

STOICHIOMETRIC THERMODYNAMIC EQUILIBRIUM MODELS FOR DOWNDRAFT GASIFIERS: A REVIEW

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Gasification is a popular biomass-to-energy production strategy due to its affordability and ease of use. Downdraft gasifiers, typically small-scale units with a maximum heat power output of 5 MW, are ideal for decentralized power generation and delivery to remote villages. Mathematical models can predict gasifier design, operating behaviour, gas composition, startup and shutdown, fuel and load changes, and other issues. Numerous numerical/mathematical models have been developed to characterize and forecast gasification processes, including drying, pyrolysis, gasification, and combustion. This article reviews the thermodynamic equilibrium model for gasification and its modifications to increase prediction accuracy. Factors such as, pressure fluctuations, equivalent ratio, biomass moisture content, and oxygen enrichment affect the quality of generated syngas. Equilibrium models are useful for predicting the maximum yield achievable by a reagent system and are ideal for initial analysis or optimization techniques.

Key words: Biomass gasification, Downdraft gasifier, Equilibrium model, Modelling

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1. Introduction

The world's energy need is growing every day because of population growth, use of electric vehicles, and the spreading of industrialization [1,2]. To cope with this increasing energy demand, alternative ways to produce energy from environment friendly and renewable sources have been focused. The biomass gasification process is one of the most useful processes to produce flammable gas, which can be used as an energy source and is renewable too [3]. Gasifiers have several positive effects on the environment, when compared to conventional methods, gasifiers allow us to produce greener energy while lowering hazardous pollutants. Gasification reduces environmental damage by effectively managing waste and lowering greenhouse gas emissions. It represents a move toward more sustainable energy options. By implementing a gasifier, we can decrease our dependence on fossil fuels, making a significant contribution towards a more environmentally friendly and sustainable future.

The two main pathways via which the biomass conversion process occurs are the thermochemical and biochemical pathways. To produce syngas/producer gas the thermochemical route is followed. Fig. 1 shows the biomass conversion process.

Downdraft gasifiers have garnered a lot of attention lately since they provide a straightforward and affordable method of generating electricity from biomass. Additionally, they address the growing need for clean and renewable energy sources. Current study aims to enhance the efficiency and performance of downdraft gasifiers [4]. The thermodynamic equilibrium condition is a useful

tool for simulation studies that assess the potential of various biomass sources for gasification. Downdraft gasifier equilibrium can be modelled in two ways. The first, known as stoichiometric equilibrium determining the equilibrium constants of certain reactions; the second, known as non-stoichiometric equilibrium modelling, entails minimising the Gibbs free energy.

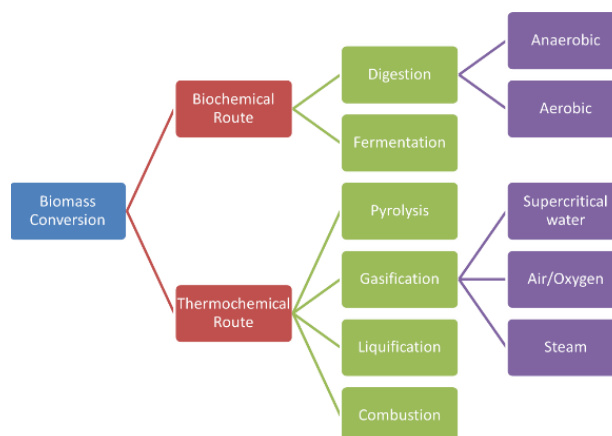


Fig. 1 Biomass conversion methods

Several studies have been conducted on the stoichiometric thermodynamic equilibrium modelling of downdraft gasifiers, and this article reviews some of them and adopts some of the methods and assumptions used by their authors to compare developed equilibrium models.

This work focuses on gasification, a well-established technique that has gained popularity recently due to its environmental sustainability and energy efficiency. The mathematical modelling of the underlying thermo-chemical processes is also considered a valuable tool for developing new reactors or choosing the appropriate control method [5]. The review of thermodynamic equilibrium models for downdraft gasifiers is the main goal of the authors. Downdraft gasifiers are the best small-scale gasifier options available, and the thermodynamic equilibrium model is quick, easy to use, and unaffected by the kind of gasifier.

The biomass gasifiers' operation involves a series of complicated chemical reactions, which include fast pyrolysis, partial oxidation of pyrolysis products, gasification of the resultant char, conversion of tar and lower hydrocarbons, and water-gas shift. Fig. 2 illustrate the biomass gasification process and energy flow. Using mathematical models, we can better understand how main parameters like biomass moisture content or the air-to-fuel ratio affect the producer-gas composition and calorific value. Despite their limitations, present work concentrates on thermo-chemical equilibrium models that are particularly useful for preliminary comparisons and studying the influence of the most critical variables. The advantage of these models is that they are independent of the specific gasifier design [6].

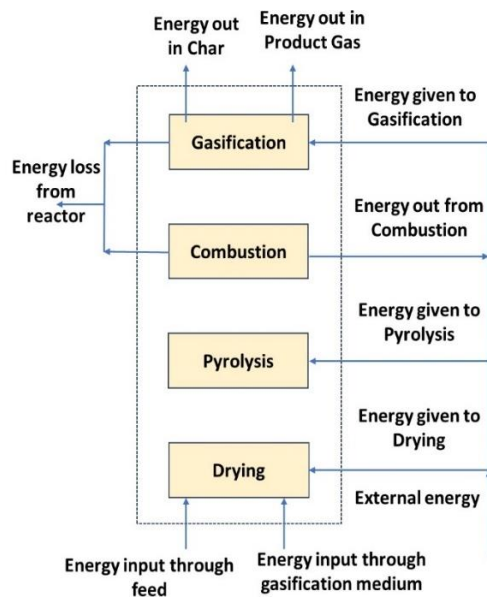


Fig. 2 Biomass gasification and energy flow

2. The gasification process

Gasification is a process that occurs when a gasifying agent, such as air, oxygen, or steam, partially oxidizes a solid fuel [7]. This partial oxidation generates heat, facilitating the drying, devolatilization, and reduction reactions. Table 1 outlines the reactions that must be considered during the gasification process. The process of gasification involves converting carbonaceous materials derived from biomass or fossil fuels into various gases, such as carbon dioxide (CO_2), nitrogen (N_2), hydrogen (H_2),

methane (CH_4), and carbon monoxide (CO) [8–10]. The feedstock material is reacted at high temperatures (usually over 700°C) without burning, and the amount of air, oxygen, or steam in the reaction is regulated to achieve this. Fig. 3 shows the gasification process with temperature ranges for each step.

After the gasification process, the resulting gas composition is known as syngas (synthesis gas) or producer gas. Because the gas is primarily made of H_2 and CO , which are flammable, the gas is used as fuel. When the compounds used in the gasification process are made from biomass sources, it is considered a renewable energy source and has the potential to provide power when the resulting gas is burned. One of the benefits of gasification is that it produces syngas, which can be burned more efficiently than the original solid biomass-based feedstock [11]. This is because syngas has a higher combustion temperature, which increases the thermodynamic efficiency limit defined by Carnot's rule. The majority of syngas is burned directly in gasoline type of engines. Syngas can also be used as a source to hydrogen and methanol production, or it can be processed through the Fischer-Tropsch process to create synthetic fuel. Gasification can reduce emissions of air pollutants like methane and particulates by replacing landfilling and incineration for certain materials.

