PARAMETERS

A sensitivity analysis was performed to evaluate each case study more comprehensively and to determine the changes in the economic potential (EP) caused by fluctuations in the basic cost and price data for products, biomasses, energy, and syngas from SMR at a rate of  $\pm 10\%$  from the base case (case studies 1 and 2). The results of the sensitivity analysis for the two case studies are shown in Figures 4 and 5, respectively, as well as Tables 8 and 9, respectively.

**7.1. Sensitivity Analysis for Case Study 1.** Based on Figure 4 and Table 8, it is noted that the cost datum with the greatest impact on the overall feasibility of the synthesized integrated biorefinery is the price of DME. As shown in Figure 4 and Table 8, a 10% increase in the DME price increases the EP by 71.67%, assuming that the rest of the cost parameters remain

**Table 11. Optimized Results for Case Study 2 with a 10% Drop in Price of DME**

Optimized Integrated Biorefinery			
biomass	235.65 kg/h wood waste at 7 wt % moisture, 764.35 kg/h EFB at 10 wt % moisture.		
product(s)	methanol, mixed-alcohol fuel		
H <sub>2</sub> /CO requirement	3.0 and 1.0–3.0		
production rate	100 kg/h methanol, 138.85 kg/h mixed-alcohol fuel		
economic potential	−0.73 \$US/h		
gasification parameters	optimized parameters		
P (atm)	36		
T (K)	1200		
optimum oxidant	steam		
steam-to-biomass ratio (mol/mol)	0.38		
additional external heating (MJ/ton of biomass)	3726.71		
dry syngas production rate (ton/ton of biomass)	1.21		
dry syngas composition	syngas to methanol synthesis (kmol/h)	syngas to mixed-alcohol synthesis (kmol/h)	mol % (dry)
H <sub>2</sub>	2.48	25.02	40.80
CO	2.48	25.02	40.80
CO <sub>2</sub>	0.62	6.21	10.13
CH <sub>4</sub>	0.50	5.08	8.28
fresh syngas from SMR	syngas to methanol synthesis (kmol/h)	syngas to mixed-alcohol synthesis (kmol/h)	mol %
H <sub>2</sub>	6.98	—	91.24
CO	0.67	—	8.76
overall syngas specification	ratio (specification)		
	methanol synthesis	DME synthesis	
H <sub>2</sub> /CO (mol/mol)	9.46/3.0 (~3.15)	25.02/25.02 (~1)	

constant. In addition, it is noted that the price of syngas from SMR, which is directly proportional to the price of natural gas, also has a significant impact on the overall EP, as syngas from SMR is required to improve the quality of the biomass syngas for the synthesis of DME. Note that a 10% increase in the syngas price reduces the overall EP by 26.93%. On the other hand, the prices of steam and wood waste have the least effect on the overall EP. However, if the price of DME decreased by 10%, the product portfolio would change to produce mixed-alcohol fuel. The detailed optimized results are reported in Table 10. As shown, the optimum gasification temperature is 1293 K, and the optimum oxidant remains as steam. As the price of DME and mixed-alcohol fuel is highly sensitive to product allocation, a more detailed analysis is required in more advanced stages of process synthesis and design.

**7.2. Sensitivity Analysis for Case Study 2.** For case study 2, the sensitivity analysis results are presented in Table 9 and Figure 5. In this case, the prices of wood waste, EFB, methanol, and steam have minimal effects on the overall EP. However, the price of DME strongly affects the overall EP, as production of DME is crucial in offsetting the high cost of producing methanol, which requires additional syngas from SMR to improve the syngas to a high H<sub>2</sub>/CO ratio of 3. Thus, the price of syngas from SMR plays an important role in



determining the overall economic feasibility of the synthesized integrated biorefinery. It is worth mentioning that, as in case study 1, a 10% decrease in the price of DME would result in a byproduct switch from DME to mixed-alcohol fuel, as shown in Table 11. This causes the whole process to have a negative economic potential.

Thus, in the presented case studies and sensitivity analyses, the prices of DME, mixed-alcohol fuel, and syngas from SMR should be considered in detail in advanced stages of the synthesis of a gasification-based integrated biorefinery to ensure its economic feasibility once equipment costs are taken into account.

## 8. CONCLUSIONS

In this work, an optimization approach is presented based on a thermodynamic equilibrium model to find the optimum operating conditions that produce the maximum amount of syngas with the correct specifications for various end-use applications in an integrated biorefinery. The modular approach presented in this work is a useful optimization strategy for processes whose underlying mechanisms are not fully understood and for the preliminary design of a process, in this case, a gasification-based integrated biorefinery. Future work will focus on extending the tools for selecting optimum feedstocks and process pathways to produce various products in an integrated biorefinery. In addition, detailed models for other processing units can easily be added to the current model if the need arises.

