Development of a modified equilibrium model for biomass pilot-scale fluidized bed gasifier performance predictions

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Abstract

The objective of this work is to develop a thermodynamic model considering non-stoichiometric restrictions. The model validation was done from experimental works using a bench-scale fluidized bed gasifier with wood chips, dairy manure, and sorghum. The model was used for a further parametric study to predict the performance of a pilot-scale fluidized biomass gasifier. The Gibbs free energy minimization was applied to the modified equilibrium model considering a heat loss to the surroundings, carbon efficiency, and two non-equilibrium factors based on empirical correlations of ER and gasification temperature. The model was in a good agreement with $RMS < 4$ for the produced gas. The parametric study ranges were $0.01 < ER < 0.99$ and $500\text{ }^{\circ}\text{C} < T < 900\text{ }^{\circ}\text{C}$ to predict syngas concentrations and its LHV (lower heating value) for the optimization. Higher aromatics in tar were contained in WC gasification compared to manure gasification. A wood gasification tar simulation was produced to predict the amount of tars at specific conditions. The operating conditions for the highest quality syngas were reconciled experimentally with three biomass wastes using a fluidized bed gasifier. The thermodynamic model was used to predict the gasification performance at conditions beyond the actual operation.

Keywords

Fluidized bed gasification; Non-equilibrium model; Experimental validation; Thermodynamic; Tar compositions;

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1. Introduction

In recent decades, biomass has recently created attention as an alternative energy source to replace the use of fossil fuels and compensate for increasing energy consumption. On a daily or yearly basis, tons of lignocellulosic biomass, municipal solid waste (MSW), and human/livestock wastes are produced and processed at high cost. Even though many commercial technologies handle the wastes, a great deal of wastes are still buried underground or burned, especially in many underdeveloped or developing countries. The abundant biomass energy resources could be converted into different forms of useful products through various commercial technologies. A strong candidate for handling the mass production of biomass wastes could be a gasification technology, one of the thermochemical conversion processes [1].

After Zainal et al. [2] proposed a Gibbs free energy minimization model, many mathematical models for gasification processes have recently been developed based on chemical equilibrium [3-11]. However, thermodynamic equilibrium calculations are independent of the gasifier type, and the model is more suitable for process studies on the influence of the fuels and process parameters [12]. Some drawbacks present in the equilibrium models are: the impossibility to consider char, the formation of tar, the underestimation of CH_4 , the overestimation of H_2 and product yield. In order to avoid these inaccuracies, authors introduced correction factors based on non-equilibrium phenomena from actual experiments. Li et al. [13] developed a correction system for an equilibrium model that described the amount of carbon and hydrogen which bypassed the equilibrium reactions in coal gasification in a fluidized bed. A similar correction system was introduced by Damiani et al. [14]. Some of basic modifications which were used by other researchers are consideration of the carbon conversion and tar formation [15]. Barman et al. [16] validated an equilibrium model based on a consideration of a tar yield of 4.5% from the experimental results. Many modified models were developed to understand the effect of parameters on the final product compositions as follows: Antonopoulos et al. [17] developed a non-stoichiometric equilibrium model using an enthalpy change term (ΔH) included in the energy balance equation. The gasification temperature was manually changed until the ΔH reached zero, and the output parameters were calculated based on the predicted temperature at a

constant $ER=0.45$. Doherty et al. [18] developed an ASPEN Plus® model based on a Gibbs free energy minimization to create a sensitivity analysis of a circulating fluidized bed biomass gasifier. Due to the sequential modular approach of the program, stream thermodynamic conditions and mass flow rates were required in each process. Two unit operation blocks were examined for heterogeneous and homogeneous reactions for gasification reaction simulation. Imorb et al. [19] also made a parametric study of a rice straw gasification system using two different gasifying agents, steam-air and steam- CO_2 , and the model was developed using Aspen Plus based on the Fischer-Tropsch method. Schuster et al. [20] performed an extensive parametric study with operating conditions of temperature, fuel composition, and amount of fluidizing agent on a dual fluidized-bed steam gasifier. An equilibrium determination was calculated from three partial mass balances (C, H and O) and three equations for the chemical equilibrium of three independent reactions considering a restriction on the model, showing that the unconverted carbon increases when the temperature decreases. Ściążko and Stępień [21] formulated a modified Gibbs energy minimization model by introducing experimental concentrations of carbon monoxide and carbon dioxide to build a regression model, and found an exponential correction function that depended only on temperature. The resultant factor was multiplied by the Boudouard reaction equilibrium constant and a water-gas shift equilibrium correction factor of 2. The actual coal gasification experiments were also done using a circulating fluid bed reactor.

Developing new technologies would be difficult and costly without a prior modelling and simulation of the process. Many modeling tools can be used such as the stoichiometric model (the simplest method), the equilibrium model (more complicated method), and kinetic and CFD models (the most advanced and effective methods) [21]. Although several different gasification designs have been proposed based on experimental data, most models still have a limitation in predicting the syngas compositions at the out-of-range boundaries because of non-linear thermodynamic reaction behaviors. Zainal et al. [22] investigated the relationship between ER and reduction temperature using woodchip gasification in a downdraft gasifier. The relationship was linear and close to the theoretical gasification ($ER = 0.19-0.43$) obtained from a stoichiometric balance. Pinto et al. [23] conducted a steam gasification experiment using a pilot-scale reactor with different feedstocks of coal, pine wood, and polyethylene (PE) waste (main plastic present in MSW). Their optimum coal mixed ratio for co-gasification was 20% (w/w) of

pine and 20% (w/w) of PE wastes at 900 °C. Sheth and Babu [24] tested sesame and rose wood in a downdraft gasifier to find the optimum ER of 0.21 to reach a calorific value of 6.3 MJ/Nm³ of producer gas. Sharma [25] studied temperature profile, pressure drop, and gas composition across a reactor in both firing and non-firing mode. Ratnadhariya and Channiwala [26] tested woody biomass materials to study the distribution of CO/CO₂ and CO/H₂ ratios along the length of the gasifier. Then they developed a correlation using an Arrhenius equation to predict the molar distributions of each gas. The average absolute error was between 9.0 and 9.5% of the CO/CO₂ ratio and between 5.7 and 9.0% of the CO/H₂ ratio.

The overall goal of the present work is to develop a user friendly program coupled with a modified thermodynamic equilibrium model using EES (engineering equation solver) so that any gasification users with the program can predict the gas compositions with known operating variables. The modification of a model by using constant factors was based on the actual experimental gasification work using bench-scale and pilot-scale bubbling fluidized bed gasifiers at Texas A&M University (TAMU).