Fossil fuels are currently widely used in industrial settings for electricity generation through gasification. Certain pollutants, like SO_x and NO_x , can be produced in smaller quantities by gasification than by combustion.

3. Types of gasifiers

Gasifiers are classified into three types: fixed beds, fluidized beds and entrained flow gasifiers (Fig 4). The entrained suspension gasifier is designed for finely split coal gasification ($<0.1\text{--}0.4\text{ mm}$) [12]. This design is not suitable for fibrous materials like wood [13]. Table 2 summarizes the key features of different gasifiers [18].

3.1. Fixed-bed gasifiers

The oldest and most widely used reactors for producing syngas are fixed-bed gasifiers. Industrial facilities are becoming less interested in large-scale (greater than 10 MW) fixed-bed gasifiers because of scale-up problems [14]. On the other hand, numerous companies employ highly efficient small-scale fixed-bed gasifiers (less than 10 MW) for thermal applications and decentralized power production [15]. Fixed-bed gasifiers are frequently used and investigated because of their straightforward functioning and ease of fabrication.

Fixed-bed gasifiers are categorized based on the fuel flow direction and entrance of airflow as:

- Updraft gasifier
- Downdraft gasifier
- Crossdraft gasifier

Different reaction distribution zones (such as drying, pyrolysis, combustion, and reduction) are positioned differently in a fixed-bed reactor, depending on the kind of gasifier.

Table 1 Typical gasification reactions at 25 °C

Reaction Type	Reaction
Carbon Reaction	
R1 (Boudouard)	$C + CO_2 \leftrightarrow 2CO + 172 \text{ kJ/mol}$
R2 (water-gas or steam)	$C + H_2O \leftrightarrow CO + H_2 + 131 \text{ kJ/mol}$
R3 (hydrogasification)	$C + 2H_2 \leftrightarrow CH_4 - 74.8 \text{ kJ/mol}$
R4	$C + 0.5 O_2 \rightarrow CO - 111 \text{ kJ/mol}$
Oxidation Reactions	
R5	$C + O_2 \rightarrow CO_2 - 394 \text{ kJ/mol}$
R6	$CO + 0.5O_2 \rightarrow CO_2 - 284 \text{ kJ/mol}$
R7	$CH_4 + 2O_2 \leftrightarrow CO_2 + 2H_2O - 803 \text{ kJ/mol}$
R8	$H_2 + 0.5 O_2 \rightarrow H_2O - 242 \text{ kJ/mol}$
Shift Reaction	
R9	$CO + H_2O \leftrightarrow CO_2 + H_2 - 41.2 \text{ kJ/mol}$
Methanation Reactions	
R10	$2CO + 2H_2 \rightarrow CH_4 + CO_2 - 247 \text{ kJ/mol}$
R11	$CO + 3H_2 \leftrightarrow CH_4 + H_2O - 206 \text{ kJ/mol}$
R14	$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O - 165 \text{ kJ/mol}$
Steam-Reforming Reactions	
R12	$CH_4 + H_2O \leftrightarrow CO + 3H_2 + 206 \text{ kJ/mol}$
R13	$CH_4 + 0.5 O_2 \rightarrow CO + 2H_2 - 36 \text{ kJ/mol}$

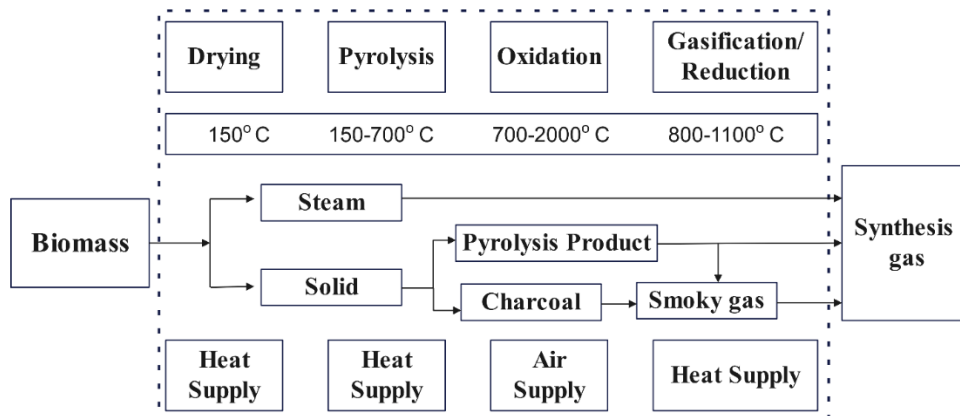


Fig. 3 Gasification process: Temperature ranges of each stage are illustrated [16]

