COMPREHENSIVE THERMODYNAMIC EQUILIBRIUM MODEL WITH MODIFIED EQUILIBRIUM CONSTANTS FOR BIOMASS DOWNDRAFT GASIFIERS

Dipakkumar J. Parmar[1], Vimal R. Patel[2*], Shyam K. Dabhi[3], Mazar A Shaikh[4]

[1]Gujarat Technological University, Gujarat, India
[2,4]Automobile Engineering Department, L.D. College of Engineering,
Gujarat Technological University, Ahmedabad, Gujarat,380 015, India
[3]Mechanical Engineering Department, Government Engineering College, Palanpur,
Gujarat Technological University, Gujarat, India
*Corresponding Author Email Addresses: vimalpatel@live.com
Automobile Engineering Department, L.D. College of Engineering, Ahmedabad, Gujarat, India

This paper proposes a novel, comprehensive stoichiometric thermodynamic equilibrium model to forecast the chemical compositions of syngas from a downdraft gasifier for various biomass fuels. The principal objective of this model is to predict the chemical compositions of syngas while reducing the individual percentage error in the estimation of moles of different species, hence attaining a minimal Root Mean Square Error (RMSE). Model is prepared as available in literature and then modified for the different kind of fuels and biomasses to minimize error in prediction. The model is developed to find out two modified equilibrium constants, 1.01 and 0.65 for water-gas-shift reaction and methane reaction respectively in thermodynamic equilibrium model (TEM) which can be applicable to all types of fuels. This will make this comprehensive stochiometric thermodynamic equilibrium model a generalized for all kind of fuels. Many researchers have modified the thermodynamic equilibrium models for different kind of fuels, which makes their model fuel specific. Here the model prepared is generalized for all kind of fuels.

Key words: Thermodynamic equilibrium model, Generalized, Gasification, Modified equilibrium constants

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1. Introduction

The energy demand of the world is continuously rising. This has resulted in increased environmental pollution. There is a need to bring and promote the technologies which may be utilized to generate energy from conventional and unconventional fuel without polluting environment. “Biomass gasification - a thermochemical conversion of biomass” may be considered to produce a high-quality syngas (clean fuel) in the gasifier and is considered as a “Carbon-neutral” fuel[1].

Gasification is typically conducted in one of three principal kinds of gasifiers: fixed bed, fluidized bed, and entrained flow gasifiers. Every type of gasifier has advantages and disadvantages [2], but a survey of gasifiers in countries of Europe, Canada, and the United States indicates that downdraft gasifiers are the predominant kind. Seventy-five percent (75 %) are downdraft, twenty percent (20 %) are fluidized beds, two-point five percent (2.5 %) are updraft, and two-point five percent (2.5 %) comprise various other types[1].

The effective functioning of a downdraft gasifier relies on various aspects, including chemical reactions, different operational parameters, design of reactor, and fuel compositions. The gasification process, along with syngas quality and gasifier performance, is significantly affected by various operational factors, including the flow rates of both feedstock and gasifying medium, equivalence ratio, and the reactor's pressure and temperature. In addition to operation parameters, composition and thermochemical properties of feedstock affects the gasification process and end products. As a result, the modeling approach may be applied to any reactive system to determine the impact of operational parameters such as moisture content (MC), equivalence ratio (ER), and fuel mixture ratio on producer gas composition, heating value, and cold gas efficiency.

TEMs are designed for reacting systems using either stoichiometric or non-stoichiometric techniques. Stoichiometric equilibrium models are founded on the equilibrium constant and can be formulated by integrating chemical and thermodynamic reactions. Using free energy data, the equilibrium constant for specific reaction may be calculated. In the stoichiometric method, not all reactions are accounted for, leading to the exclusion of less significant events, which may cause deviations in model predictions. The stoichiometric equilibrium model accounts just for species with the minimum free energy of production. The predominant species under gasification conditions (temperature range of 600 to 1500 K) include CO, CO_2, H_2, H_2O, CH_4, N_2, and solid carbon[3].

Numerous models exist in the literature for the biomass and coal gasification process in downdraft gasifiers. Conclusion of thorough study of these models shows, models are either fuel specific or some parameter specific. A more advanced model is required that can be generalized for all types of fuels. The modifications done to the TEM are for accurate prediction for particular fuels only. Parmar et al.[2] compared many models and findings of them are tabulated to get the overall idea of kind of modifications done to the models to improve model’s

accuracy. Zainal et al.[4] has prepared a TEM to forecast the effect of Moisture Content (MC) on producer gas compositions and effect of gasification temperature on Calorific Value (CV). The limitation of this model is, it takes gasification temperature of 800 °C constant for parametric study. Jayah et al.[5] developed a model to examine the influence of chip size, MC, temperature of inlet air, heat loss, and throat angle on conversion efficiency. The model was employed to ascertain the variation of the CO:H_2 ratio with fuel MC at a constant pressure. The projected methane quantity was modified to match the experimentally measured amount of methane in the produced gas. This model was fuel specific for rubber wood. S. Jarungthammachote et al. [6] has used modified TEM for municipal solid waste. They have introduced coefficient of 0.91 for the equilibrium constant of water-gas-shift reaction (K_{wgs}) and 11.28 for equilibrium constant of methane reaction (K_m).

Darshit et al.[7] has prepared a modified TEM to calibrate his experimental work and to predict the effect of ER on the performance of the gasifier. Fuel used here for experimental work is mixture of lignite (70%) and sawdust pallets (30 %) respectively. The correction factor for equilibrium constants of methane reaction (K_m) and water-gas-shift reaction (K_{wgs}) are formulated by using regression method. These correction factors are based on ER only.

Aydin et al.[8] formulated a semi empirical equilibrium model for downdraft gasification systems to forecast the syngas compositions, as well as the yields of tar and char from various wood-based fuels across different equivalence ratios. The model proposed by Chaurasia [9] integrates crucial effects of the pyrolysis fraction and char reactivity factor in its simulations for downdraft biomass gasification. Patra et al. [10] proposed a dynamic multiphase model that combines mass and energy transfer with kinetics for wood gasification in a downdraft gasifier. A stochiometric and non-stochiometric model proposed to study parameter effects in the gasification process of a feedstock in downdraft gasifiers [11], [12], [13]. Babu and Seth[14] presented a modified model for reduction zone of downdraft biomass gasifier incorporating the variation of the char reactivity factor (CRF). A mathematical model for studying the effect of fuel/air ratio and the moisture content of the biomass on producer gas composition is presented by Melgar et al. [15]. Gao and Li [16] proposed a model to predict the behavior of global fixed bed biomass gasification reactor. An equilibrium model is also proposed by numerous researchers[17], [18], [19].

This paper develops a novel comprehensive thermodynamic equilibrium model to simulate the gasification process of various fuels and biomass. The integration of mass balance, energy balance, and equilibrium constant equations provide a method for estimating gas compositions. The model was then adjusted to enhance its predictive accuracy by multiplying equilibrium constants with corrective factors. This model seeks to improve the forecasting precision of TEM across a wide range of fuels, positioning it as a versatile model rather than one tailored to a specific fuel type.

2. The Model

The thermodynamic equilibrium model defines the feedstock as $CH_xO_yN_z$, with the global gasification reaction process expressed as follows:

$$CH_xO_yN_z + wH_2O + m(O_2 + 3.76N_2) = n_{H_2}H_2 + n_{CO}CO + n_{CO_2}CO_2 + n_{H_2O}H_2O + n_{CH_4}CH_4 + \left(\frac{z}{2} + 3.76m\right)N_2 \quad (1)$$

In this context, suffixes *x*, *y*, and *z* signify the amounts of hydrogen, oxygen, and nitrogen atoms, respectively, per carbon atom in the feedstock. Additionally, *w* signifies the amount of moisture per kmol of feedstock, while *m* indicates the quantity of oxygen per kmol of feedstock.