In this paper,

- a) Experimental data was obtained from both bench-scale and pilot-scale reactors in order to achieve suitable correspondence to the actual system.
- b) An equilibrium model was developed based on three modification factors based on the actual experimental results.
- c) The effects of gasification parameters (ER, temperature and fuel) were investigated to improve the reaction operation to find an optimized condition for syngas quality.
- d) A simple and rigorous model was implemented for predicting the gasification performance of a bubbling fluidized bed gasifier.

2. Experimental

The experimental data for high tonnage sorghum (HTS) and dairy manure (DM) was imported from Maglinao Jr. et al [27] and Nam et al. [28]. Woodchip (WC) gasification was conducted for this work.

2.1 Sample preparation and characterization

HTS was introduced in a pilot-scale fluidized bed gasification system while WC and DM were utilized in a bench-scale fluidized bed gasification system. High-tonnage sorghum was planted and harvested at the Texas Agrilife farm in Burleson, Texas [27]. The HTS was an ES 5150 variety composed of low lignin content. The feedstock was shredded to an average particle size of less than 10 mm. The dairy manure was collected directly from an open pit at the Dairy Center at Tarleton State University in Stephenville, Texas [28]. The biomass wastes were initially air-dried. Then, only the dairy manure was further dried to reduce the moisture content enough to remove the sand bedding which was used at the dairy farm. A detailed sand removal study with manure from the Sierra Dairy in Texas was investigated [29]. The DM and WC were further milled through a 2 mm sieve using Wiley Laboratory Mill model #4 in order to be fed into a bench-scale gasifier. The characteristics of the three biomass samples were analyzed for their high heating value (HHV) using a Parr bomb calorimeter, a proximate analysis in accordance with ASTM standard E1775, ASTM D3175, and ASTM E871, and an ultimate analysis using a Vario MICRO Elemental analyzer.

The characteristics of biomass wastes used for the experimental gasification process are shown in Table 1. The HHV of the dry basis of the processed manure at 12.3 MJ/kg is comparable to the HHV of energy sorghum at 19.6 MJ/kg and its woodchip at 17.5 MJ/kg. The large difference in the HHV can be explained by the ash and carbon content. The carbon and ash contents were determined to be 33% and 36% for DM, and 46% and 16% for WC, while the HTS showed 42% carbon and 14% ash. The chemical composition can be expressed as $C_{3.52}H_{5.74}N_{0.02}O_{2.33}S_{0.002}$ for HTS, $C_{4.07}H_{6.6}N_{0.01}O_{2.79}S_{0.003}$ for the WC, and $C_{2.7}H_{2.5}N_{0.3}O_{1.53}S_{0.007}$ for the processed DM. This information is needed for the equivalence ratio (ER) calculations.

2.2 Experimental setup and procedure

The fluidized bed gasification experiments were conducted using dairy manure and woodchip as shown in Figure 1. A bench-scale fluidized bed reactor of 2 inches in diameter and 33 inches in length made of AISI 316 S.S was covered with an electric tube furnace. The bed material for fluidization (Mulgrain 47-10 x18, CE Minerals, Andersonville, GA) was used after being sieved

with -20 and +40 meshes consisting of 50% SiO₂ and 46.8% Al₂O₃ [30]. The syngas flow rate was measured using an orifice meter placed after the wet scrubber.

Both the bench- and pilot-scale gasifiers were first preheated to 400 °C for the initial bed fluidization at a minimum air flow velocity. Then, feedstock was inserted into the main reactor to increase its temperature. The reactor temperature was maintained only by the feedstock flow rate, in other words, of the equivalence ratio (ER). And three replicate experiments were done for each condition. The flow of cooled and cleaned gas was measured. The syngas was analyzed with a gas chromatograph (GC) with a thermal conductivity detector (TCD). The GC was calibrated using two different standard gases offered by Airgas Distribution at ± 2%. Detailed gasification reactor setups and procedures are explained in previous studies [27, 28].

An isokinetic tar sampler designed based on a report by Van de Kamp et al. [32] was located after the TAMU cyclone to capture tars in syngas. Isokinetic sampling was recognized from the equalized static pressure of interior and exterior tubes, which was immersed in the sampling outlet. Six bottles were connected to a pump with flowmeter set at 2 ml/min after a gas filter. The first three bottles with isopropanol solvent were placed in a room temperature water bath, while the next three bottles were placed in a -2 °C glycol water. The last bottle was emptied to capture possible moisture or vaporized solvent. Then the captured tar was separated from solvent using a rotor evaporator for further GC-MS analysis.

2.3 Data analysis

The stoichiometric combustion reaction can be expressed as shown in equation (1-3) using the elemental compositions. Based on the ER (equivalence ratio), for example, one kg of WC (woodchips) requires 5.97 kg of air for the stoichiometric combustion reaction. The equations of ER, LHV (lower heating value) of syngas, CGE (cold gas efficiency), and CCE (carbon conversion efficiency) for actual syngas analysis are described in Nam et al. [28].

3. Model formulation

The fluidized bed air gasification model was developed based on the non-stoichiometric equilibrium, also known as the Gibbs free energy minimization method. The actual experimental data were used to validate and modify the developed thermodynamic equilibrium model. The amount of oxygen, nitrogen, and relative humidity was considered in the composition of air used for the model.

3.1. Chemical equilibrium

First, the model was solved using eight equations based on a thermodynamic equilibrium method; gasification reaction (Eq. 4), chemical balances (Eq. 5-9) representing the molar balance for each element, and the two reaction equilibrium constants (Eq. 10) and (Eq. 11).

where: n_1, n_2, n_3, n_4 and n_5 are the molar relation C/C, H/C, O/C, N/C, and S/C respectively:

$$n_1 = 1, n_2 = \frac{x_H/M_H}{x_C/M_C}, n_3 = \frac{x_O/M_O}{x_C/M_C}, n_4 = \frac{x_N/M_N}{x_C/M_C}, n_5 = \frac{x_S/M_S}{x_C/M_C}$$

The moisture content of biomass is included in Equation 4, and is defined as:

$$MC = \frac{M_{H_2O} w_{bio}}{M_{Bio} + M_{H_2O} w_{bio}} 100\%$$

Carbon balance

$$n_1 = x_2 + x_3 + x_5 \quad (5)$$

Oxygen balance

$$n_3 + w + w_{air} + 2m = x_2 + 2x_3 + x_4 \quad (6)$$

Hydrogen balance

$$n_2 + 2(w + w_{air}) = 2x_1 + 2x_4 + 4x_5 + x_6 \quad (7)$$

Sulfur balance

$$n_5 = x_6 \quad (8)$$

Nitrogen balance

$$n_4 + \frac{r_{N_2}}{r_{O_2}} m = x_7 \quad (9)$$

According to Equation (4), there are 8 unknown variables: m , x_1 , x_2 , x_3 , x_4 , x_5 , x_6 , and x_7 with only 6 molar balance equations (Eq. 4-9), which require two more equations to find all the unknown variables. The chemical equilibrium constants from the chemical reactions (R3) of methanation and the reaction (R4) of the water gas-shift reaction can be applied. The water gas-shift reaction (R4) is a combination of the chemical reactions of the water-gas (R1) and Boudouard (R2) reactions. The chemical reactions of (R1 – R4) are most descriptive of an ideal gasification process model according to Zainal et al. [2].