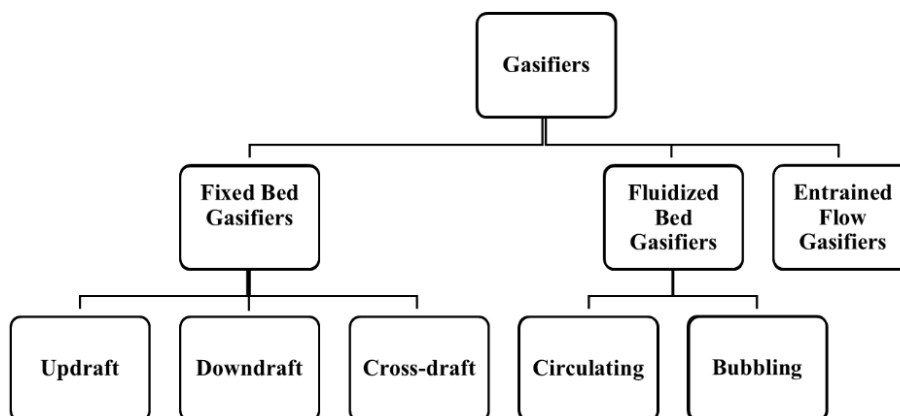


Fig. 4 Types of gasifiers

Table 2 Features of different gasifiers

Gasifier	Downdraft	Updraft	Fluidized bed	Entrained bed flow
Technology	Simple, reliable and proven. A reactor with low investment cost. A relatively simple construction	Simple, reliable and proven. A reactor with low investment cost. A simple and robust construction	Proven technology with coal. Plant with relatively high investment cost	Complex construction
Feed size	<51 mm	<51 mm	<6 mm	<0.15 mm
Tolerance for fines/coarse particle	Limited/very good	Limited/very good	Good/good	Excellent/poor
Oxidant requirements	Low	Low	Moderate	High
Maximum fuel moisture (%)	25	60	55	15
Gas LHV (MJ/m ³) at (NC)	4.5-5.0	5-6	3.7-8.4 (BFB), 4.5-13 (CFB)	4-6
Tar (g/m ³) at (NC)	0.015-3.0	30-150	3.7-61.9 (BFB), 4-20 (CFB)	0.01-4
Ash and particles in syngas	Low	High	High	Low
Reaction temperature	1090 °C	1090 °C	800-1000 °C	1990 °C
Ash melting point	>1250 °C	> 1000 °C	>1000 °C	>1250 °C
Exit gas temperature	400-700 °C	200-400 °C	800-1000 °C	>1260 °C
Admissible power	Up to 1 MW _e	Up to 10 MW _e	1-100 MW _e	5-100 MW _e
Residence time	Particles are in bed until its discharge	Particles are in bed until its discharge	Particles spend substantial time	Very short time (few seconds)
Carbon conversion efficiency	High	High	High. Loss of carbon in ash	High. Carbon loss with ash
Scale up potential	500 kg/h feed rate (limited)	4 dry t/h feed rate (good)	10-15 dry t/h feed rate (good)	>20 dry t/h feed rate (very good)
Turn-down capability	Limited	Good	Limited	Limited
Specific capacity	Low	-	High	High
Process flexibility	Very limited, any change in process variables need a new design	Very limited, any change in process variables need a new design	Flexible to loads less than design	Very limited. Size and energy content of the fuel must be in a narrow range
Temperature profile	High gradient	High gradient	Vertically almost constant	Temperature above the ash melting temperature
Hot gas efficiency	85-90%	90-95%	89%	80%
Cold gas efficiency	80%	80%	89%	80%
Nature of ash produced	Dry	Dry	Dry	Slagging
Application	Small scale	Small scale	Medium scale	Large scale
Problem areas	Utilization of fines	Tar production	Carbon conversion	Raw gas cooling

NC= Normal condition (101.325 kPa, 0°C)

3.1.1. Downdraft gasifier

Downdraft gasifier (Fig 5), in which both biomass (fuel) and air move downward in the lower section of the gasifier unit. The downdraft gasifier has four distinct zones: (1) drying zone, (2) pyrolysis zone, (3) oxidation zone, and (4) reduction zone. The product gases exit the

gasifier immediately below the grate, allowing partial breaking of the generated tars in high temperature oxidation and reduction zones and therefore producing a gas with minimal tar concentration. The resulting gas typically has a low content of particles and tars (about 1 g/m³). The downdraft gasifier is suitable for producing clean gas [17].

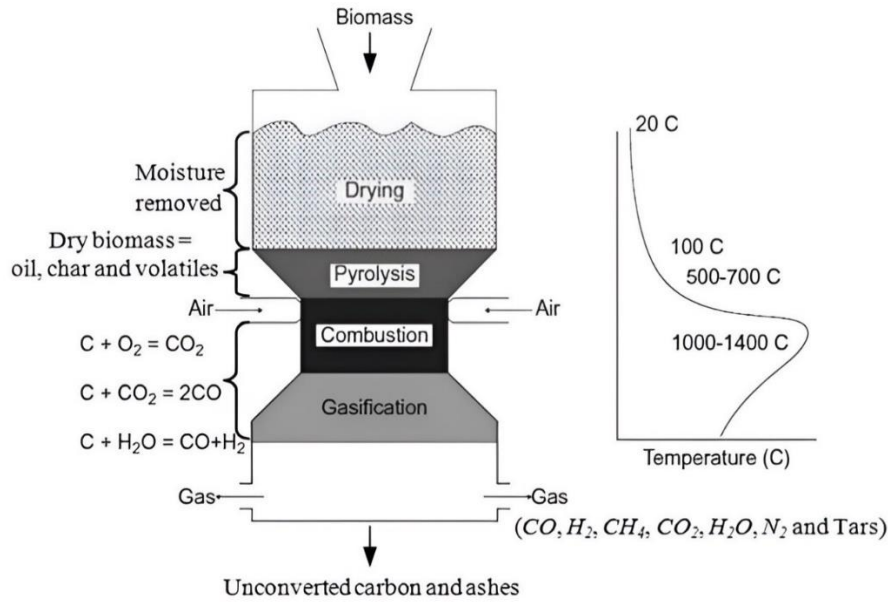


Fig. 5 Downdraft gasifier as layers [26]

3.2. Fluidized-bed gasifiers

Fluidized beds are emerging as the finest biomass combustion technology because of their versatility in fuel type and great efficiency. Fluidized bed (FB) gasification has been widely employed in coal gasification for many years. Its benefit over fixed-bed gasifiers is constant temperature distribution throughout the fluidised bed. This temperature consistency is achieved by intensive circulating of fine granular material (such as sand) in the fluidised bed of the gasifier. Fluidized beds are utilized for a wide range of fuels. Bed agglomeration causes inadequate fluidization or de-fluidization, which is a serious issue in fluidized bed gasifiers. However, viable solutions have been described for various biomass feedstocks [19]. These solutions are primarily based on lowering and controlling the fluidised bed temperature. Two main types of fluidized bed gasifiers are in current use:

- Circulating fluidized bed
- Stationary (Bubbling) fluidised bed.

4. Models for biomass gasification

Mathematical modelling may be used for a variety of purposes, including the basic design of an industrial process and the complicated simulation of a single unit [20]. Simulation of gasification improves understanding of the physical and chemical factors that underpin the gasification process. It aids in the design of new systems or the development of effective control techniques for existing units, hence optimising produced syngas quality.

Models assist in determining the sensitivity of gasifier performance to various operating or design parameter alterations [21]. Models can be used for design, predicting operating behaviour, predicting emissions under

normal conditions, start-up, shut-down, fuel and load changes, and decreasing char and tar formation concerns. A significant amount of work has been done to construct gasifier simulation models. These can be classed as belonging to the following groups [22,23].

- Thermodynamic equilibrium models;
- Kinetic models;
- Phenomenological models;
- Artificial Neural Network (ANN) models.

4.1. Thermodynamic equilibrium models

Thermodynamic Equilibrium (TE) simulations which are independent of gasifier design and useful for evaluating the impact of solid material composition and process parameters. Although chemical or thermodynamic equilibrium may not be reached within the gasifier, this model provides designers with a reasonable prediction of the maximum achievable yield of a desired product. However, TE models are unable to predict the impact of fluid kinetic or geometric characteristics, such as fluidizing velocity, or design variables like gasifier height. In contrast to equilibrium models, the kinetic model considers the hydrodynamics of the gasifier reactor as well as the kinetics of the gasification events occurring inside the gasifier. This becomes significant when the dwell time needed for full conversion is prolonged, which happens at low reaction temperatures when the reaction rate is extremely slow. As a result, it is discovered that, when compared to equilibrium models, kinetic modelling is more accurate and appropriate at relatively low working temperatures. The total performance of the system, including the producer gas yield and the temperature and composition profiles of the gas along the gasifier, can be predicted using kinetic models. Although kinetic models need a lot of calculation, they

are precise and thorough. The equilibrium model, on the other hand, is independent of the particular gasifier design and is comparatively simple to implement with quick convergence. An equilibrium model is very helpful for making initial comparisons and examining the impact of the most important variables [24,25].