From the ultimate analysis of fuel/feedstock (Table 2) the percentage of carbon, hydrogen, oxygen, nitrogen, sulphur and ash is determined. From the known percentage of different constituents, the 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 the aforementioned equation, *'C%', 'H%', 'O%'*, and *'N%*' represent the mass fractions of carbon, hydrogen, oxygen, and nitrogen in the fuel, whereas *'Mi'* denotes their molecular weights. The variable 'w' in Equation 1 denotes the molar amount of water per kilomole of fuel mixture, whereas '*m*' signifies the molar quantity of oxygen per kilomole of fuel mixture, which is contingent upon the stoichiometric molar quantity of oxygen and the equivalence ratio; it may be computed using the following expression:

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

where '*ER'* is equivalence ratio and '*WC'* is moisture content in fuel.

Every input on the left side of Equation (1) is set to 25 °C. The number of moles of species *'i'* that are unknown is represented by *'n_i'* on the right-hand side.

2.1. Model assumptions

The gasifier may be seen as thermodynamic system, whereby biomass enters and producer gas exits the reactor. The model assumes that the feedstock for a gasifier is composed of carbon, hydrogen, oxygen, and nitrogen, with no sulphur or other minerals. The gasifier operates under steady state conditions with uniform temperature and pressure. The reaction is auto thermal, with high temperature and fast reaction rates. The products are CO, CO_2, H_2, H_2O, CH_4, and N_2, with higher order hydrocarbons neglected. Nitrogen is considered an inert gas, and no tar is present in the product gas. All gases behave ideally, and ash is an inert substance[20].

2.2. Mass balance

To identify the five unknown species, a total of five equations is necessary. Among these five equations, three are derived from the conservation of elemental mass in the reactants and products, while the other two are based on the connection of equilibrium constants.

Carbon balance:

$$1 = n_{CO} + n_{CO_2} + n_{CH_4} \quad (4)$$

Hydrogen balance:

$$x + 2w = 2n_{H_2} + 2n_{H_2O} + 4n_{CH_4} \quad (5)$$

Oxygen balance:

$$w + 2m + y = n_{CO} + 2n_{CO_2} + n_{H_2O} \quad (6)$$

2.3. The thermodynamic equilibrium

Chemical equilibrium is often elucidated using two distinct approaches: the reduction of Gibbs free energy or the application of an equilibrium constant. The current thermodynamic equilibrium model is formulated based on the equilibrium constant rather than the Gibbs free energy. To analyse the global gasification process, a total of five equations are necessary for resolution. Three equations are derived from mass balance, while the other two are generated from the equilibrium constants of the reactions happening in the gasification zone, as seen below.

Boudouard reaction:

$$C + CO_2 \leftrightarrow 2CO \ (+172\ MJ/kmol) \quad (7)$$

Steam forming reaction:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \ (+206\ MJ/kmol) \quad (8)$$

Methane reaction:

$$C + 2H_2 \leftrightarrow CH_4 \ (-75\ MJ/kmol) \quad (9)$$

Water gas reaction:

$$C + H_2O \leftrightarrow CO + H_2 \ (+131\ MJ/kmol) \quad (10)$$

Water gas shift reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \ (-41\ MJ/kmol) \quad (11)$$

To create the equilibrium model, the reactions must be identified and confirmed for their independence. If the chosen reactions belong to a certain group and none can be expressed as a combination of at least two others, this group is termed independent. If the generated group lacks independence, the model may compute redundant information. When unconverted carbon persists in the equilibrium state, three distinct processes must be accounted for to finalize the equilibrium model. If three independent reactions must be selected, then 10 possible groups may be formed from equations 07-11. Of the 10 groupings, two are dependent, while the remaining eight are independent.[11]. There is no compelling rationale to choose one independent group over another for the validation of the model against experimental results. Numerous scholars have examined the solid (unconverted carbon or char) result in the global gasification process and produced a model.[21], [22]. The water-gas-shift reaction (Eqn-11) and Methane reaction (Eqn-9) were used by S. Jarungthammachote et al.[6], [7] and many more for their models.

As discussed earlier, three equations are generated using mass balance of elements, two more equations are formulated for methane and water-gas-shift reactions (Eqs. 9, 11).

Methane reaction:

$$C + 2H_2 \leftrightarrow CH_4 \ (-75\ MJ/kmol)$$

Water gas shift reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \ (-41\ MJ/kmol)$$

2.4. The equilibrium constant formulation

Assuming all gases participating in the process exhibit perfect behaviour and all reactions occur at low working pressure (1 atmosphere), the equilibrium constant for methane and water-gas-shift reactions as a function of their molar content may be expressed as follows:

$$\mathrm{K_m} = \frac{\mathrm{P_{CH_4}}}{(\mathrm{P_{H_2}})^2} = \frac{\mathrm{n_{CH_4}}}{(\mathrm{n_{H_2}})^2} \quad (12)$$

$$\mathrm{K_{wgs}} = \frac{\mathrm{P_{CO_2} P_{H_2}}}{\mathrm{P_{CO} P_{H_2O}}} = \frac{\mathrm{n_{CO_2} n_{H_2}}}{\mathrm{n_{CO} n_{H_2O}}} \quad (13)$$

Eqs. (14) and (15) were used for the equilibrium state of ideal gas mixture because of the requirements of K_m and K_{wgs} values

$$\ln \mathrm{K} = -\frac{\Delta \mathrm{G^o_T}}{\bar{\mathrm{R}}\mathrm{T}} \quad (14)$$

$$\Delta \mathrm{G^o_T} = \textstyle\sum_{\mathrm{i}} \mathrm{v_i}\, \Delta \bar{g}^o{}_{f,T,i} \quad (15)$$

Where $\bar{R}$ is the universal gas constant, 8.314 kJ/kmol K, $\Delta G^o{}_T$ is the standard Gibbs function of reaction, and $\Delta \bar{g}^o{}_{f,T,i}$ represents the standard Gibbs function of formation at given temperature T of the gas species *i* which can be expressed by the empirical equation below

$$\Delta \bar{g}^o{}_{f,T} = \bar{h}^o{}_f - a'T\,ln(T) - b'T^2 - \left(\frac{c'}{2}\right)T^3 - \left(\frac{d'}{3}\right)T^4 + \left(\frac{e'}{2T}\right) + f' + g'T \quad (16)$$

The values of coefficients a'- g' and enthalpy of formation of the gases are presented in Table 3.[6]

2.5. Energy Balance

The gasification zone temperature must be estimated to determine the equilibrium constants (Eqs. 12-13). For this reason, either an energy or enthalpy balance was done for the gasification process, which was normally believed to be an adiabatic process.[4].

The enthalpy balance for the gasification process may be expressed as follows, with the gasification zone temperature denoted as T and the input state temperature assumed to be 298 K.

$$\textstyle\sum_{j=react} \bar{h}^o{}_{f,j} = \sum_{i=prod} ni\left(\bar{h}^o{}_{f,i} + \Delta \bar{h}^o{}_{T,i}\right) \quad (17)$$

Where $\bar{h}^o{}_{f,j}$ is the enthalpy of formation in kJ/kmol and for all chemical elements at reference state (298 K and 1 atm) its value is zero. $\Delta \bar{h}^o{}_{T,i}$ represents the enthalpy difference between any given state and at reference state. It can be approximated by

$$\Delta \bar{h}_T = \int_{298}^{T} \bar{C}_p(T)\,dT \quad (18)$$

Where $\bar{C}_p(T)$ is specific heat at constant pressure in kJ/kmol-K and is a function of temperature. It can be defined by empirical equation below

$$\bar{C}_p(T) = a + bT + cT^2 + dT^3 \quad (19)$$

Where T is temperature in K and

$$\int_{298}^{T} \bar{C}_p(T)dT = aT + bT^2 + cT^3 + dT^4 + k \quad (20)$$

Where k is a constant obtained from the integration and a, b, c, and d are the specific gas species coefficients, which are shown in Table 4[23]

Equation 17 can be rewritten as

$$\sum_{j=react} \overline{h_{f_j}}^{o} = \sum_{i=prod} ni\, \overline{h_{f_i}}^{o} + [(\sum_i n_i a_i)T + (\sum_i n_i b_i)T^2 + (\sum_i n_i c_i)T^3 + (\sum_i n_i d_i)T^4 + (\sum_i n_i k_i)] \quad (21)$$

To find the enthalpy of formation for any solid fuel in reactant, De Souza-Satos[24] suggested

$$\bar{h}^o_{f,fuel} = LHV + \sum_{k=product} \left[n_k \left(\bar{h}^o_f\right)_k \right] \quad (22)$$

where $\left(\bar{h}^o_f\right)_k$ represents the enthalpy of formation of product 'k' during the entire combustion of the solid fuel, and LHV denotes the lower heating value of the solid fuel in kJ/kmol. The temperature in the gasification zone may now be computed from Eq. (17) using the Newton-Raphson approach. This correlation can forecast the reaction temperature based on the quantity of oxygen present. This makes the model an effective instrument for demonstrating the fluctuation in reaction temperature when the mole of oxygen is altered.