The equilibrium constants for (R3) and (R4) are given as K_3 (Eq. 10) and K_4 (Eq. 11). The constants can be obtained using the Gibbs function equation (Eq. 12)

$$K_3 = \frac{p_{CH_4}}{(p_{H_2})^2} = \frac{x_{CH_4}}{(x_{H_2})^2} \left(\frac{p}{p_0} \right)^{-1} \quad (10)$$

$$K_4 = \frac{p_{CO_2} p_{H_2}}{p_{CO} p_{H_2O}} = \frac{x_{CO_2} x_{H_2}}{x_{CO} x_{H_2O}} \quad (11)$$

$$-R \cdot T \cdot \ln K = \Delta G^0 \quad (12)$$

where ΔG^0 is the Gibbs function calculated for each chemical specie i , defined as:

$$\Delta G^0 = \sum v_i g_i^0(T) \quad (13)$$

The Gibbs free energy for a singular specie has been obtained using the NASA polynomial for the data from the JANAF thermochemical tables available in the literature [33, 34] as given by:

$$\frac{g_i^0(T)}{R \cdot T} = Ag_i + Bg_i T + Cg_i T^2 + Dg_i T^3 + Eg_i T^4 + \frac{Fg_i}{T} + Gg_i \ln T \quad (14)$$

The values of constants from Ag_i to Gg_i for the i th components used can be referenced in Table 2 and Table 3 [33].

The energy balance equation was constructed assuming an adiabatic gasification process in which the bed gasification temperature changes according to the ER. Because of the adiabatic process assumption, the energy balance equation can be completed by adding the heat loss term that exists in an actual gasification process. The global energy equation is as follows:

$$\sum_{in} (h_f^0 + \Delta h(T_{in})) = \sum_{out} (h_f^0 + \Delta h(T_{gasif})) \quad (15)$$

Developing the term of enthalpies formation h_f^0 , equation (15) is disaggregated as:

$$\begin{aligned} h_{fbio}^0 + w(h_{fH_2O}^0 + h_{fH_2Og}^0) + w_{air} h_{fH_2Og}^0 + m h_{fO_2}^0 + \frac{r_{N_2}}{r_{O_2}} m h_{fN_2}^0 + \Delta h(T_{in}) = x_1 h_{fH_2}^0 \\ + x_2 h_{fCO}^0 + x_3 h_{fCO_2}^0 + x_4 h_{fH_2O}^0 + x_5 h_{fCH_4}^0 + x_5 h_{fH_2S}^0 + x_7 h_{fN_2}^0 + \Delta h(T_{gasif}) \end{aligned} \quad (16)$$

where the values of the enthalpies formation (h_f^0 , kJ/kmol) at the standard ambient temperature and pressure (298.15 K, 1 bar) are obtained from Stull et al. [35]. The sensible heat term for reactant and product gases are rearranged depending on the specific heat of the gas mixture that can be obtained from Perry et al. [36]:

$$\Delta h(T_{in}) = \Delta T_{in} \left(w_{bio} (C_{pH_2O} + C_{pH_2Og}) + w_{air} C_{pH_2Og} + m C_{pO_2} + \frac{r_{N_2}}{r_{O_2}} m C_{pN_2} \right) \quad (17)$$

$$\Delta h(T_{gasif}) = \Delta T_{gasif} \sum_{gases} x_i C_{p_i} \quad (18)$$

The specific heat for each species in the products is calculated according to the following:

$$C_{p_i} = R \cdot \left(A_{cp_i} + B_{cp_i} \cdot T_{ave} + \frac{C_{cp_i}}{3} (4 \cdot T_{ave}^2 - T_{ref} \cdot T_{gasif}) + \frac{D_{cp_i}}{T_{ref} \cdot T_{gasif}} \right) \quad (19)$$

A correlation extensively used to estimate the formation of heat for several biomass is given by Bain et al. [37]:

$$h_{fbio}^0 = (-190.3 - 1407n_2) \cdot 2.326 \cdot M_{bio} \quad (20)$$

where M_{bio} is the molar mass of biomass and the factor 2.326 is the conversion value of Btu/lbm to kJ/kg to obtain the enthalpy of the formation in kJ/kmol.

3.2. Process performance evaluation

The best performance parameters to validate the thermodynamic model for reactor operating conditions are the gasification temperature and the dimensionless variable of the ER ratio. Hence, the calculation of the equivalence ratio is as follows:

$$ER = \frac{(R_{A/F})_{real}}{(R_{A/F})_{stoich}} \quad (21)$$

where the term $(R_{A/F})_{real}$ is the actual air-fuel ratio and $(R_{A/F})_{stoich}$ is calculated as follows [38]:

$$(R_{A/F})_{stoich} = \frac{M_{O_2} + r_{N_2}/r_{O_2} M_{N_2}}{100} \left(\frac{C}{M_C} + \frac{H}{2M_{H_2}} + \frac{S}{M_S} - \frac{O_2}{M_{O_2}} \right) \quad (22)$$

where C, H, S and O are the percentages in weight of elemental species for carbon, hydrogen, sulfur and oxygen, respectively from ultimate analysis in dry-ash free basis.

The two thermodynamic parameters usually applied to evaluate the gasification performance are the syngas heating value and cold gas efficiency. The syngas heating value is determined for a dry basis shown as [39]:

$$LHV_{syn} = 4.2 \cdot (2.57Yd_{H_2} + 3Yd_{CO} + 8.54Yd_{CH_4}) \quad (23)$$

where the considered gases are in volume and the heating value of the producer gas is in MJ/Nm³.

Cold gas efficiency of the gasifier is defined as the ratio between the produced gas energy and the energy content of the biomass:

$$\eta_{CGE} = \frac{\dot{V}_{syn} \cdot LHV_{syn}}{\dot{m}_{bio} \cdot LHV_{bio}} \quad (24)$$

HHV of the biomass is determined using an equation from Channiwala and Parikh [40] based on the mass percentages of elemental data. LHV can be found by just removing the latent heat of moisture content in the biomass.

$$HHV_{bio} = 0.3491C + 1.1738H + 0.1005S - 0.1034O - 0.0151N - 0.0211ASH \quad (25)$$

3.3. Proposed modified equilibrium model

The thermodynamic chemical equilibrium model was improved based on the actual experimental gasification work of HTS, DM, and WC. The aim of the developed model was the prediction of syngas compositions and efficiencies not just from the bench-scale gasifier, but also the pilot-scale gasifier. Some assumptions were made for the current model: tar free syngas, no reactions with the nitrogen element, and no further reactions with SO₂.