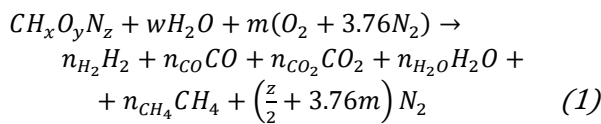
Chemical equilibrium can be obtained by:

- Equilibrium constant (stoichiometric method)
- Minimization of the Gibbs free energy (non-stoichiometric method)

Stoichiometric models are based on evaluating the equilibrium constants of an independent set of reactions (Table 1) that can be associated with Gibbs' free energy. The non-stoichiometric equilibrium modelling approach, often referred to as the “Gibbs free energy minimisation approach”, is developed on the direct minimisation of the Gibbs free energy of the reaction. This method is standard among many researchers [27,28] and is claimed to apply to complex reaction pathways, avoiding the need to identify the independent set of reactions. The solutions to the resulting equilibrium model equations can be obtained using different algorithms. However, despite the differences in the two approaches, both produce similar results [29]. Generally, equilibrium models are relatively more straightforward to implement and converge faster [30].

4.2. Stoichiometric thermodynamic equilibrium model steps

The model based on Stoichiometric thermodynamic equilibrium follows the following steps for prediction of syngas composition. The feedstock's chemical formula is defined as $CH_xO_yN_z$. The global gasification reaction can be written as:



where x, y, and z are the number of atoms of hydrogen, oxygen and nitrogen per number of atoms of carbon in the feedstock, respectively; w is the amount of moisture per kmol of feedstock; m is the amount of oxygen per kmol of feedstock, and n_i are the amounts (kmol) of formed products.

From the ultimate analysis of fuel/feedstock the percentage of carbon, hydrogen, oxygen, nitrogen, sulphur and ash is determined [31,32]. From known percentage of different constituents, number of atoms can be calculated by following expressions:

$$x = \frac{H\% \times M_C}{C\% \times M_H}, y = \frac{O\% \times M_C}{C\% \times M_O}, z = \frac{N\% \times M_C}{C\% \times M_N} \quad (2)$$

In above equation, C%, H%, O% and N% are mass fraction of carbon, hydrogen, oxygen and nitrogen of fuel and M_i is their molecular weight.

$$w = \frac{M_{fuel} \times WC}{M_{H_2O} \times (1 - WC)} \quad m = ER \times \left(1 + \frac{x}{4} - \frac{y}{2}\right) \quad (3)$$

where ER is equivalence ratio. Which is defined as actual air fuel to stoichiometric air fuel ratio.

All inputs on left hand side of Eq. (1) are defined at 25°C. On the right-hand side, n_i are the numbers of kmol of species i . that are unknown.

4.3. Mass balance

To find the amount of unknown species n_i of the producer gas, same number of equations (equals to number of unknown species i) are needed. After considering mass balance equations, remaining equations are generated from equilibrium constant relations. Relationships between equilibrium constants and mass balance are used to create those equations. Once equations are formed, they are solved (simultaneously) to find the moles of different species taken in to consideration. Heat balance is done to calculate the gasification temperature. Here iterative method is used to calculate gasification temperature. The flow diagram as shown is Fig. 6 illustrate the calculation process.

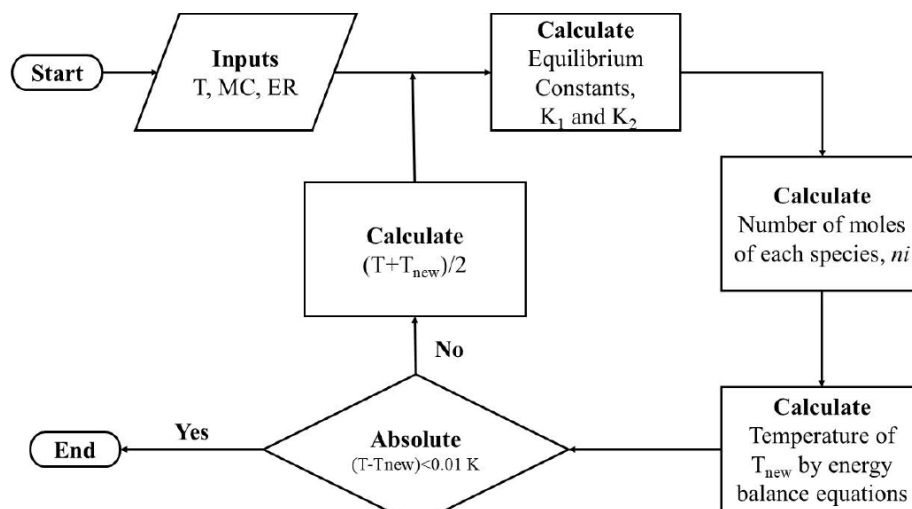


Fig. 6 Thermodynamic equilibrium model flow diagram

5. Development of stoichiometric thermodynamic equilibrium models

This section describes the most pertinent stoichiometric equilibrium models in historical sequence. The main findings of parametric analyses that evaluate the effects of the equivalence ratio, biomass's initial moisture content and gasification pressure on syngas composition and calorimetric value, and the temperature and efficiency of gasification are presented for each model. The validation of models has been grounded in a variety of experimental works: stratified gasifiers [21,30,33,34], Imbert gasifier [35–37], double-stage air supply gasifiers [38,39] gasifiers with an internal separate combustion chamber [40], and catalytic steam gasifiers [41], among other stratified gasifiers that have been built and tested by multiple researchers.

Chern's model (1991) [42] is applied to the downdraft gasification of wood to calculate the temperature and char yield at the gasifier's exit, as well as the syngas composition in terms of N_2 , H_2 , CO , CH_4 , H_2O , and CO_2 (a reference composition that is also utilized by all other researchers in their models), for a given set of heat loss and input conditions. This model uses the following reactions: Boudouard reaction, Water-gas heterogeneous reaction, Methane formation reaction, Water-gas shift reaction, and $CO_2 + CH_4 \rightarrow 2H_2 + 2CO$. Experimental data from wood gasification in a downdraft gasifier on a commercial scale is used to validate the model.

Zainal's model (2001) [43] use the equilibrium model for the prediction of the gasification process for the downdraft gasifier and to predict the composition (H_2 , CO , CO_2 , H_2O , CH_4 , and N_2) as well as calorific value. A parametric study is carried out after validating the model with the experimental results available from the literature [44]. It was found that the calorific value of the produced gas decreases with increasing moisture content in the raw material as well as an increase in the gasification temperature. Initially, the fuel used is wood chips. Then, the same model is applied to different fuels: paddy husk, paper, and municipal waste. The gasification temperature is taken at $800^\circ C$ constant, and the effect of moisture content in wood chips is analysed. Compared to experimental results, the hydrogen percentage predicted is higher, while the carbon monoxide percentage indicated is lower than the practical result. The most important results are: content of H_2 in the producer gas increases almost linearly with the increase in the moisture content for all the considered materials; CO content in the producer gas decreases almost linearly with the increase in moisture, while CH_4 increases linearly, although its percentage is small (of the order of 1%).