Formula for finding the enthalpy of formation of solid fuel in reactant is (HHV in MJ/kg) [25]

$$HHV\left({}^{MJ}/_{kg}\right) = 0.3491 \times C\% + 1.1783 \times H\% + 0.1005 \times S\% - 0.1034 \times O\% - 0.0151 \times N\% - 0.0211 \times A\% \quad (23)$$

$$LHV = HHV - \left(\frac{9 \times H\% \times hfg}{100}\right) \quad (24)$$

2.6. Calculation Procedure

To calculate the values of $n_{H_2}, n_{CO}, n_{CO_2}, n_{H_2O}, and\ n_{CH_4}$ an initial temperature was assumed and used into Eqs. (16) and (14) to initially compute K_m and K_{wgs}. Then both the equilibrium constants were substituted into Eqs. (12) and (13) respectively. The five simultaneous equations, Eqs. (4), (5), (6), (12), and (13), were ultimately solved using the Newton-Raphson technique. Using Eqn. (21), the new value of temperature is calculated. The specified method was repeated until the temperature value converged. The computation technique is shown in Figure 1. The initial model which is TEM is termed as M1.

3. Validation and modification in the model

The model constructed (M1) in this work was evaluated by juxtaposing the computational findings with the experimental data found in the literature. Table 2 presents a total of 17 distinct fuels together with their experimental findings used for model testing. The root-mean-square error (RMSE) quantifies the discrepancy in this comparison and is defined as

$$RMSE = \sqrt{\frac{\sum_i^N (Exp_i - Mod_i)^2}{D}} \quad (25)$$

where D is the number of data values, Exp is the value derived from the experimental results, and Mod is the value projected by the model.[6]

Considering different fuels from research articles of many researchers, it is found that the number of moles of different species varies in the range of following

Tab. 1 Name of species with percentage of moles and effect on RMSE

Sr. No.	Name of Species	Number of moles (%) of total moles	Effect of % error of individual on RMSE
1	CO	16 % to 24 %	Moderate
2	CO_2	11 % to 17 %	Moderate
3	CH_4	2 % to 4 %	Minimum
4	H_2	12 % to 20 %	Moderate

It is very much clear from data that CH_4 varies from 2 % to 4 % only. Considering very low value of CH_4, it is obvious that its impact on RMSE value is very less. This model neglects individual percentage error of CH_4. Remaining species values are calculated using algorithm as mentioned in figure 1. Total 17 cases are taken for calculation of moles of species. (Table 2)

After testing all the biomass/feedstock into model, the results predicted by model is as below in Table 5. Initial model M1 predicts the average moles of CO more by 16.71 %, moles of CO_2 less by 6.11 %, moles of H_2 more by 28.79 %, moles of N_2 less by 12.3 %

As mentioned in above table, to reduce the RMSE and individual percentage error, the major concern is to focus on moles of CO, CO_2, and H_2 and not on the CH_4. A new improved model is made to minimize the RMSE and individual percentage errors by doing certain modifications in Model M1.

Many studies indicate that the TEM requires correction factors to accurately predict syngas compositions. Numerous researchers have proposed correction factors for equilibrium constants; however, these factors are specific to individual fuels and lack general applicability. This study aims to derive a generalised correction factor applicable to any fuel or biomass. The modified model is designated as M2. This novel approach is outlined sequentially as follows:

The TEM is initially applied to the collection of fuels or biomass for which experimental results are documented in the literature. Following the application of the TEM to the fuel/biomass, the results are compared with experimental values for validation purposes. The TEM results are deemed reliable. Researchers typically employ the RMSE method to compare model predictions with experimental values. Although the RMSE values are approximately 6 or lower, it is occasionally noted that individual percentage errors in predictions can be significantly high.

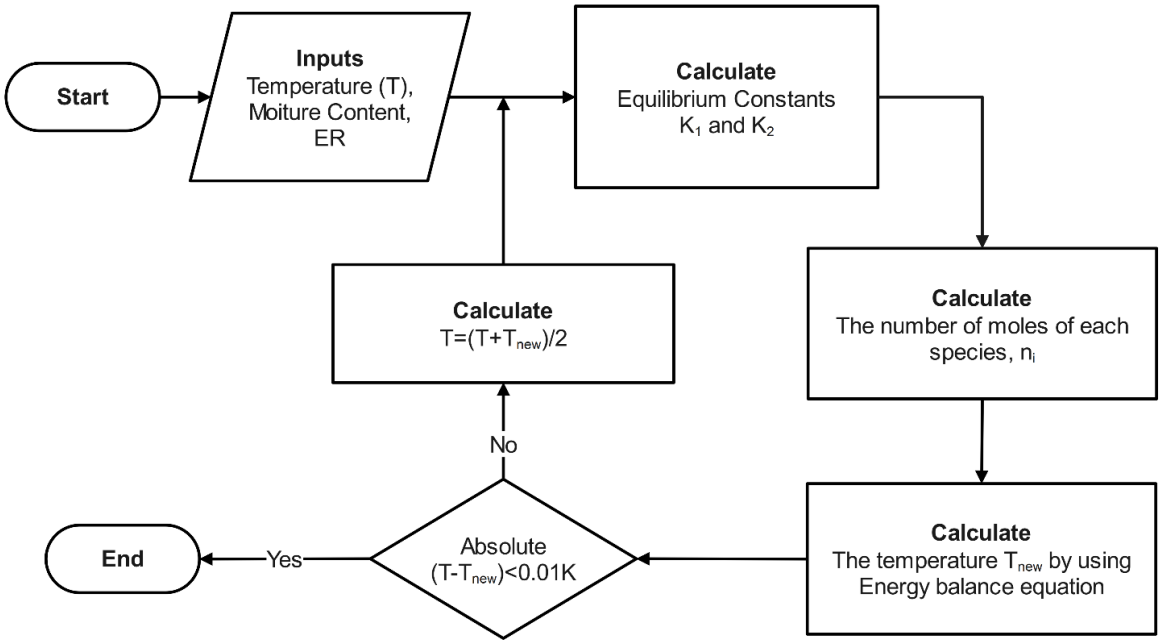

Fig. 1 Flowchart for calculation process of TEM (M1)