The developed modified equilibrium model considered three important factors; 1) heat loss, 2) carbon conversion efficiency, and 3) non-equilibrium reactions. First, the temperature and oxidizing agent were the most important variables when the model was under consideration in the adiabatic state. The actual processes, however, had considerable heat losses, up to 20%, that required a modification of the energy balance equation (Eq. 15) by including the dissipating heat from the gasifier to the surroundings.

$$\sum_{in} (h_f^0 + \Delta h(T_{in})) = \sum_{out} (h_f^0 + \Delta h(T_{gasif})) + Q_{loss} \quad (26)$$

Second, as the thermodynamic equilibrium model overestimated the carbon conversion, an additional modification factor for carbon conversion efficiency was included based on the stoichiometric balance (Eq. 4). By considering the incomplete conversion, the unconverted

carbon (Eq. 27) imported from the GCE (carbon conversion efficiency) from experimental work was determined and applied to the model. A different carbon conversion efficiency (50 – 98%) was reported from different biomass wastes by Lapuerta et al. [41]. Kaewluan et al. [42] also determined a carbon conversion efficiency from 79 to 87% from woodchips in a bubbling fluidized bed gasification. Damiani and Trucco [14] proposed exponential correlations between the ER and unreacted carbon flow. These modifications were also used in other studies Azzone et al. [43], and Ghassemi and Shahsavan-Markadeh [44].

$$n_{UC} = n_1(1 - \eta_{carb}) \quad (27)$$

The last modifiers were the two non-equilibrium factors of the water-gas shift and methanation reactions, which do not always reach thermodynamic equilibrium in actual experiments. The unknown factors of actual mass transfer and incomplete reactions, engaged in the gasification reactions, result in a large deviation between experimental and calculated values from equilibrium models [45,46]. A thermodynamic model based on the Gibbs free energy minimization method generally underestimates the CH₄ content and overestimates H₂ gas. Thus the CH₄ content should be adjusted [3]. Ngo et al. [45] constructed a model to predict the synthesis gas compositions from a dual circulating fluidized bed gasifier. They developed a three stage quasi-equilibrium model using two empirical equations from Boudouard and methanation reactions to correct the production of carbonic elements and methane formation. Mendiburu et al. [47] also developed a model combining empirical correlations to predict methane using hydrogen and moisture content in the biomass, ER, and gasification temperature along with two chemical kinetic constraints.

The methanation reaction (R3), also called hydrogasification, takes place during devolatilization. The produced methane barely undergoes any secondary reactions unless it is exposed to a high temperature with a catalyst [47]. In other words, methane doesn't form through any thermodynamic equilibrium reactions, but only through devolatilization [48]. A much larger amount of methane is produced through the pyrolysis process where no oxidant agent is supplied than in the gasification process, which supports the fact that the thermal cracking or devolatilization is mainly involved in methane production [49-51]. The water-gas shift reaction (R4) of hydrogen and carbon monoxide exothermically changes, and the hydrogen equilibrium yield decreases slowly as the temperature rises. Also, the thermodynamic equilibrium is affected

by the exposure residence time of gas staying in a given biomass gasifier [48]. Therefore, a smaller H_2/CO ratio than an equilibrium ratio must be proposed as the fluidization minimized the reaction time under a high temperature. The two equilibrium constants are shown as:

$$\begin{aligned} K_3^* &= K_3 F_{K3}(T, ER) \\ K_4^* &= K_4 F_{K4}(T, ER) \end{aligned} \quad (28)$$

The approximation of non-equilibrium factors is solved based on a ramp function. Although it is desirable to propose a continuous mathematical function, it requires many more experimental data points for the minimum deviation when a linear regression is calculated. The non-equilibrium factors for the coded simulation are designated to fit the experimental results. F_{K3} helps decrease the error of methane, while F_{K4} gives more accurate result of carbon monoxide yield compared to the values from the non-modified thermodynamic model. Also, both factors are necessary to improve the hydrogen yield expectation from the developed model. When the factor values are greater than 1.0, the gas reactions or formation of products happen faster in a real experiment than in a condition of equilibrium. Table 4 shows empirical correlations governing factors used for the new non-equilibrium constants. The experimental data used to designate F_{K3} and F_{K4} were imported from Maglinao Jr. et al. [27] for sorghum gasification with experimental conditions of $0.3 \leq ER \leq 0.5$ and $730 \text{ }^\circ\text{C} \leq T \leq 800 \text{ }^\circ\text{C}$, Nam et. al. [28] for processed dairy manure gasification with conditions of $0.12 \leq ER \leq 0.48$ and $700 \text{ }^\circ\text{C} \leq T \leq 830 \text{ }^\circ\text{C}$, and woodchip gasification with conditions of $0.15 \leq ER \leq 0.5$ and $540 \text{ }^\circ\text{C} \leq T \leq 780 \text{ }^\circ\text{C}$ using a bench-scale fluidized bed gasifier at Texas A&M University.

An optimization logic algorithm was applied to obtain less than 4.0 of the RMS (root mean square) in order to obtain acceptable predictions [8,9,47,52]. This function considers the volume percent of syngas from a dry basis, as shown in Eq. (29). The RMS values obtained from the equilibrium model and the modified equilibrium model are compared and summarized in Table 5.

$$RMS_i = \sqrt{\frac{\sum_{i=1}^N |y_{i,\text{exp}} - y_{i,\text{cal}}|}{N}} \quad (29)$$

where y_{exp} is the experimental syngas composition in vol%, y_{cal} is the calculated value from the modified model, N is the number of data, and i refers to the syngas components taken into account for the synthesis gas: H_2 , CO , and CH_4 .

The overall logic algorithm for determining the equilibrium correction constants is presented as a block diagram in Figure 3. The algorithm, similar to the neural network optimization method, helped to find the best solution from a considerable amount of data. The current logic was sufficient to validate the biomass conversion processes to predict the syngas composition from TAMU pilot-scale gasifier. Figure 2 shows a screen shot of the developed program for the gasification performance prediction based on a consideration of a heat loss to surroundings, carbon conversion efficiency, non-equilibrium factors in accordance with temperature and ER.