Jayah's model (2003) [33] consists of two sub-models of the pyrolysis and gasification zones, respectively. The gas's maximum temperature and makeup entering the gasification zone have been ascertained using the pyrolysis sub-model. Data from the experiments have been used to calibrate the gasification zone sub-model. In-

stead of using Chen's algorithms [42], the flaming pyrolysis model created by Milligan [45] has been used to overcome the overprediction of the pyrolysis zone exit temperature. The gasification zone sub-model predicts gas compositions of N_2 , H_2 , CO , CH_4 , and CO_2 that are within $\pm 5.8\%$ of the measured values.

S. Jarungthammachote's model (2007) [46] is a thermodynamic equilibrium model based on equilibrium constant was developed to predict the makeup of producer gas in a downdraft waste gasifier. As a raw material/fuel, municipal solid waste (MSW) is used, unlike Zainal's model [43] known value of oxygen. The iterative method is used to predict the gasification temperature based on the initially guessed value of temperature. Simulations reveal that the effects of moisture content (MC) of the waste are as follows: the mole fraction of H_2 gradually increases; CO decreases; CH_4 , which has a meagre percentage in the producer gas, increases; N_2 slightly decreases; and CO_2 increases with increasing MC. As MC rises, the reaction temperature, the calorific value, and the second law efficiency all fall. Data reported by Jayah et al. [33] was used for model validation. Initially, the model assumes an adiabatic process, and results obtained assuming gasification temperature as 1100 K constant, just like Zainal the predicted results show that mole fraction of CH_4 is predicted very low compared to experimental results but higher amounts of H_2 . To enhance the model's prediction, some modifications in the form of coefficient multiplication with equilibrium constants are done. Coefficients equal to 11.28 and 0.91 multiply the equilibrium constant of the methane reaction and water-gas shift reaction respectively. This modified model predicts results that are more accurate and in line with the experimental data available in the literature [27,33,43].

Hua-Jiang Huang's model (2009) [47], two models are built and based on the three equilibrium reactions, Water-gas heterogeneous reaction, Water-gas shift reaction, and Methane reforming reaction to simulate a downdraft gasifier. Model-1 omits the char, while Model-2 considers the char. Equilibrium constants for all reactions are calculated for a given gasification temperature and pressure. Moles of all constituents are obtained by solving the nonlinear equation for the elemental balance of C, H, and O and the equilibrium constant under the given amount of air. As in [46], the partial equilibrium is considered through a coefficient β_1 that multiplies the equilibrium constant associated with the Methane reforming reaction and β_2 associated with the water-gas shift reaction. β_1 can be determined by fixing the fraction of CH_4 in the dry syngas at its average value of the experimental data, and β_2 estimated by fixing the fraction of CO in the dry syngas at its average value. For the first model, the modifications resulting from β_1 improve the predictive capability, whereas the modification by β_1 and β_2 leads to poorer predictive capability. The results of the second model, considering char, are far from the experimental data, and specifically, the simulation value of

CO is much higher than in experimental data, while the value of CO₂ is much lower.

Vaezi's model (2011) [48] is prepared to check the feasibility of the equilibrium model for downdraft gasifiers for heavy fuel oil. This work used an innovative numerical method to forecast the performance of a heavy fuel oil gasifier based on thermochemical equilibrium modelling. After obtaining the composition of the produced syngas, various parameters were studied. H₂:CO ratio, gasification temperature, heating value of produced gas, cold gas efficiency, and carbon conversion efficiency. Analysis is done on how the equivalent ratio, pressure, and oxygen enrichment—or how much oxygen is present in the gasification agent—affect the gasification properties. Since it is assumed that all of the carbon in the feedstock has been gasified, the creation of char is disregarded; the syngas is made up of H₂, CO, CO₂, H₂O, CH₄, and N₂, and the gasification process is thought to be adiabatic. The model predicted results were validated with Ashizawa et al. [49] results. In this model, oxygen is used as a gasification agent. The results of the composition of the produced gas are in good agreement with the experimental results. A parametric study demonstrated that syngas with a significant calorific value of roughly 15 MJ/m³ could be produced by gasifying heavy fuel oil at a low equivalent ratio of 0.32. Such a heating value for syngas makes it appropriate for gas turbines and other devices that burn gases with high specific gravity. Using pure oxygen as a gasification agent produces high specific gravity and hydrogen-rich syngas with a 42.5% hydrogen content by volume and an approximate H₂:CO ratio of 0.76. Such a high H₂:CO ratio syngas can be used to produce pure hydrogen for fuel cell applications and synthesize methanol. This study also reveals that gasification pressure does not significantly affect the gasification process.

Mendiburu's model (2014) [50], In this paper four models with modification of one over other are made and tested namely M1, M2, M3 and M4. These four models were tested to predict the syngas composition based on given input data, in which fuel blend, equivalence ratio, moisture content, and oxygen percentage in gasification agent are the variables. Model M1 is created based on Zainal et al. [43] and Mountouris et al. [51] model which assumes gasification temperature to predict the results (syngas compositions). Model M2 was a modified version of M1 in which the iterative method calculates gasification temperature. To improve model prediction accuracy, equilibrium constants are multiplied by variables α and β respectively as presented in Table 3. Model M3 utilize different correlation in the form of ration of CO/CO₂ and CO/H₂ as mentioned in Table 3. Model M4 implements a modification of the equilibrium equations of the water-gas homogeneous reaction and the Methane reforming reaction by substituting their respective equilibrium constants with the relations shown in Table 3.

The root mean square error was calculated to compare the numerical results predicted by the models with experimental results available in literature. Based on root mean square error, the conclusion is that Model M2 is best among all others.

Costa's model (2015) [52], A new model is created to combine a thermo-chemical equilibrium model which takes into account the formation of tar and char with an evolutionary algorithm-based optimization program (MOGA II) to determine the best correction factors to reduce the discrepancy between calculated and experimentally measured yields and temperatures. The procedure is repeated to replicate the thermal treatment of various biomasses with increasing carbon content, such as sawdust, rubber wood, treated wood, and straw. Comparable considerations are made for tar and char, respectively, as suggested by [53]. The experimental data for biomass rubber wood presented in ref. [54] is used to validate the model.

Aydin's model (2017) [55], The stoichiometric equilibrium model (SEM) proposed in this study can be used to predict, for a range of wood-based fuels and equivalent ratios (ER), the chemical composition of the syngas (hydrogen, carbon monoxide, carbon dioxide, methane) as well as the yield of tar and char produced by a downdraft gasifier. Global Stoichiometric equilibrium approach is used to make the model and predict the dry gas compositions. Three different models SEM1-3 are prepared and validated with the experimental data available. SEM1 is a full model, while SEM2 exclude tar and SEM3 exclude char. Two correction factors are introduced for Water gas shift reaction and Methanation reaction as a function of gasification temperature, equilibrium temperature, and ER (Table 3). These correction factors are obtained by comparison of theoretical model data with experimental data from literature using the Levenberg-Marquardt algorithm. The equilibrium temperature is calculated according to the following equation.

$$T_{eq} = \frac{-12400}{1.98 \ln \left(10^{-3.4} \frac{y_{CO}}{y_{CO_2}} \right)} \quad (4)$$

Where y_{CO} and y_{CO_2} are molar fractions of respective components. Models with correction factor increase the accuracy of models and RMSE decreases.