Tab. 2[7] Ultimate and proximate analysis of fuels

Components	Ultimate Analysis				Proximate Analysis					
Biomass/Feedstock	C	H	O	N	FC	VM	MC	Ash	HHV	Ref.
	wt % db	wt % db	wt % db	wt % db	wt % db	wt % db	wt % db	wt % db	MJ/kg	
Aspen Chips	49.30	5.50	45.20	N/A	14.70	84.90	6.80	0.40	19.88	[26]
Wood Chip	46.50	5.80	43.50	0.20	14.30	60.90	21.70	3.90	18.66	[27]
HWC 20	52.58	6.61	41.05	0.10	N/A	N/A	N/A	1.14	18.71	[28]
Wood	50.60	6.50	42.00	0.20	19.20	80.10	14.00	0.70	20.50	[5]
Rubber Wood	50.70	6.90	42.40	0.30	N/A	N/A	7.58	0.39	18.86	[29]
Corn Cobs	47.60	6.10	45.78	0.52	17.82	80.06	10.01	2.12	18.56	[30]
Soft Wood	49.20	6.20	44.06	0.08	15.20	79.20	5.20	0.40	19.00	[31]
Depleted pomace	51.31	6.40	35.01	2.00	NA	NA	6.80	5.00	NA	
Wood Pellets	48.91	5.80	45.11	0.18	17.27	80.63	9.50	2.10	18.40	[30]
Rice Husk	49.44	6.25	43.77	0.54	15.45	67.95	12.50	16.60	15.60	[30]
Eucalyptus	46.78	5.92	45.55	0.32	15.66	83.01	12.23	1.34	18.78	[32]
Municipal Solid Waste	50.60	6.50	42.00	0.20	NA	NA	16.00	0.70	NA	[6]
Wood sawdust pellets	48.91	5.80	45.11	0.18	17.27	80.63	9.50	2.10	18.43	[33]
Mixed Wood	48.77	5.85	44.52	0.05	12.80	75.80	10.60	0.80	17.30	[31]
Oil Palm Fronds	42.40	5.80	48.20	3.60	11.50	85.10	N/A	3.40	15.72	[34]
Vine Pruning	50.84	5.82	42.46	0.88	16.54	80.84	17.60	2.62	18.10	[30]
Lignite and wood mixture	37.80	4.93	55.50	1.63	NA	NA	12.00	0.00	NA	[20]

Tab. 3 The values of $\overline{h_f}^o$ (kJ/mol) and coefficients of the empirical equation for $\Delta\overline{g_{f,T}}^o$ (kJ/mol) [6]

Compound	hf	a'	b'	c'	d'	e'	f'	g'
CO	110.5	5.619 x 10^{-3}	-1.190 x 10^{-5}	6.383 x 10^{-9}	-1.846 x 10^{-12}	-4.891 x 10^{2}	8.684 x 10^{-1}	-6.131 x 10^{-2}
CO_2	-393.5	-1.949 x 10^{-2}	-3.122 x 10^{-5}	-2.448 x 10^{-8}	6.946 x 10^{-12}	-4.891 x 10^{2}	5.270	-1.20 x 10^{-1}
H_2O	-241.8	-8.950 x 10^{-3}	-3.62 x 10^{-6}	5.209 x 10^{-9}	-1.478 x 10^{-12}	0.00	2.868	-1.722 x 10^{-2}
CH_4	-74.8	-4.620 x 10^{-2}	1.130 x 10^{-5}	1.319 x 10^{-8}	-6.647 x 10^{-12}	-4.891 x 10^{2}	1.411 x 10^{1}	-2.234 x 10^{-1}

Tab. 4 The coefficients of specific heat for the empirical equation [6]

Gas Species	a	b	c	d	Temperature Range (K)
Hydrogen	29.11	-1.92 x 10-3	4.0030 x 10-6	-8.7040 x 10-10	273-1800
Carbon monoxide	28.16	1.68 x 10-3	5.3720 x 10-6	-2.2220 x 10-9	273-1800
Carbon dioxide	22.26	5.98 x 10-2	-3.5010 x 10-5	-7.4690 x 10-9	273-1800
Water vapour	32.24	1.92 x 10-3	1.0550 x 10-5	-3.5950 x 10-9	273-1800
Methane	19.89	5.20 x 10-2	1.2690 x 10-5	-1.1010 x 10-8	273-1800
Nitrogen	28.90	-1.57 x 10-3	8.0810 x 10-6	-2.8730 x 10-9	273-1800

A novel approach is applied to the TEM to reduce individual percentage error and, consequently, RMSE. Literature indicates that correction factors enhance the accuracy of model predictions. Optimisation techniques are employed to identify the optimal correction factor that minimises the RMSE. This model utilises two independent reactions: the methane reaction and the water-gas shift reaction. The value of 'K_m' is initially optimised while maintaining 'K_{wgs}' constant to assess its impact on RMSE. The 'K_m' corresponding to the minimum RMSE has been recorded. The same process is employed for 'K_{wgs}' optimisation. The model is then tested for simultaneous values of the newly optimised 'K_m' and 'K_{wgs}'.

The RSME identified a minimum in this instance. This protocol is applied consistently across all 17 fuels and biomasses. The results were analysed in relation to the experimental values and the predicted values from TEM M1. After the application of both modified equilibrium constants, a decrease in the RMSE value is observed, along with a simultaneous reduction in individual percentage errors. The procedure is illustrated in the flowchart below (Figure 2).

Results as tabulated in Table 5 shows that average of individual percentage error decreases, and hence the results are more accurate compared to model M1

4. Results and discussion

Due to variations in design, the producer gases generated by downdraft gasifiers exhibit distinct compositions. Prediction results of two models M1 and M2 are tabulated in Table 5.

The two distinct coefficients are obtained from model M2 for the equilibrium constants K_m and K_{wgs}. After multiplying the coefficients by the equilibrium constants, two modified equilibrium constants, 1.01 and 0.65 were obtained. These numbers were derived from the average of 17 distinct fuels.

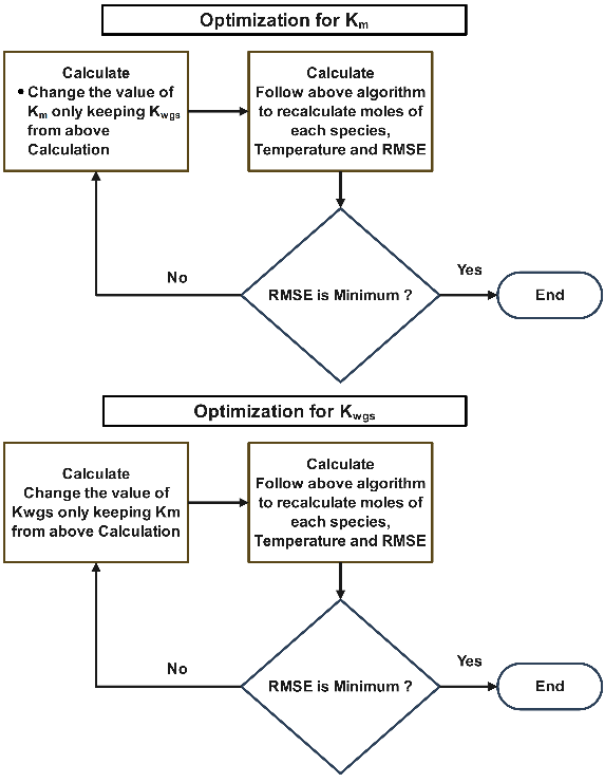

Fig. 2 Optimization for Km and Kwgs

The M1 model estimates the average moles of CO for 17 fuels to be 23.55, above the experimental value of 20.18, which is more by 16.71 %. The estimated moles of CO_2 are 10.97, which is 6.11 % lower than the experimental value of 11.68.

Tab. 5 Comparison of predicted results from model M1 and M2 with experimental values.