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## NOMENCLATURE

### Constants

$\alpha$  = stoichiometric coefficient of CO<sub>2</sub> from complete combustion of a specific biomass  
 $\beta$  = stoichiometric coefficient of H<sub>2</sub>O from complete combustion of a specific biomass  
 $\phi_{\text{Bio}}^{\text{CO}}$  = molar fraction of CO in syngas from biomass gasification  
 $\phi_{\text{Bio}}^{\text{H}_2}$  = molar fraction of H<sub>2</sub> in syngas from biomass gasification  
 $\phi_{\text{SMR}}^{\text{CO}}$  = molar fraction of CO in syngas from SMR  
 $\phi_{\text{SMR}}^{\text{H}_2}$  = molar fraction of H<sub>2</sub> in syngas from SMR  
 $a$  = number of C atoms per mole of biomass  
 $\text{ash\%}$  = weight percentage of ash in a specific biomass  
 $b$  = number of H atoms per mole of biomass  
 $c$  = number of O atoms per mole of biomass  
 $C\%$  = weight percentage of C in a specific biomass  
 $C_{p,C}$  = specific heat capacity of C, cal/(mol·K)  
 $C_{p,\text{CH}_4}$  = specific heat capacity of CH<sub>4</sub>, cal/(mol·K)  
 $C_{p,\text{CO}}$  = specific heat capacity of CO, cal/(mol·K)  
 $C_{p,\text{CO}_2}$  = specific heat capacity of CO<sub>2</sub>, cal/(mol·K)  
 $C_{p,\text{H}_2}$  = specific heat capacity of H<sub>2</sub>, cal/(mol·K)  
 $C_{p,\text{H}_2\text{O(g)}}$  = specific heat capacity of H<sub>2</sub>O(g), cal/(mol·K)  
 $C_{p,\text{N}_2}$  = specific heat capacity of N<sub>2</sub>, cal/(mol·K)

$d$  = number of N atoms per mole of biomass  
 $e$  = number of moles of water (moisture content) per mole of biomass  
 $H\%$  = weight percentage of H in a specific biomass  
 $H^{\text{Cr}}$  = total enthalpy of char at temperature  $T$  (kJ/mol, MJ/kmol)  
 $H^{\text{PG}}$  = total enthalpy of product gases at temperature  $T$  (kJ/mol, MJ/kmol)  
 $H^{\text{RMs}}$  = total enthalpy of raw materials at standard condition (1 atm, 298 K)  
 $H_{f,C}^{\circ}$  = standard heat of formation of C at 298 K (kJ/mol, MJ/kmol)  
 $H_{f,\text{CH}_4}^{\circ}$  = standard heat of formation of CH<sub>4</sub> at 298 K (kJ/mol, MJ/kmol)  
 $H_{f,\text{CO}}^{\circ}$  = standard heat of formation of CO at 298 K (kJ/mol, MJ/kmol)  
 $H_{f,\text{CO}_2}^{\circ}$  = standard heat of formation of CO<sub>2</sub> at 298 K (kJ/mol, MJ/kmol)  
 $H_{f,\text{H}_2}^{\circ}$  = standard heat of formation of H<sub>2</sub> at 298 K (kJ/mol, MJ/kmol)  
 $H_{f,\text{H}_2\text{O(g)}}^{\circ}$  = standard heat of formation of steam, H<sub>2</sub>O(g), at 298 K (kJ/mol, MJ/kmol)  
 $H_{f,\text{H}_2\text{O(l)}}^{\circ}$  = standard heat of formation of H<sub>2</sub>O(l) of biomass at 298 K (kJ/mol, MJ/kmol)  
 $H_{f,i}^{\circ}$  = standard heat of formation of biomass  $i$  at 298 K (kJ/mol, MJ/kmol)  
 $H_{f,\text{O}_2}^{\circ}$  = standard heat of formation of O<sub>2</sub> at 298 K (kJ/mol, MJ/kmol)  
 $H_{f,\text{N}_2}^{\circ}$  = standard heat of formation of N<sub>2</sub> at 298 K (kJ/mol, MJ/kmol)  
 $\text{HHV}$  = higher heating value of biomass, kJ/g  
 $i$  = component  $i$  in the biomass gasification product, syngas  
 $\text{MW}_i$  = molecular weight of a specific biomass component  $i$   
 $\text{O}\%$  = weight percentage of O and elements other than C, H, and ash in a specific biomass  
 $T^{\circ}$  = standard temperature, 25 °C (298 K)  
 $T^{\text{max}}$  = maximum gasification temperature, K  
 $T^{\text{supply}}$  = steam supply temperature for steam gasification, K  
 $P$  = operating pressure of the gasifier, atm  
 $P^{\text{CO}_2}$  = price per unit mass of CO<sub>2</sub>, \$US/kg  
 $P^{\text{H}_2\text{O}}$  = price per unit mass of steam, \$US/kg  
 $P^i$  = price per unit mass of biomass  $i$ , \$US/kg  
 $P^{\text{O}_2}$  = price per unit mass of O<sub>2</sub>, \$US/kg  
 $P^p$  = price per unit mass of product  $p$ , \$US/kg  
 $P^Q$  = price per unit heat input, \$US/MJ  
 $P^{\text{SMR}}$  = price per unit molar flow rate of syngas (corresponding CO molar flow rate), \$US/kg  
 $q$  = number of product components,  $y$ , in an equilibrium reaction for eqs 19–23  
 $r$  = number of reactant components,  $z$ , in an equilibrium reaction for eqs 19–23  
 $\nu_y$  = stoichiometric coefficient of component  $y$  in a closed system  
 $\nu_z$  = stoichiometric coefficient of component  $z$  in a closed system  
 $X_{\text{upper}}^p$  = upper limit of H<sub>2</sub>/CO specification required for the different synthesis processes to produce products  $p$   
 $X_{\text{lower}}^p$  = lower limit of H<sub>2</sub>/CO specification required for the different synthesis processes to produce products  $p$   
 $y$  = product component in an equilibrium reaction for eqs 19–23  
 $Y^p$  = molar CO conversion factor  
 $Y_m^p$  = molar to mass conversion factor for product  $p$   
 $z$  = reactant component in an equilibrium reaction for eqs 19–23