Upadhyay's model (2018) [31] in this paper, the thermodynamic equilibrium model is used to predict the producer gas compositions and lower heating value for seven different values of equivalent ratios (ER) ranging from 0.24 to 0.386 for the lignite and sawdust briquette (70:30, % wt) as fuel. The model predicts the gasification temperature by an iterative method using EES (Engineering equation solver) and then estimates the producer gas compositions. To avoid conversion issues, it is specifically mentioned not to assume temperature initially below 650 K and more than 1500 K. To increase the accuracy of predicted values correction factors based on ER (as shown in Table 3) for methane reaction and water gas shift reactions are developed by trial-and-error methods.

Table 3 Models with corrections or coefficients

Author(s) (Year)	Reference	Model	Constant(s)/Coefficient(s) or Modifications
S. Jarungham-machote et al.	[46]	M2	$0.91 \times K_2$ and $11.28 \times K_1$, where $K_2 = \frac{(nCH_4)}{(nH_2)^2}$ and $K_1 = \frac{(nCO_2)(nH_2)}{(nCO)(nH_2O)}$
Mendiburu et al. (2014)	[58]	M2	$\alpha = \max \left[\left(-\frac{1.639}{10^4} T^2 + 0.3518T - 128.7 \right), 1 \right]$, $\beta = 2.8 - 0.372\lambda$
		M3	$\frac{CO}{CO_2} = 2.18e^{-\frac{450.893}{T}}$, $\frac{CO}{H_2} = 0.92e^{-\frac{110.11}{T}}$
		M4	$K_{wgs} = e^{\left(\frac{4276}{T} - 3.961\right)}$, $K_{mr} = 1.198 \times 10^{13} e^{\left(\frac{-26830}{T}\right)}$
Aydin et al. (2017)	[55]	SEM2	$Cf_m = -778.4(ER) + 774.6e^{\frac{0.6639(ER)}{\left(\frac{T_{eq}}{T^*_{gas}}\right)^{-2}}} + 666.6$ $Cf_{wgs} = 3.194(ER) + 0.02912e^{\frac{4.23(ER)}{\left(\frac{T_{eq}}{T^*_{gas}}\right)^{-2}}} - 0.6354$
		SEM3	$Cf_{m,tar} = 2678 - 19920(ER) - 441.3 \left(\frac{T_{eq}}{T^*_{gas}}\right) + 23220(ER) \left(\frac{T_{eq}}{T^*_{gas}}\right) - 3069 \left(\frac{T_{eq}}{T^*_{gas}}\right)^2$ $Cf_{wgs,tar} = 1.183 - 46.06(ER) + 10.09 \left(\frac{T_{eq}}{T^*_{gas}}\right) + 56.56(ER) \left(\frac{T_{eq}}{T^*_{gas}}\right) - 13.72 \left(\frac{T_{eq}}{T^*_{gas}}\right)^2$
Upadhyay et al. (2018)	[31]		$Cf_m = 245104(ER)^4 - 296964(ER)^3 + 134912(ER)^2 - 26993(ER) + 2024.4$ $Cf_{wgs} = -6334.5(ER)^5 + 13593(ER)^4 - 11130(ER)^3 + 4399.3(ER)^2 - 846.18(ER) + 64.286$
Mazhko et al. (2021)	[57]		$Cf_m = -27.09 - 89.16(ER) + 65.96(e^{-0.17(ER)})$ $Cf_{wgs} = 1.49 + 11.79(ER) - 2.33(e^{2.31(ER)})$ $Cf_{tar} = -0.98 + 2.18(ER)$ $Cf_{char} = 0.02 + 7.58(ER)$

Different cases (total 65) based on combination of fuel, ER and moisture content were used for validation purposes. Major findings of this study is that, increment in ER increases the gasification temperature. With increment in ER, CO₂ content decreases, CO and N₂ increases, CH₄ and H₂ decreases.

Chidiebere Diyokey's model (2018) [56] A thermodynamic equilibrium gasification model is developed for the wood as fuel for downdraft gasifier and implemented in MATLAB to simulate. The downdraft gasifier was conceptually divided into three zones: the pyrolysis zone, the combustion/oxidation zone, and the reduction zone. Tar compositions and mole fractions are taken from the literature available as input parameters. By solving energy balance and mass conservation across each control volume and taking into account the rate of formation/consumption of the species according to different gasification kinetics, the concentration of syngas

and profiles of temperature along the reduction zone length were obtained. The simulations' results were in good agreement with the experimental data available. The syngas concentration was found to be about 1.1%, 17.3%, 22.8%, 9.0% and 49.8% for CH₄, H₂, CO, CO₂, and N₂ respectively and the corresponding LHV, CGE, CCE, and yield were 4.7 MJ/m³, 59.9%, 85.5% and 2.5 m³/kg-biomass respectively at ER of 3.1 and fuel moisture content of 18.5 wt.%. Sensitivity analysis was carried out with this validated model for different air-fuel ratios, moisture contents, and inlet air temperature. The analysis can be applied to produce specific design data or a downdraft biomass reactor, given the fuel composition and operating conditions. As the ER and MC increases, the LHV, CGE, and CCE decreases. The performance of the biomass gasifier in terms of yield, LCV, CGE, and CCE increases with inlet air temperature. The temperatures in the pyrolysis, oxidation, and reduction

zone of the gasifier lie between 654-510 K, 1221-1094 K, and 964-862K, respectively, at ER range of 3-5.2 and MC of 18 %. In this article author has defined ER as (A/F)stoichiometric/(A/F)Actual.

Mazhko's model (2021) [57] is a modified quasi-thermo-equilibrium model prepared to predict the syngas composition of H₂, CO, CO₂, H₂O, CH₄, and N₂ for the walnut shell as fuel. This model also predicts yields of tar and char during the gasification process. For model prediction improvisation, non-equilibrium correction factors are estimated and validated with the 40 experimental data available in literature with 25 various biomass feedstocks. The parameters varied in ER (0.2 to 0.45) and temperature (740K to 1300K). Two correction factors shown in Table 3 for Water-gas shift reaction and Methanation reaction are predicted from experimental data available and using Levenberg-Marquardt algorithm. To avoid convergence-related issues, the gasification temperature is calculated using the following equation [49].

$$T_{eq} = \frac{-12400}{1.98 \ln \left(10^{-3.4} \frac{y_{CO}}{y_{CO_2}} \right)} \quad (5)$$

After applying the correction factors, the RMSE was reduced from 5.02 to 2.19.