Fuel Name	Exp n_co_exp	M1 n_co	M2 n_co	Exp n_co2_exp	M1 n_co2	M2 n_co2	Exp n_ch4_exp	M1 n_ch4	M2 n_ch4	Exp n_h2_exp	M1 n_h2	M2 n_h2	Exp n_n2_exp	M1 n_n2	M2 n_n2	M1 RMS	M2 RMS
Aspen Chips	23.60	27.51	26.07	9.10	9.64	11.06	3.10	1.66	4.19	17.60	21.39	16.31	38.10	39.80	42.37	2.64	2.49
Wood Chips	15.90	16.09	15.25	15.30	15.70	16.52	2.30	1.93	4.29	16.50	20.93	15.43	50.20	45.35	48.50	2.95	1.41
HWC 20	21.62	29.26	26.32	11.58	5.55	7.94	2.41	1.02	4.18	19.20	21.46	15.73	45.20	42.72	45.83	4.65	3.19
Wood	18.40	22.17	19.16	10.60	10.52	12.95	1.30	1.25	4.55	17.00	22.27	16.03	52.70	43.79	47.31	4.93	3.06
Rubber Wood	19.10	25.09	23.24	13.00	8.78	10.36	1.20	2.14	5.16	13.00	23.42	17.55	54.00	40.58	43.69	8.29	5.78
Corn Cobs	21.30	23.53	18.36	11.76	10.11	14.18	2.05	0.35	3.82	16.80	20.18	14.62	47.74	45.83	49.02	2.26	2.19
Soft Wood	24.27	26.69	26.86	11.80	9.55	9.67	4.12	3.16	5.00	14.00	22.08	17.88	47.07	38.52	40.60	5.48	3.71
Depleted pomace	19.00	22.18	20.60	10.00	8.90	10.11	3.00	1.51	3.81	18.00	19.03	14.22	50.00	48.38	51.25	1.86	1.95
Wood Pellets	21.29	25.14	24.23	12.39	10.95	11.95	2.28	2.19	4.64	16.40	22.24	17.07	46.59	39.49	42.11	4.50	2.64
Rice Husk	20.04	22.60	16.55	10.58	9.71	14.35	0.69	0.18	3.55	17.97	18.62	13.72	50.50	48.89	51.83	1.46	3.30
Eucalyptus	19.52	21.59	21.51	13.73	13.29	13.65	1.92	2.70	4.89	17.20	22.43	17.35	47.64	39.99	42.61	4.26	2.76
Municipal Solid Waste	18.40	21.38	17.08	10.60	10.56	13.92	1.30	0.68	4.21	17.00	21.33	15.10	52.70	46.05	49.69	3.80	2.60
Wood sawdust pellets	21.30	24.61	19.60	13.30	9.69	13.66	3.10	0.31	3.59	17.50	19.47	14.27	44.20	45.92	48.89	2.78	2.67
Mixed Wood	22.60	23.86	25.16	11.05	12.33	11.62	4.80	3.71	5.11	16.40	22.02	18.15	44.90	38.08	39.97	4.06	2.62
Oil Palm	16.71	26.76	28.22	8.70	11.48	10.69	4.95	3.89	5.13	15.60	22.15	18.64	54.00	35.72	37.33	9.87	9.20
Vine Pruning	21.74	21.20	22.70	13.02	13.68	12.80	2.55	3.90	5.34	17.10	22.42	18.31	45.07	38.80	40.85	3.75	2.37
Lignite and wood mixure	18.28	20.74	13.81	12.12	16.05	21.49	1.71	0.07	2.89	10.27	16.01	13.02	56.06	47.12	48.80	5.24	5.82
Average	20.18	23.55	21.45	11.68	10.97	12.76	2.52	1.80	4.37	16.33	21.03	16.08	48.63	42.65	45.33	4.28	3.40