## Variables

- $\gamma_i$  = mixing ratio of multiple biomass  $i$   
 EP = economic potential (i.e., the profit excluding the capital costs and operating and maintenance costs), \$/US/h  
 $f(n_i)$  = optimization objective in the function of syngas components  $n_i$   
 $F_m^p$  = mass production rate of product  $p$ , kg/h  
 $F^p$  = molar production rate of product  $p$ , kmol/h  
 $g$  = number of moles of steam per mole of biomass for biomass gasification using steam  
 $h$  = number of moles of  $O_2$  per mole of biomass for biomass gasification using  $O_2$ /air  
 $Q^T$  = minimum heat required to maintain the gasification temperature at  $T$  without supplying excess oxidants, MJ  
 $j$  = number of moles of  $CO_2$  per mole of biomass for biomass gasification using  $CO_2$   
 $K_{20}$  = equilibrium constant of the gasification reaction as represented by eq 20  
 $K_{21}$  = equilibrium constant of the gasification reaction as represented by eq 21  
 $K_{22}$  = equilibrium constant of the gasification reaction as represented by eq 22  
 $k_{CH_4}$  = thermodynamic equilibrium constant for the formation reaction of the  $CH_4$   
 $k_{CO}$  = thermodynamic equilibrium constant for the formation reaction of the CO  
 $k_{CO_2}$  = thermodynamic equilibrium constant for the formation reaction of the  $CO_2$   
 $K_{eqn}$  = equilibrium constant of the gasification reaction as represented by eqs 19–23  
 $k_{H_2O}$  = thermodynamic equilibrium constant for the formation reaction of the  $H_2O(g)$   
 $k_{prod}$  = thermodynamic equilibrium constant for the formation reaction of the products in an equilibrium reaction  
 $k_{reac}$  = thermodynamic equilibrium constant for the formation reaction of the reactants in an equilibrium reaction  
 $n_1$  = stoichiometric coefficient of  $H_2$  in the gasification product, syngas  
 $n_2$  = stoichiometric coefficient of CO in the gasification product, syngas  
 $n_3$  = stoichiometric coefficient of  $CO_2$  in the gasification product, syngas  
 $n_4$  = stoichiometric coefficient of  $H_2O(g)$  in the gasification product, syngas  
 $n_5$  = stoichiometric coefficient of  $CH_4$  in the gasification product, syngas  
 $n_6$  = stoichiometric coefficient of  $N_2$  in the gasification product, syngas  
 $n_7$  = stoichiometric coefficient of C in the gasification product, syngas  
 $n_{SMR}$  = total molar flow rate of syngas from steam methane reforming (SMR) required, kmol/h  
 $n_T$  = total molar flow rate of all components in the gasification product, syngas, kmol/h  
 $n_{Bio}^p$  = distribution of gasification product, syngas, to various synthesis processes to produce product  $p$   
 $n_{SMR}^p$  = distribution of syngas from SMR to various synthesis processes to produce product  $p$   
 $(\bar{n}\bar{C}_p)$  = mean heat capacity flow rate of gaseous products  
 $T$  = optimum gasification temperature, K  
 $x_u$  = molar fraction of component  $u$  in the gasification product, syngas

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