4. Simulation results and discussion

The developed equilibrium model was compared to the experimental data of HTS gasification from Maglinao Jr. et al. [27], DM gasification from Nam et al. [28], and WC gasification performed for this work. The results of syngas composition, heating value, CGE (cold gas efficiency), and CCE (carbon conversion efficiency) were used for the comparison between the calculated and the experimental data based on the operating conditions of temperature and ER as shown in Table 6. Also, the hydrocarbon contents over C_2 gases were observed to have a brief indication of the tar content as indicated in Table 7. At a higher temperature, more hydrocarbon compositions were obtained. The quadratic regression equations were used to predict the optimal condition of temperature and ER for the highest CCE and CGE for each biomass gasification.

4.1. Model validation

The model was developed using EES (Engineering Equation Solver) V9.433-3D, licensed by the University of Guanajuato, and used to reconcile the performance of a pilot-scale mobile gasification system at TAMU. Figure 4 (a) shows the model validation of syngas compositions for a dry basis at the operating conditions of $740\text{ }^{\circ}\text{C} \leq T \leq 800\text{ }^{\circ}\text{C}$ and an $ER=0.35$. The volume concentration difference of CO between experimental and calculated data was only about 1% and 1.5% at the temperature of $740\text{ }^{\circ}\text{C}$ and $800\text{ }^{\circ}\text{C}$, respectively. However, the error was increased by 14% at $770\text{ }^{\circ}\text{C}$ as the regression curve was based on a second order function. There were not significant deviations with H_2 data. In the case of CH_4 , the maximum different

deviation was determined to be 1.5%. In order to include other hydrocarbons of acetylene, ethylene and ethane obtained from experimental work, the amount of CH_4 represented the sum of all the hydrocarbons. This was also applied in other studies for a better modified model [4,6,10,15,43,44]. Figure 4(b) shows a comparison between the experimental and calculated LHV of syngas. Although the two trends showed similar, a higher experimental LHV than the calculated was obtained by a difference of 15% at 740 °C and 20% at 800 °C. The consequence of this difference was caused by the discrepancy of methane, which had much higher energy content per volume. Figure 5 shows the relationship of ER against the adiabatic gasification temperature and experimental temperature. It is important to know both trends in order to calculate heat losses that take place in every reaction. Some authors [15,52] explained that this was due to the poor insulation of the reactor and unburned solid feedstock that were converted into heat energy, reported as a heat loss from 5% to 48%, depending on the geometry and type of gasifiers.

Figure 6 (a) shows the results of woodchip gasification at the operating conditions of $540 < T < 780$ °C and $\text{ER} = 0.33$. The differences were 1.5% for CH_4 , 1% for H_2 , and 2% for CO. Figure 6 (b) represents syngas LHVs that show a maximum of about 5.5 MJ/Nm^3 at 700°C. The regression curve was based on a parabolic equation. Figure 6 shows a similar performance between an adiabatic and actual WC gasification at the conditions of $500 \leq T \leq 700$ °C. The results indicate that more air was required to increase the temperature above 700 °C, which led to a higher ER of 0.5.

Woody wastes have been extensively studied in gasifiers because of low ash content and high carbon content, resulting in small error deviations between the calculated and the experimental results. Ash is defined as an inorganic mineral mixture of metal oxides and silicon oxide [53]. The thermodynamic equilibrium model doesn't consider the chemical transformations of inorganics so that the high inclusion of ash in fuel samples is directly related to the inaccuracy of equilibrium model. In a study by Vassileve et al. [54], an appropriated model including ash components as inert mixture reactants (wt%: $\text{SiO}_2 - 23.0$, $\text{CaO} - 44.5$, $\text{K}_2\text{O} - 7.7$, $\text{Al}_2\text{O}_3 - 5.3$, $\text{MgO} - 6.3$, $\text{Fe}_2\text{O}_3 - 3.6$, $\text{K}_2\text{SO}_4 - 6.3$, Na_2O) for an energy balance and a recalculated system temperature led to corrected syngas volume fractions.

In a state of equilibrium, a thermodynamically stable solid carbon (or char) can be obtained. The gasification conditions can achieve the maximum energy efficiency of the process when the solid carbon fuel has completely reacted [55]. Hence, when the carbon content is high in a biomass, the experimental results of gasification are closer to the thermodynamic models. In other words, gasification with a high ash biomass leads to difficulty in finding an accurate non-equilibrium constant.

Figure 8 (a) presents molar concentrations of the syngas from the developed model and experimental work of processed DM from Nam et al. [28]. They replicated the experimental work at least 3 times as the physicochemical properties of the processed DM showed much variation, which significantly affected the syngas compositions. This made it difficult to develop an accurate mathematical model. The volumetric percent of CO was determined to be from 7.5 to 10.5%. The highest peak of CO concentration was at 700 °C from the experimental work, while the peak was found at 730 °C from the model. The largest error was found at the lowest temperatures of 625 °C at a 6% difference, and the curves intersected at 675 °C. Then the error was reduced by a 2% at 780 °C. The regression curve of H₂ was linear from 2.5% H₂ concentration at 625 °C to 8% at 780 °C. The largest difference between 675 and 750 °C was 4%. The developed model predicted 2% higher methane concentration compared to the experimental concentration throughout the temperature ranges.

9 indicates the performance of the gasification of processed DM in an adiabatic case and experimental case. The two trajectories were opposite each other. The experimental process had to increase air flow to raise the gasification temperature.

4.2. Parametric Studies

To determine the effects of temperature and ER with a pilot-scale gasifier, the modified thermodynamic equilibrium model was used to predict the syngas compositions from HTS, WC, and DM biomass gasification in the range of $0.01 \leq ER \leq 0.99$ and $500 \leq T \leq 950$ °C. The methanation reaction actively occurred in lower temperatures between 500 to 600 °C as indicated in the red zone of Figure 10 (a). Also, the ER is an important factor for the production of CH₄ due to thermal cracking (devolatilization) which occurs intensively in the absence of an oxidizing agent. The theoretical conditions of $ER \leq 0.2$ and $T \leq 650$ °C produces up to 20% CH₄, which is close to the amount of CH₄ produced from a pyrolysis process. Figures 10 (b) and (c)

show similar production trends of CO and H₂ volumetric concentrations depending on the operating conditions. The highest concentration of CO and H₂ from the model is close to T = 800 °C and ER = 0.25. Figure 10 (d) represents the CO₂ composition indicating a complete combustion where the ER is above 0.5. Figure 11 shows LHV from sorghum gasification indicating that the heating value significantly depends on the ER. Consequently, higher values of the LHV are determined at a lower ER and gasification temperature due to a large production of methane. High LHV values were obtained at conditions ranging from 500 °C to 700 °C at ER ≤ 0.1 because of a large CH₄ production as the active methanation reaction occurs at lower temperatures as indicated in Figure 10 (a).