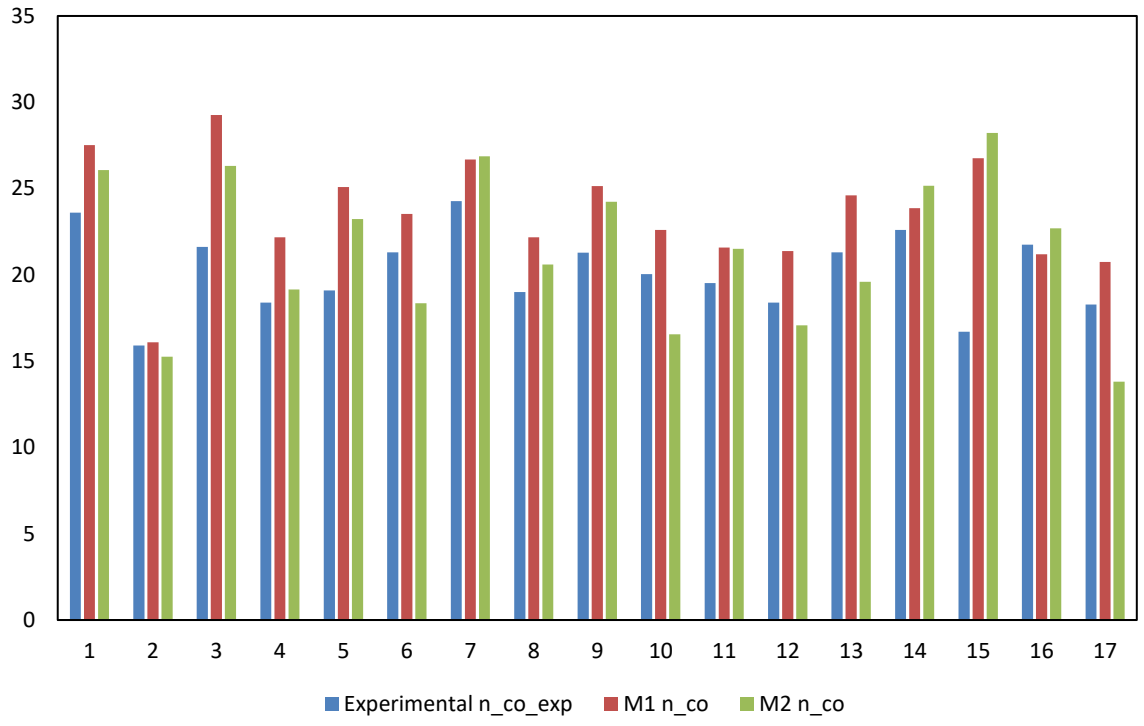

Fig.3 Predicted moles of CO

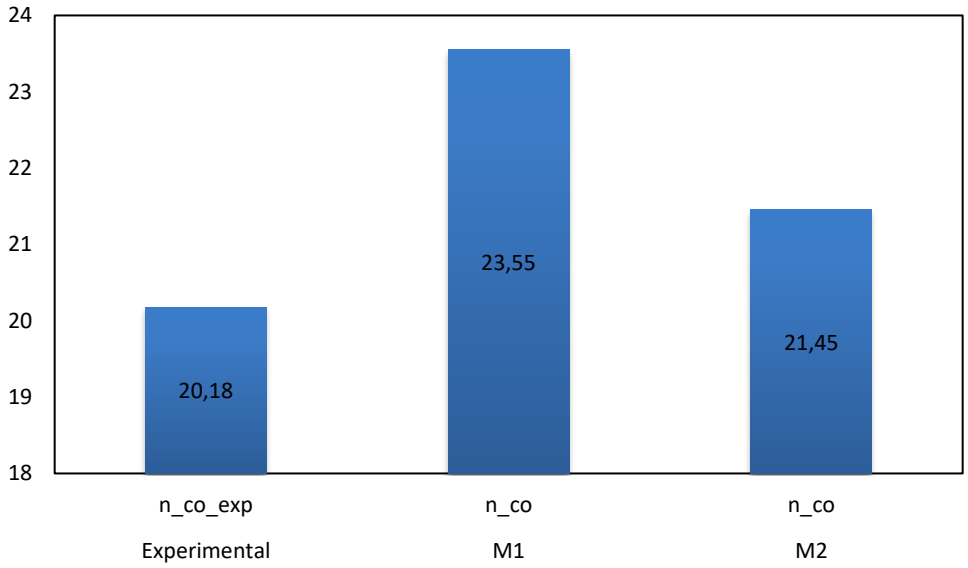

Fig. 4 Average moles of CO

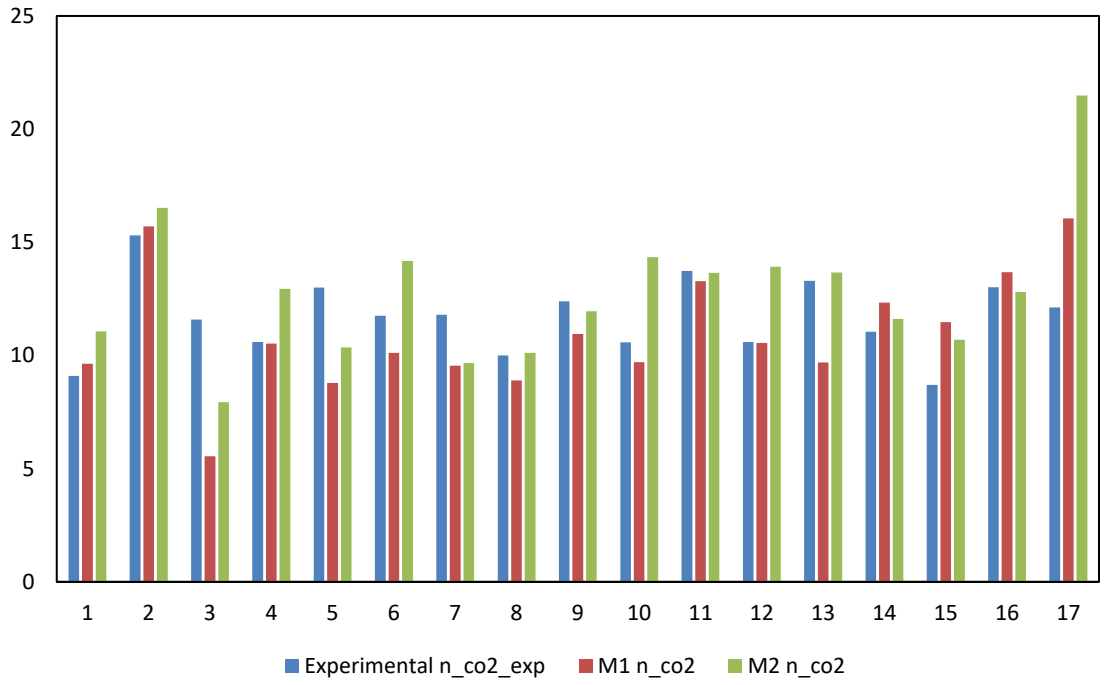

Fig. 5 Predicted moles of CO2

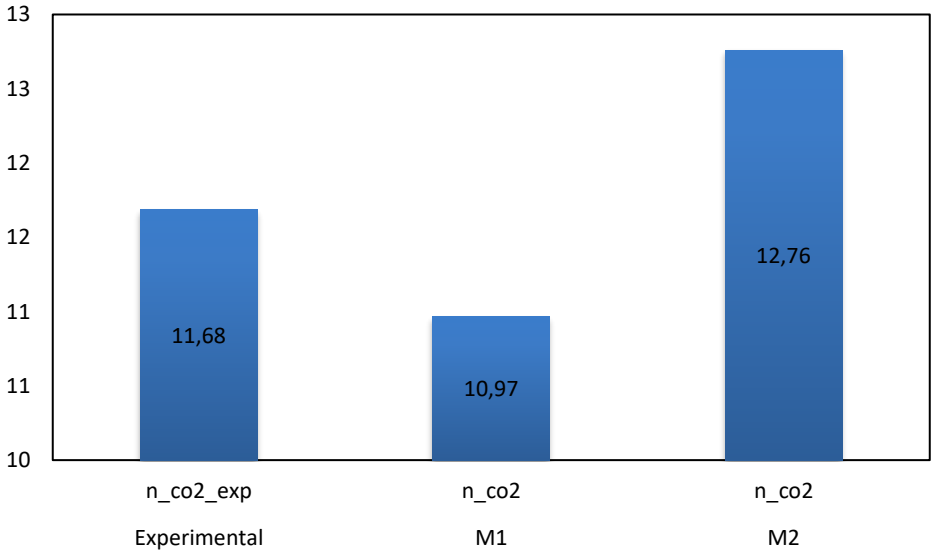

Fig. 6 Average moles of CO2

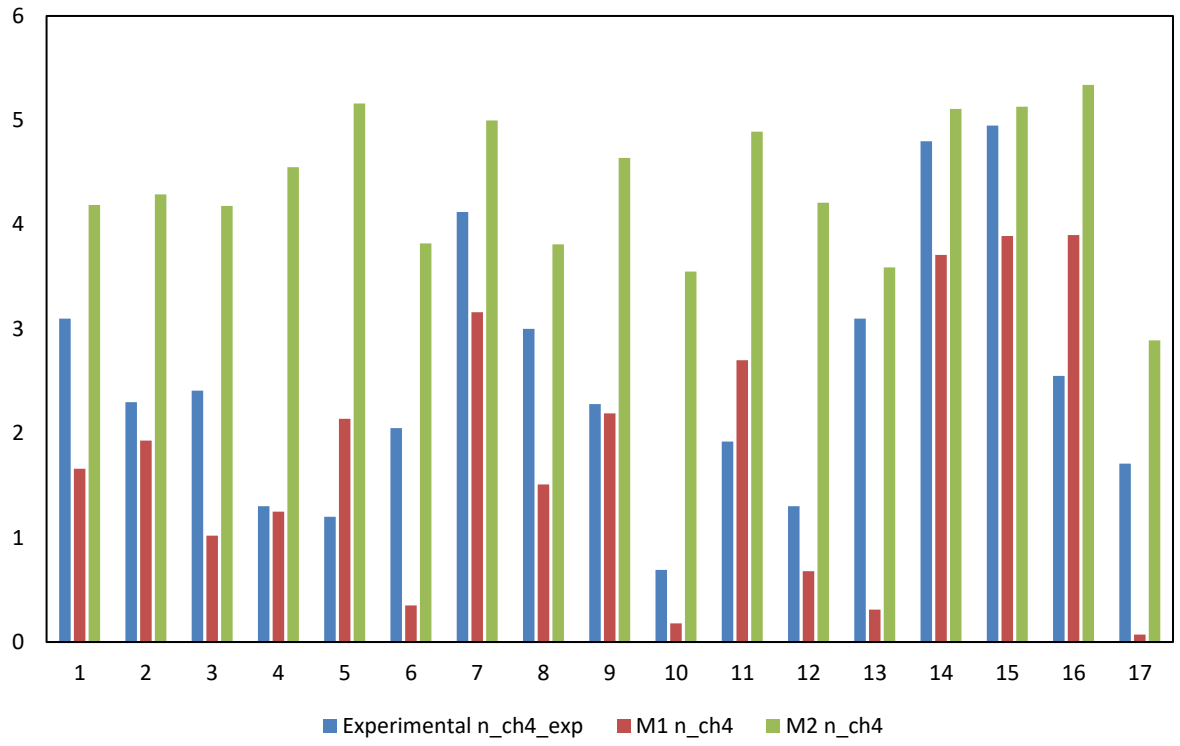