Ibrahim's model (2022) [6] takes into account the thermodynamic equilibrium of the global gasification reaction, forecasts the concentration of the minor gasification products of ammonia and hydrogen sulphide as the nitrogen- and sulphur-based contaminants, respectively, and applies a new empirical correlation to account for the mass tar yield that was developed using relevant experimental data that is currently available. The set of governing model equations are solved in fully coupled manner, to predict the char and ammonia Boudouard reaction and Ammonia synthesis reaction were used respectively. This model does not require the correction factor, which is almost necessary for existing equilibrium models. The producer gas composition, char, tar yields, lower heating value, and cold gas efficiency are obtained for different fuels with variable ER and moisture contents (MC). Results shows that as MC increases H₂, CH₄ and CO₂ increases but CO decreases. Gasification temperature increases ER and decreases with MC. As ER and T rise, the LHV and CGE also fall. While the concentration of H₂S stays nearly constant and slightly decreases with increasing ER and MC, the concentration of NH₃ decreases with increasing ER

Table 3 summerizes models with corrections and coefficients and Table 4 shows comparative analysis of different models.

6. Conclusions

Modelling and simulation studies may be very useful for studying complicated processes such as gasification without relying on time-consuming and expensive experimental approaches. Because of its simplicity, the thermodynamic equilibrium hypothesis is frequently

used in modelling investigations. However, equilibrium modelling offers the greatest yield possible under equilibrium circumstances, which are not the actual parameters of gasifier operation. As a result, the results are less dependable, and more precise modelling approaches, such as kinetic modelling, should be employed instead.

The present work reviews the most important models in the scientific literature applying the so-called stoichiometric method. The authors' aim is to discuss dedicated analyses regarding the effect of biomass moisture content (MC), gasification equivalence ratio (ER), pressure variations, and oxygen enrichment on the quality of the produced syngas, in particular in terms of lower heating value and cold gas efficiency (CGE) and how TEM were refined to improve their predictions. Researchers have prepared models that can predict the syngas constituents and modifications to improve the predicted values. Many researchers have modified their models by multiplying coefficients to equilibrium constants using either the trial-and-error method, regression, or multi-variable optimization methods. Many have taken the CH₄ constant as found in the experimental literature. Coefficient of equilibrium constants are function of temperature and/or ER.

Essentially, almost all presented models show that an increase in moisture content produces a decrease of lower heating value due to a reduction of the CO yield that has a greater weight with respect to the increase of H₂; an increase of equivalence ratio and pressure variations produce a decrease of lower heating value, due to the simultaneous decrease of CO and H₂; an increase of oxygen enrichment produces an increase of lower heating value, due to the simultaneous increase of CO and H₂. Analogous considerations are applicable to the cold gas efficiency of the gasification process.

7. Abbreviations

CCE	Carbon conversion efficiency
CGE	Cold gas efficiency
CV	Calorific Value
EES	Engineering Equation Solver
ER	Equivalence ratio
HHV	Higher heating value
LHV	Lower heating value
MC	Moisture content
QTEM	Quasi-Thermodynamic equilibrium model
RSME	Root means square error
SEM	Stoichiometric equilibrium model
SGY	Syngas yield
STEM	Stoichiometric thermodynamic equilibrium model
TEM	Thermodynamic equilibrium model
NC	Normal condition

Table 4 Comparative analysis of different models

Author(s) reference	Model and its predictions	Variables/Parameters	Model's Assumptions	Fuel Used	Parametric Study	Findings	Modification(s) in model if any
S. M. Chem et al [42]	Model predicts temperature, gas compositions and char yield.	Heat Loss (5% of wood HHV) Input conditions i.e Air/feed mass ratio (1.1 to 2.1) and moisture/feed mass ratio (0.05 to 0.3)	Output stream of the gasifier approaches an equilibrium Steady-state & Isobaric operation	Wood (CHL) 50300.681	Air/feed (1.1 to 2.1) and Moisture/feed (0.005 to 0.3) mass ratio	For all W/F, and A/F the model predicted results are in line with experimental results.	No modifications
Z. A. Zainal et al [43]	TEM (Gasification temperature is assumed not calculated) Compositions of producer gas and Calorific value	Moisture content in wood Temperature in gasification zone	All the reactions in thermodynamic equilibrium	Wood Paddy husk Paper Municipal-waste.	MC (0% to 40%) Temperature (750°C to 900°C)	Effect if MC on gas compositions (at 800°C) MC(I)→H ₂ (I), MC(I)→CO(D) MC(I)→CH ₄ (I), MC(I)→CV(D) At MC=20% T(I)→CV(D), (I=Increase, D=Decrease)	No modifications
S. Jarungthamachote et al [46]	TEM Second law efficiency of producer gas	Moisture content in wood	No heat loss All the reactions in thermodynamic equilibrium	MSW	For constant ER=0.4 MC (0% to 40%)	MC(I)→H ₂ (I) MC(I)→CO(D) MC(I)→CH ₄ (I) MC(I)→CV(D) MC(I)→CO ₂ (I) MC(I)→Temp(D)	Multiplying the equilibrium constants with coefficients Equilibrium constant for methane reaction (K2) is multiplied by 11.28* The equilibrium constant for water-gas shift reaction (K1) is multiplied by 0.91*
J. Huang et al [47]	TEM Compositions of producer gas	Four different models are tested to increase the model accuracy	All the reactions in thermodynamic equilibrium	lignocellulosic biomass Rubber wood Sawdust Biomass Solid waste	No parametric study is done	For the first model, the modifications resulting from β1 improve the predictive capability, whereas the modification by β1 and β2 leads to poorer predictive capability. The results of the second model, considering char, are far from the experimental data, and specifically, the simulation value of CO is much higher than in experimental data, while the value of CO ₂ is much lower.	M1(model without considering the char) M1F1(model M1 by fixing the fraction of CH ₄ only) M1F2(modification of Model 1 by fixing both yCH ₄ and yCO) M2(model with consideration of char) M2F1 (model M2 by fixing the fraction of CH ₄ only) M2F2(modification of Model 2 by fixing both yCH ₄ and yCO)

Table 4 Comparative analysis of different models (continuation)