Figure 12 shows the volumetric percentages of CH₄, CO, H₂ and CO₂, from the WC gasification obtained from the modified equilibrium model. The maximum methane at 10.9% is produced at two operating conditions, T ≥ 750 °C at ER ≤ 0.25 and T ≤ 650 °C at ER ≥ 0.9. In an agreement to reach acceptable results for the producer gas, WC gasification should be operated at the conditions of T ≥ 600°C and ER ≤ 0.6 to obtain a minimum of 5 % CH₄. Other components showed variations from 13 to 19% for CO, and from 16 to 22 % for CO₂ in the operating conditions of 0.3 ≤ ER ≤ 0.4 and 600 °C ≤ T ≤ 800 °C. Similar results are also reported from experimental works performed by Kim et al. [56]. Figure 13 represents the LHV graph that show intersecting contour domains of temperature (600 °C ≤ T ≤ 800 °C) and ER (0.2 ≤ ER ≤ 0.3) covering the LHV between 4 and 7.5 MJ/Nm³.

Figure 13 illustrates LHV of syngas from woodchip gasification, which indirectly indicate the tar (heavy hydrocarbons) destruction. The increased LHV at a higher temperature was led by the cracking reactions of R5-R8 that encourage the production of H₂ and CO as well as light hydrocarbon gases. This behavior was investigated by Yu et al. [57] with the result that tar yield with woody materials decreases from 2.05 mg/g to 1.1 mg/g at temperatures from 800 to 950 °C at ER=0.2. Therefore, the syngas of woodchips included a large amount of H₂ and CO within the range, which led to an increase in LHV.

Figure 14 (a) shows the volumetric concentration of CH₄ in the syngas from DM, the average yield is 6 ± 1.5 % of methane in the range of $0.2 \leq ER \leq 0.4$ over all the temperature conditions. Since thermodynamic equilibrium simulation consider the ER from 0.0 to 1.0, the CO concentration was reached at 65% at the condition of $ER < 0.05$, which is unrealistic as shown in Figure 14 (b). On the other hand, the results from the present model show 15 to 30% CO concentration at $ER \approx 0.2$ over all temperatures conditions, at which gas concentrations are within the ranges of previous fluidized bed gasification studies [52,58]. H₂ concentration was from 6 to 11.5% at the operating conditions from 700 to 800 °C at $ER = 0.3$ as shown in Figure 14 (c). These results are close to the values determined by Nam et al. [28]. The CO₂ production is significantly influenced by the amount of air. As the ER increases to 1.0, CO₂ is raised to the maximum level concentration. An average value of 27% is reached when the system is operated from 600 to 800 °C at $ER = 0.45$. Figure 15 represents the LHV of syngas from DM indicating that the best quality of syngas is obtained at the operating conditions of $ER < 0.25$ and $T > 700$ °C. High LHV values of DM gasification at a lower ER and higher temperature are in agreement with the thermogravimetric analysis of DM pyrolysis and combustion by Wu et al [59]. The DM gasification experiences a large heat loss caused by the significant reduction reactions of high ash contents and unfiltered sand. Almost 20% of heat is lost to maintain the gasification process. Also, the low carbon content doesn't help keep up the operating temperature.

4.3. Tar analysis

Table 8 shows tar contaminations from WC and manure gasification at around 650 – 700 °C, which were grouped by major functional chemical groups such as phenol, furans, aromatics, and PAHs. The majority of chemicals in woodchip gasification tar were phenols, furans, and aromatic compounds, which can be considered secondary tar but not tertiary tar which is normally produced above 800 °C. An NREL report by Milne et al. [60] also suggested that a transition of major chemicals in tars at 500, 600, and 700 °C are phenolic ethers, alkyl phenolics,

and heterocyclic ethers, respectively. Wolfesberger et al. [61] studied the effect of temperature on tars from wood fluidized bed gasification. They determined that the amounts of tar (phenols, and aromatics) decreased with a temperature increasing from 800 to 870 °C, while PAHs increased. On the other hand, tar from manure gasification showed a totally different chemical composition trend in that the majority of the tar chemicals belonged to aliphatic hydrocarbons, non-aromatic oxygenates, and siloxane. As the high ash content (36%) of dairy manure was composed of mostly 87% SiO₂ and some AAEMs (alkali and alkaline earth metals, 4.9% CaO, 1.6% Na₂O, and 0.52% K₂O) [62], the inorganics resulted in significant catalytic conversions of breaking down the possible secondary and tertiary tar into primary tars. The presence of potassium in biomass reduced the yield of aromatic rings, while CO₂ and char contents increased [63]. This explains the lower CO composition from DM gasification compared to HTS and WC gasification. The high silicate composition from manure mixed sand resulted in a large amount of siloxane tar production. Table 8 (b) also indicates that a larger chemical distribution of one or two aromatic rings were found from WC gasification when manure tar did not include a majority of aromatic aliphatic compounds.

Additionally, a tar production simulation was established to understand the effect of temperature on tar production based on an experimental gasification tar study by Yu et al. [64] with the general compositional data of wood [65]. Polynomial coefficients were first obtained from each tar yield of pure lignin, cellulose, and hemicellulose gasification at two ERs (0.2 and 0.35) over temperature conditions from 800 to 1100 °C [64]. Then, different fractions of a general wood composition (35% lignin, 28% hemicellulose, and 24% cellulose) were applied to obtain a total tar production from wood gasification. To specify the effect of operating conditions on tar production, different ERs other than 0.2 and 0.35 were calculated over temperatures from 600 to 900 °C. Figure 16 clearly showed that a decrease in tar yield was achieved at increasing temperature mainly due to thermal cracking. The tar yield at ER = 0.35 ranged from 5 to 15 g/Nm³ when that at ER = 0.2 ranged from 12.5 to 38 g/Nm³. A similar tar production was also obtained from a wood pellet pilot-scale fluidized bed gasifier; 8 g/Nm³ at 750°C and 4.2 g/Nm³ at 870 °C [66]. The more oxygen at a higher ER reduced tar production compared to less oxygen at a lower ER.

4.4. Condition optimization through the developed model

The optimized conditions for the highest CCE and CGE were obtained through the developed equilibrium model with a genetic algorithm with two independent variables ranging from an ER of 0.15 to 0.5 and a temperature of 600 to 900 °C. The genetic method was used because of its robust optimization algorithm, designed to give a reliable global optimum even in the presence of local optima. For computation, the quadratic regression equations of heavy hydrocarbons shown in Table 7 were considered to obtain computed LHVs. Then the optimized gasification conditions of the highest CCE and CGE were obtained through the optimization computation. on the real experimental measures in order to get the highest possible value of CGE as shown in Table 9. As discussed in a previous section, the lowest carbon conversion efficiency (CCE) was obtained from DM gasification due to it's a high ash content. The shortest computing time for sorghum gasification results was because of the simplest data variation compared to other fuel gasification cases.