Fig. 7 Predicted moles of CH4

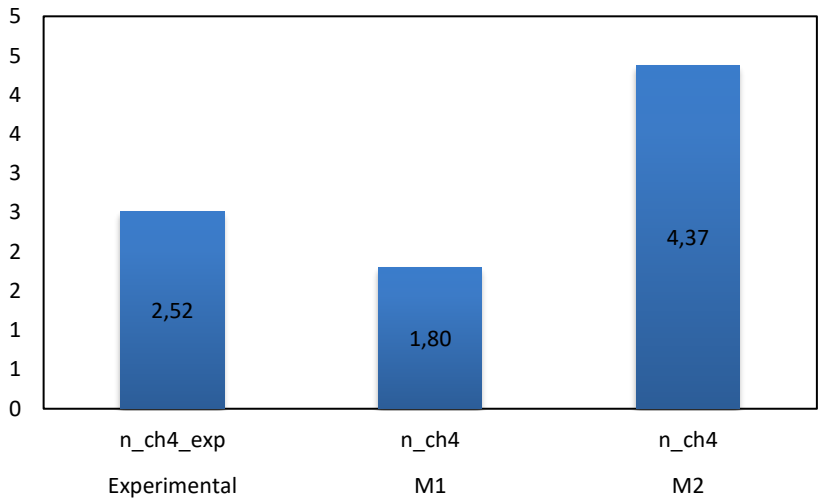

Fig. 8 Average moles of CH4

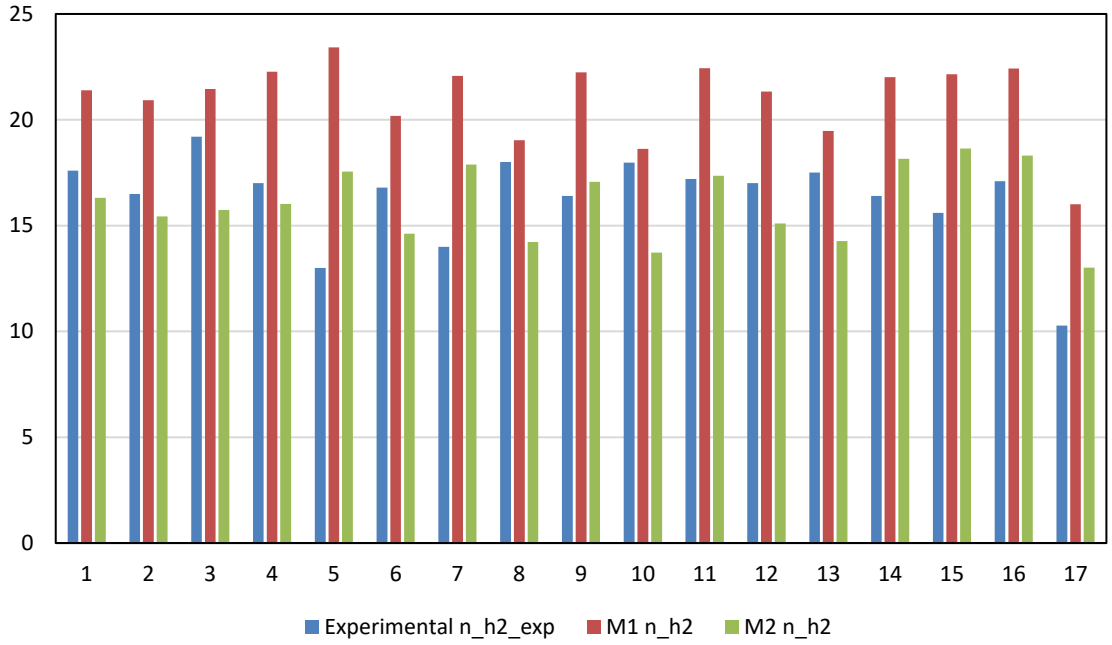

Fig. 9 Predicted moles of H2

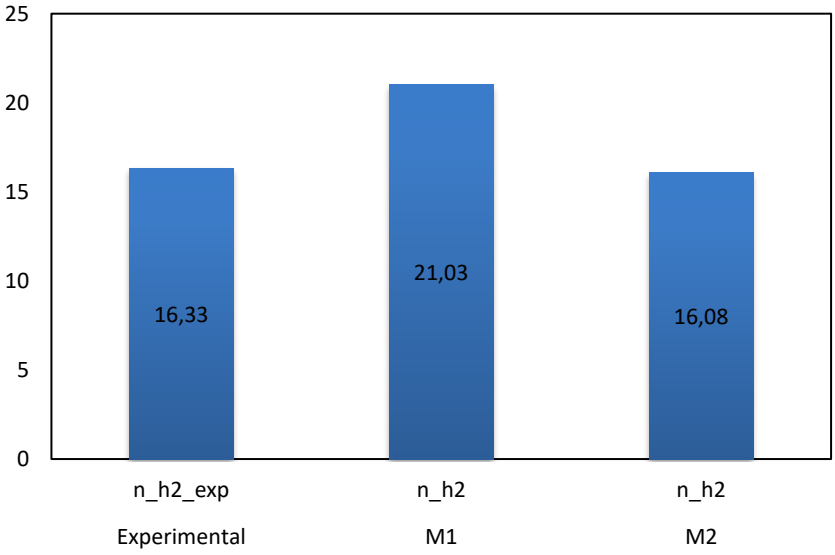

Fig. 10 Average moles of H2

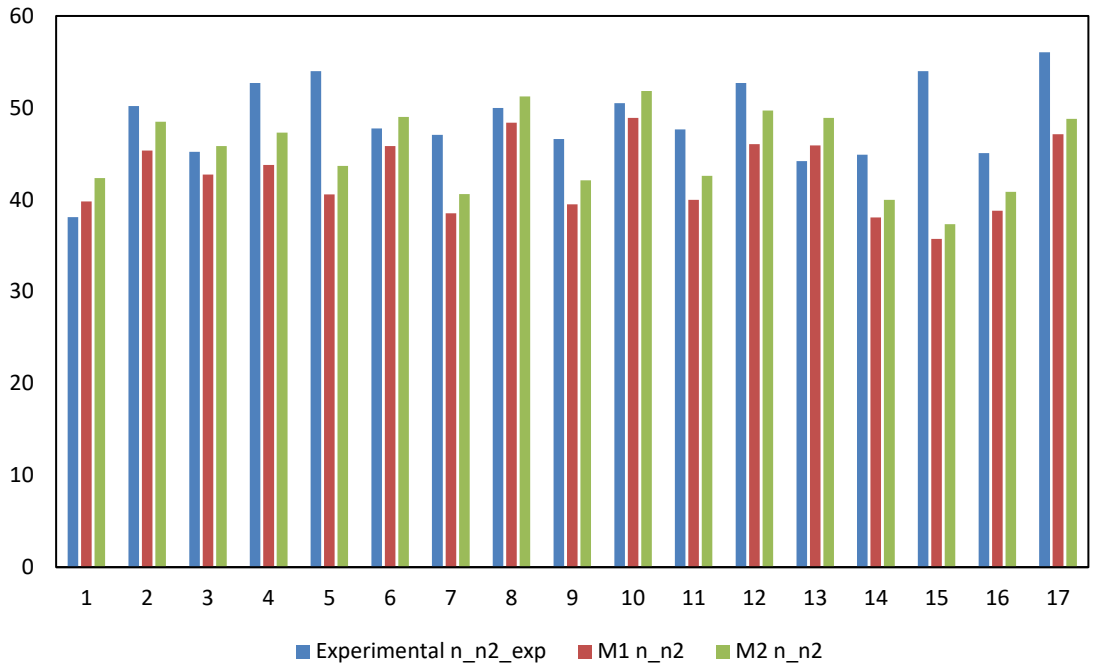

Fig. 11 Predicted moles of N2