Author(s), reference	Model and its predictions	Variables/Parameters	Model's Assumptions	Fuel Used	Parametric Study	Findings	Modification(s) in model if any
M. Vaezi et al [48]	TEM Predict the performance of a heavy fuel oil gasifier and Composition of produced syngas, and various characteristics of the gasification process like: H ₂ :CO ratio, process temperature, heating value of produced gas, cold gas efficiency and carbon conversion efficiency.	ER Oxygen enrichment Pressure	Chemical and thermodynamic equilibrium is considered. The residence time of the reactants are supposed to be high enough to reach chemical equilibrium. All carbon in feedstock is assumed to be gasified and, therefore, the formation of char is neglected; the syngas is comprised of H ₂ , CO, CO ₂ , H ₂ O, CH ₄ and N ₂ ; and the gasifier is considered to be adiabatic.	Heavy oil	ER:0.32 to 0.7 Oxygen enrichment: 21% to 100% Pressure: 10 atm to 80 atm Effect of ER, oxygen enrichment and pressure on H ₂ :CO ratio	study reveals that the heavy oil gasification is a feasible process that can be utilized to generate a syngas for various industrial applications	
A. Z. Mendiburu et al [58]	TEM Syngas compositions	Fuel-Blend ER MC Oxygen Percentage	No heat loss All the reactions in thermodynamic equilibrium	Hardwood-Glycerol mixture 80% and 20% respectively	ER:0.3 to 0.5 MC:0% to 20% Oxygen percentage: 100%, 60% and 21%	Out of four different modified models M1 to M4. Model M2 predicts the result most accurately.	M1: TEM model without any modification M2: variables were multiplied to the equilibrium constants of the methane formation reaction and the water-gas shift reaction respectively. (Refer Table 3) M3: implements correlations presented in Eq. (1) and Eq. (2) (Refer Table 3) M4: implements a modification of the equilibrium equations of the water-gas homogeneous reaction and the methane reforming reaction by substitution of their respective equilibrium constants with the relations shown in Eq. (32) and Eq. (33). (Refer Table 3)
M. Costa et al [52]	TEM predicts the released syngas composition, char, tar content and temperature in biomass gasifiers	Equilibrium Constants (EC) Multiplier to EC	Not specified But common is All the reactions in thermodynamic equilibrium	Rubber Wood Straw Treated Wood Sawdust	EC of water gas shift reaction EC of methane formation reaction EC of Boudouard reaction	Although a unique set of correction factors is not found, the procedure leads to quite reliable results under all the considered situations.	TEM is modified to find optimum EC for different reactions by using multi-objective genetic algorithm (optimization technique) using MATLAB.

Table 4 Comparative analysis of different models (continuation)

Author(s), reference	Model and its predictions	Variables/Parameters	Model's Assumptions	Fuel Used	Parametric Study	Findings	Modification(s) in model if any
E. S. Aydin et al [55]	TEM Predicts chemical composition of the syngas, yield of char and tar.	ER	The biomass consists of carbon, hydrogen, oxygen and nitrogen only. Gasifier is in thermodynamic equilibrium. Oxidizing agent is dry at a temperature of 25 C and the system is at a pressure of 101.13 kPa. The syngas includes CO, CO ₂ , H ₂ , H ₄ , N ₂ , H ₂ O and Tar. Nitrogen is not involved in any chemical reaction inside the system. The gasifier is completely adiabatic and there is no heat loss from the gasifier. Gasification reaction rates are fast enough and residence time is sufficiently long to reach the equilibrium state. Ashes are inert.	Various wood-based fuels	Gasification Temperature: 973-1390 K ER: 0.21 to 0.5	Models with correction factor increase the accuracy of models and RMSE decreases.	Introduced two correction factors for altering the equilibrium constant of methanation and the water-gas shift reaction as a function of gasification temperature, equilibrium temperature and ER (Refer Table 3) by using Levenberg-Marquadt algorithm.
D. S. Upadhyay et al [31]	TEM Syngas Composition Gasification temperature & LHV	ER	No heat loss All the reactions in thermodynamic equilibrium	lignite and sawdust briquette (70:30,%wt.)	ER: 0.24, 0.274, 0.296, 0.322, 0.346, 0.376, 0.386	Modified model is more accurate than unmodified. Then parametric study is performed to understand the effect of particular parameter on output.	Two correction factors for methane reaction and water gas shift reactions were developed to increase the accuracy of model by trial-and-error method, based on polynomial relations. (Refer Table 3)
C. Divoke et al [56]	TEM Syngas concentration Profiles of temperature along the reduction zone. LHV CGE CCE	ER ER = (A/F)stochastic/(A/F)Actual MC	All the elemental hydrogen and oxygen in fuel is released during de-volatilisation; and hence the char formed is modelled as pure carbon Char yield in the gasifier is insensitive to pyrolysis temperatures encountered in the pyrolysis zone Temperature of the volatiles is the same as char temperature at every point in the gasifier (i.e. transfer of heat between gas and solid is instantaneous) The nitrogen content of the biomass (if any) is presumed to form inert nitrogen gas and the thermal formation of nitrogenous compounds such as HCN and NH ₃ is ignored. Heat Loss is 12% of the product of LHV	Wood (CH1.54O0.63)	Chip Size: 3.3 to 5.5 cm MC: 11-18% ER=3 to 5.2	Initial prediction of model was not in agreement of experimental data. After multiplying with coefficient of 0.05, results got improved.	to increase the accuracy of the model prediction results, modifications were done to the (CO ₂ /CO) molar ratio (NCO/NCO ₂) by multiplying it by a coefficient (K) in the calculation procedure. K=0.05 is taken.

Table 4 Comparative analysis of different models (continuation)

Author(s), reference	Model and its predictions	Variables/ Parameters	Model's Assumptions	Fuel Used	Parametric Study	Findings	Modification(s) in model if any
Shahin Mahkoo et al [57]	QTEM Syngas Composition Yield of Char and Tar	ER Reduction temperature	No heat loss All the reactions in thermodynamic equilibrium	Walnut shell	ER: 0.2 to 0.45 Reduction temperature: 740 to 1300 K	The syngas composition was found to be 15.42–14.78 % H ₂ , 17.31–16.87% CO, 6.93–7.29% CO ₂ , 3.41–2.77% CH ₄ , and 56.93–58.29% N ₂	TEM1: Model without char and Tar TEM2: Model with Char TEM3: Model with Tar TEM4: Model with char and Tar TEM5: Modified model (Optimized Model)
A. Ibrahim et al [6]	TEM Syngas yield Also predicts concentration of minor gasification products like: Hydrogen sulphide and ammonia tar and char yields, gasification temperature, cold gas efficiency and lower heating value.	ER MC	1. The gasifier operates under steady state conditions; 2. The residence time is infinite; 3. Nitrogen is considered inert; 4. The process is adiabatic; 5. The contribution of char and ash to the energy balance equation is negligible; 6. The total pressure is assumed constant (i.e. P ₀ = 101, 325 Pa), however, the partial pressure of the syngas components is not and is determined via their chemical equilibrium; 7. reactants are at standard temperature (i.e. T ₀ =298.15 K), while products are at the unknown T. 8. tar, at standard conditions, is a mixture of liquid and gas, with its thermodynamic properties taken to be those of benzene; 9. char is assumed to have the same thermodynamic properties as graphite.	various biomass feedstock	ER: 0.2 to 0.4 MC: 0% to 40%	1. The concentrations of H ₂ and CO ₂ increase with MC, while the CO concentration decreases. N ₂ concentration remains constant while CH ₄ concentration gradually increases with increasing MC. 2. T increases with ER and decreases with MC for gasification reasons mentioned in 3.1.2. 3. The tar yield decreases with increasing ER and MC due to a better-quality syngas. 4. The Boudouard reaction is a reliable approach for predicting char yield. 5. The LHV and CGE decrease with an increase in ER and T. 6. The concentration of NH ₃ decreases with increasing ER values and increases with increasing MC, while the concentration of H ₂ S remains almost constant, decreasing slight with increasing ER and MC. 7. It is shown that equilibrium models are able to provide reliable predictions of syngas composition.	Implements a new empirical correlation, formulated using existing pertinent experimental data, to account for the mass tar yield.

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