5. Conclusions

A modified equilibrium model based on the free Gibbs energy minimization method was developed for simulating a bubbling fluidized bed gasification process. The model was analyzed and validated by comparing it to the experimental data from HTS (high tonnage sorghum), WC (woodchip), and DM (dairy manure) in bench and pilot scale reactors by determining the non-equilibrium factors of F_{k3} and F_{k4} for each biomass gasification. The developed model can be considered a suitable model to predict the syngas composition (H_2 , CO and CH_4) and LHV for a TAMU pilot-scale gasification reactor. The equilibrium model was modified and improved by considering three correction factors for meet the actual process: 1) heat loss, 2) carbon conversion efficiency, and 3) chemical reactions. The developed thermodynamic simulator was used to investigate the effects of a wide range of temperatures and ERs (equivalence ratios) on the produced syngas. Tar compositions from WC and manure gasification was determined as well as the tar yield was simulated at various operating conditions. Also, condition optimization for the highest CCE and CGE was predicted from the combination of the developed equilibrium model and a genetic algorithm considering the heavy hydrocarbon contents. A more exhaustive study is planned to understand the effects of other thermodynamic parameters (moisture content,

H/C ratio, and ash content of biomass) on the syngas compositions and gasification tar compositions.

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Nomenclature

a	number of carbon atoms in hydrocarbons
Cp_i	specific heat at constant pressure [kJ/kmol-K]
F_{Ki}	non-equilibrium factors
g_i^0	specific Gibbs free energy formation [kJk/mol]
ΔG^0	Gibbs function [kJ/kmol]
h_i	enthalpy for i chemical species [kJk/mol]
h_f^0	enthalpy of formation [kJk/mol]
HHV	Higher heating value [kJ/kmol]
K	equilibrium constants
K^*	modified equilibrium constants
LHV	lower heating value [kJ/kmol] [kJ/Nm ³]
m	oxygen [mol/mol biomass]
$\dot{m}$	mas flow rate [kg/s]
M_i	molar weight of i chemical species [kg/kmol]
n_1	number of carbon atoms per carbon in biomass molecule
n_2	number of hydrogen atoms per carbon in biomass molecule
n_3	number of oxygen atoms per carbon in biomass molecule
n_4	number of nitrogen atoms per carbon in biomass molecule
n_5	number of sulfur atoms per carbon in biomass molecule
η	efficiency
p	<i>stoichiometric coefficient for heavy hydrocarbons of cracking reaction</i>
P	pressure [kPa]
P_0	standard pressure [kPa]
q	<i>stoichiometric coefficient of cracking reaction</i>
Q_{loss}	loss heat to surroundings [kJ/kmol]
r	<i>stoichiometric coefficient for H₂ of cracking reaction</i>
R	universal constant of ideal gases [kJ/kmol-K]
T	Temperature [K]
T_{in}	reagent temperature [K]
T_{gasif}	gasification temperature [K]

$\dot{V}$	volume flow rate [m ³ /s]
w_{bio}	moisture of biomass [mol/mol biomass]
w_{air}	moisture of air [mol/mol air]
x	number of hydrogen atoms in hydrocarbons
x_i	gas molar ratio of i chemical species with respect to biomass [mol/mol]
Y_d	volume fraction of dry gas

Subscripts

ave	arithmetic mean
bio	biomass
carb	carbon
CGE	cold gas efficiency
gasif	gasification
ref	standard condition
syn	syngas
UC	unconverted carbon

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(a) Bench scale gasification system [28]

(b) TAMU pilot scale gasification system [31]

Figure. 1. Bench scale and pilot scale gasifiers at Texas A&M University.

Figure 2. Diagram window of model simulator

Figure 3. Scheme of solution algorithm for modified equilibrium model

Figure 4. Comparison of experimental results vs. present model for sorghum: (a) volume fraction of syngas components, and (b) syngas heating value.

Figure 5. Comparison of experimental results vs. present model for sorghum

Figure 6. Comparison of experimental results vs present model for wood chips: (a) volume fraction of syngas components, and (b) lower heat value.

Figure 7. Comparison of experimental results vs. present model for wood chips

Figure 8. Comparison of experimental results vs. present model for DM: (a) volume fraction of syngas components, and (b) lower heating value

Figure 9. Comparison of equivalence ratio between the actual and adiabatic processes for DM gasification.

Figure 10. Product gas composition by volume percent for sorghum gasification: (a) CH₄, (b) CO, (c) H₂ and (d) CO₂.

Figure 11. Influence of reaction temperature and ER on the LHV of syngas for sorghum gasification.

Figure 12. Product gas composition by volume percent for wood chips gasification: (a) CH_4 , (a) CO , (a) H_2 , (a) CO_2

Figure 13. Influence of reaction temperature and ER on the LHV of syngas for woodchips gasification.

Figure 14. Product gas composition by volume percent for dairy manure: (a) CH_4 , (b) CO , (c) H_2 , (d) CO_2 .

Figure 15. Influence of reaction temperature and ER on the LHV of syngas for dairy manure gasification.

Figure 16. Tar production simulation from wood gasification at various ER and temperature.

Table 1. Biomass characteristics (db: dry basis; *: by difference).

Biomass Material	Proximate Analysis % _{wt} (db)			Ultimate Analysis % _{wt} (db)					Bomb calorimeter
	VCM	FC	ASH	C	H	O*	N	S	HHV(MJ/kg)
Sorghum (HTS)	71.40 ± 0.012	14.45 ± 0.080	14.16 ± 0.90	42.29	5.74	37.32	0.42	0.07	19.58 ± 0.13
Wood chips (WC)	85.62 ± 1.61	13.44 ± 1.67	0.93 ± 0.18	48.32	6.62	44.58	0.14	0.32	17.52 ± 0.08
Dairy manure (DM)	60.5 ± 2.8	3.6 ± 2.7	35.9 ± 1.7	32.8	2.48	24.46	4.16	0.21	12.3 ± 1.4

Table 2. Constants of Gibbs free energy for temperature range from 300 K to 1000 K

Species	Ag _i	Bg _i	Cg _i	Dg _i	Eg _i	Fg _i	Gg _i
CO	-1.586446E+00	-7.559705E-04	-6.469592E-07	-4.651620E-10	4.124918E-13	-1.431054E+04	-3.262451E+00
CO ₂	-7.912764E+00	-4.961036E-03	1.734852E-06	-5.722238E-10	3.528800E-13	-4.837314E+04	-2.275724E+00
H ₂	6.592218E+00	-4.124721E-04	1.357169E-07	7.896195E-12	-6.891453E-14	-1.012521E+03	-3.298124E+00
H ₂ O	7.966100E-01	-1.737491E-03	1.059116E-06	-5.807151E-10	4.177647E-13	-3.020811E+04	-3.386842E+00
CH ₄	-1.294345E+01	-8.738340E-03	-5.722238E-10	-2.541423E-09	2.039885E-12	-9.825229E+03	-7.787415E-01

Table 3. Constants of Gibbs free energy for temperature range from 1000 K to 5000 K

Species	A_{gi}	B_{gi}	C_{gi}	D_{gi}	E_{gi}	F_{gi}	G_{gi}
CO	-3.083139E+00	-7.213443E-04	9.384712E-08	-8.488178E-12	1.151825E-15	-1.426835E+04	-3.025078E+00
CO ₂	5.409019E+00	-1.570084E-03	2.130684E-07	-1.994997E-11	2.781722E-15	-4.896696E+04	-4.453623E+00
H ₂	4.346533E+00	-3.500322E-04	9.389713E-09	7.692982E-13	-2.637920E-16	-8.350340E+02	-2.991423E+00
H ₂ O	-4.190672E+00	-1.528147E-03	1.455043E-07	-1.000830E-11	1.065270E-15	-2.989921E+04	-2.672145E+00
CH ₄	-7.939917E+00	-5.118618E-03	6.458547E-07	-5.654654E-11	7.505705E-15	-1.008079E+04	-1.683478E+00

Table 4. Correlations for non-equilibrium factors and carbon conversion efficiency

$F_{Ki}(T, ER)$	Sorghum		Wood chips		Dairy Manure	
$T_{gasif} [^{\circ}C]$	$720 \leq T < 740$	$740 \leq T \leq 810$	$540 \leq T < 700$	$700 \leq T \leq 800$	$610 \leq T \leq 820$	$610 \leq T \leq 820$
ER [-]	0.3-0.5		0.15-0.5		0.1-0.2	0.2-0.5
$F_{K3} [-]$	0.2	0.15	0.045	$F_{K3} = -0.6556 + 0.0009T_{gasif}$	0.0001	$F_{K3} = -0.1056 + 0.0002T_{gasif}$
$F_{K4} [-]$	$F_{K4} = -9.281 + 0.0141T_{gasif}$		$F_{K4} = -1.572 + 0.0027T_{gasif}$	$F_{K4} = -0.5655 + 0.0013T_{gasif}$	11	
$\eta_{carb} [-]$	$\eta_{carb} = 0.0881 + 0.0011 T_{gasif}$		$\eta_{carb} = 0.1007 + 0.0011 T_{gasif}$	0.55	$\eta_{carb} = -0.6118 + 0.0016T_{gasif}$	

Table 5. Average RMS errors obtained from model validation.

	Sorghum		Wood chips		Dairy Manure	
	Equilibrium model	Modified model	Equilibrium Model	Modified model	Equilibrium model	Modified model
RMS error	9.0131	1.2065	9.0466	3.2823	8.7081	3.5273

Table 6. Comparison of results obtained with the present model and experimental results (HTS: high tonnage sorhum, WC: woodchip, and DM: dairy manure).

	HTS [27]		WC		DM[28]	
	Exp	Calc	Exp	Calc	Exp	Calc
H ₂ (%)	5.24	5.115	9.03	9.849	3.90	6.75
CO (%)	13.56	13.11	18.34	18.16	11.10	12.5
CO ₂ (%)	14.06	15.02	17.94	15.47	17.50	23.71
CH ₄ (%)	4.53 ^a	3.18	4.80 ^a	6.51	2.50	5.07
LHV (MJ/Nm ³)	4.09	3.35	5.63	5.69	3.25	4.12
CGE (%)	42.64	36.79	66.8	67	26	24.05
η_{carb} (%)	82.28	90	86.68	99	63	48.5
T (°C)	730		707		635	
ER	0.35		0.33		0.18	

Table 7. The hydrocarbon contents during the fluidized bed gasification process at different temperatures.

	(%)	Ranges of temperature			Quadratic regression
		500-600 [°C]	600-700 [°C]	700-800 [°C]	
Wood chips	C ₂ H ₄	0.21	0.87	1.37	$C_2H_4 = -8.82899347 + 0.0245761026 * T_{gasif} - 0.0000146377839 * T_{gasif}^2$
	C ₂ H ₆	0.11	0.41	0.25	$C_2H_6 = -5.93664314 + 0.0186935899 * T_{gasif} - 0.0000138714824 * T_{gasif}^2$
Dairy Manure	C ₂ H ₂	0	0.013	0.07	$C_2H_2 = -1.99674273 + 0.00568790498 * T_{gasif} - 0.00000399290969 * T_{gasif}^2$
	C ₂ H ₄	0.52	0.94	1.15	$C_2H_4 = -36.482326 + 0.104373369 * T_{gasif} - 0.0000721716527 * T_{gasif}^2$
	C ₂ H ₆	0.1	0.193	0.81	$C_2H_6 = -11.7159867 + 0.0334659636 * T_{gasif} - 0.0000233093674 * T_{gasif}^2$
	C ₃ H ₆	0	0.283	0.63	$C_3H_6 = -23.0589535 + 0.0664461844 * T_{gasif} - 0.0000471728599 * T_{gasif}^2$

Table 8. Tar analysis of WC and manure gasification (a) relative % chemical groups by GC-MS and (b) relative % of different aromatic rings.

(a)

Chemical group	Relative amount %	
	WC	Manure
<i>Phenols</i>	59.8	19.8
<i>Furans</i>	7.1	0.0
<i>Aromatic compounds</i>	19.1	18.6
<i>N containing aromatics</i>	5.3	3.4
<i>Naphthalene</i>	4.4	0.0
<i>PAHs</i>	3.0	0.0
<i>Siloxane</i>	0.0	13.4
<i>Phthalates</i>	0.0	3.5
<i>Aliphatic HC</i>	0.7	26.5
<i>Other oxygenates</i>	0.6	14.8

(b)

# of aromatic ring	Relative amount %	
	WC	Manure
0	1.4	41.3
1	75.6	27.3
2	19.0	17.0
3	3.9	0.9
4 <	0.1	0.0

Other	0.0	13.4
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Table 9. Gasification condition optimization and its best efficiencies.

Biomass	Constraints				Optimal Value		CCE [%]	CGE [%]	Computing time [s]
	Temp [°C]		ER [-]		T [°C]	ER[-]			
	Min	Max	Min	Max					
HTS	600	900	0.15	0.5	600	0.16	85.84	52.44	296.5
WC	600	900	0.15	0.5	849	0.25	99.07	77.73	444.5
DM	600	900	0.15	0.5	748	0.15	64.9	55.48	1082.9