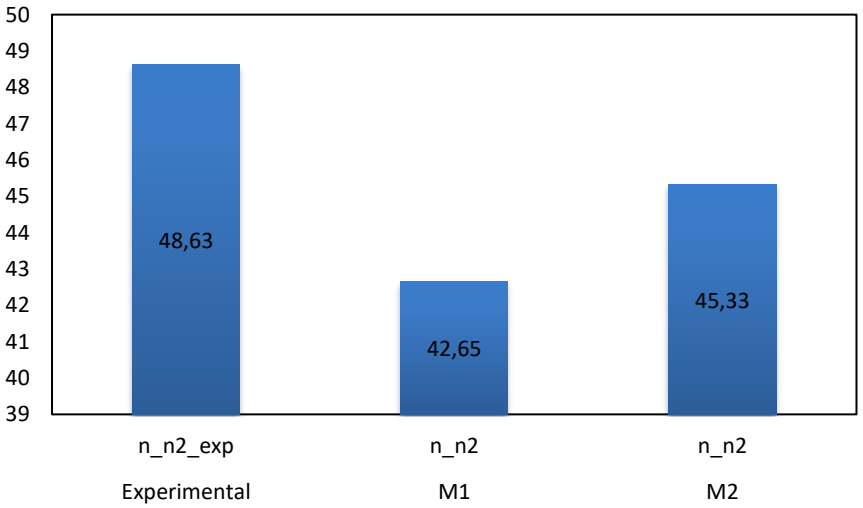

Fig. 12 Average moles of N2

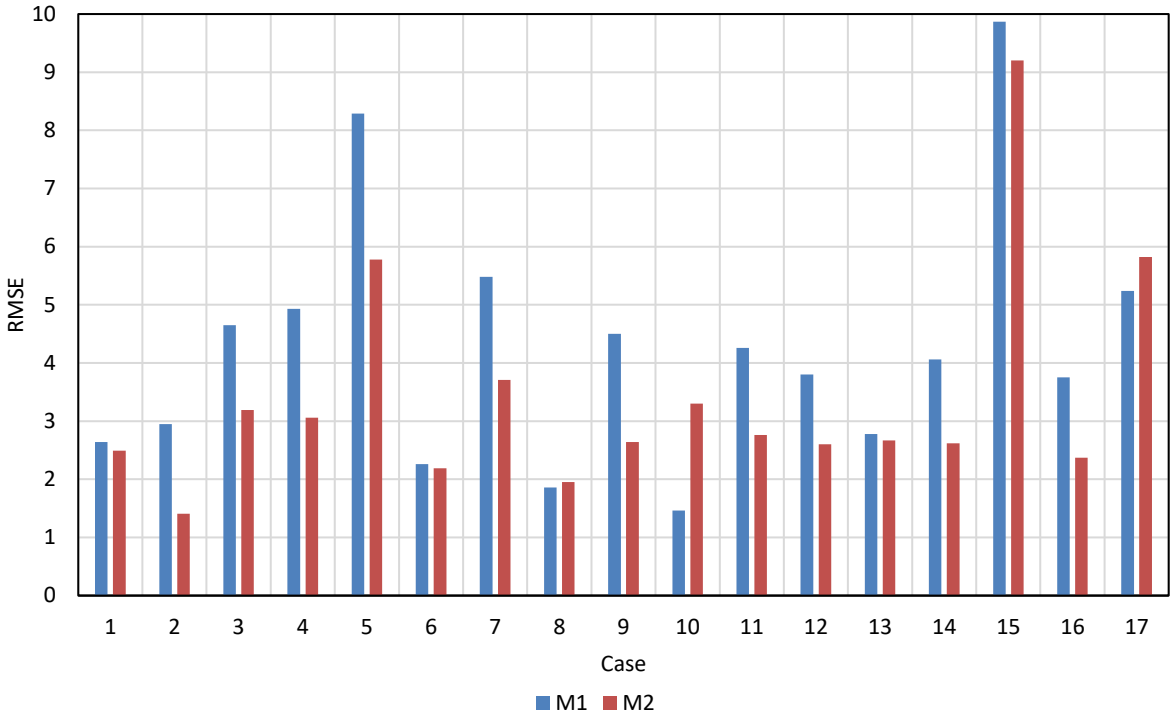

Fig. 13 RMSE comparison

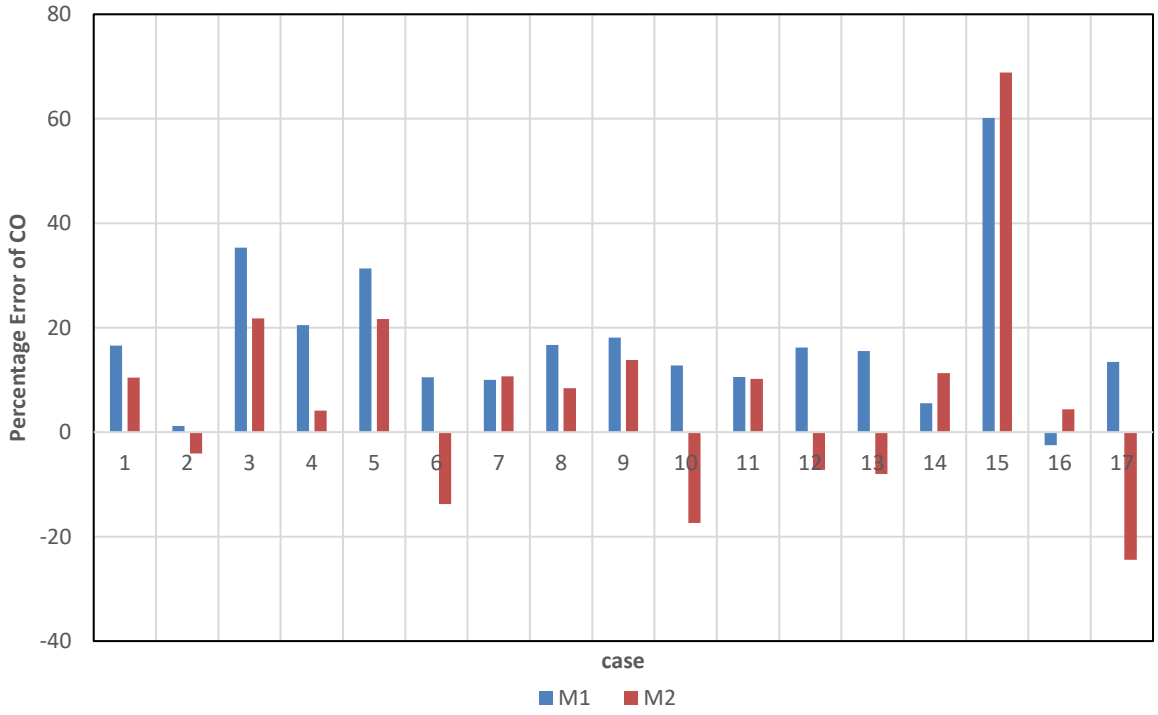

Fig. 14 Comparison of percentage error of CO

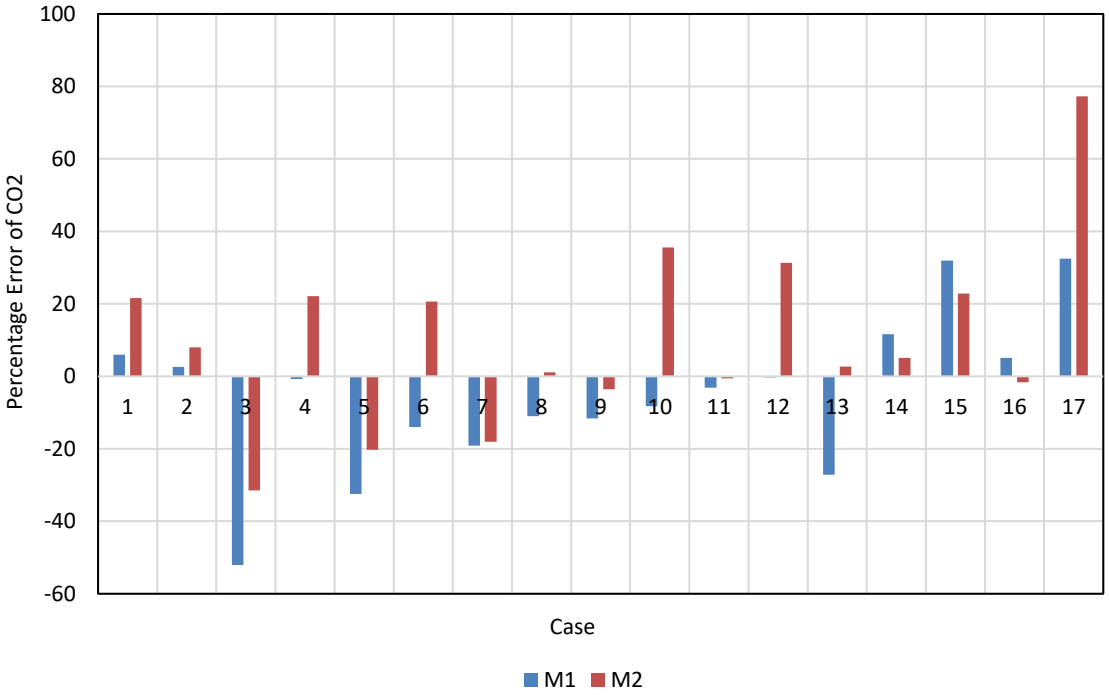

Fig. 15 Comparison of Percentage error of CO2

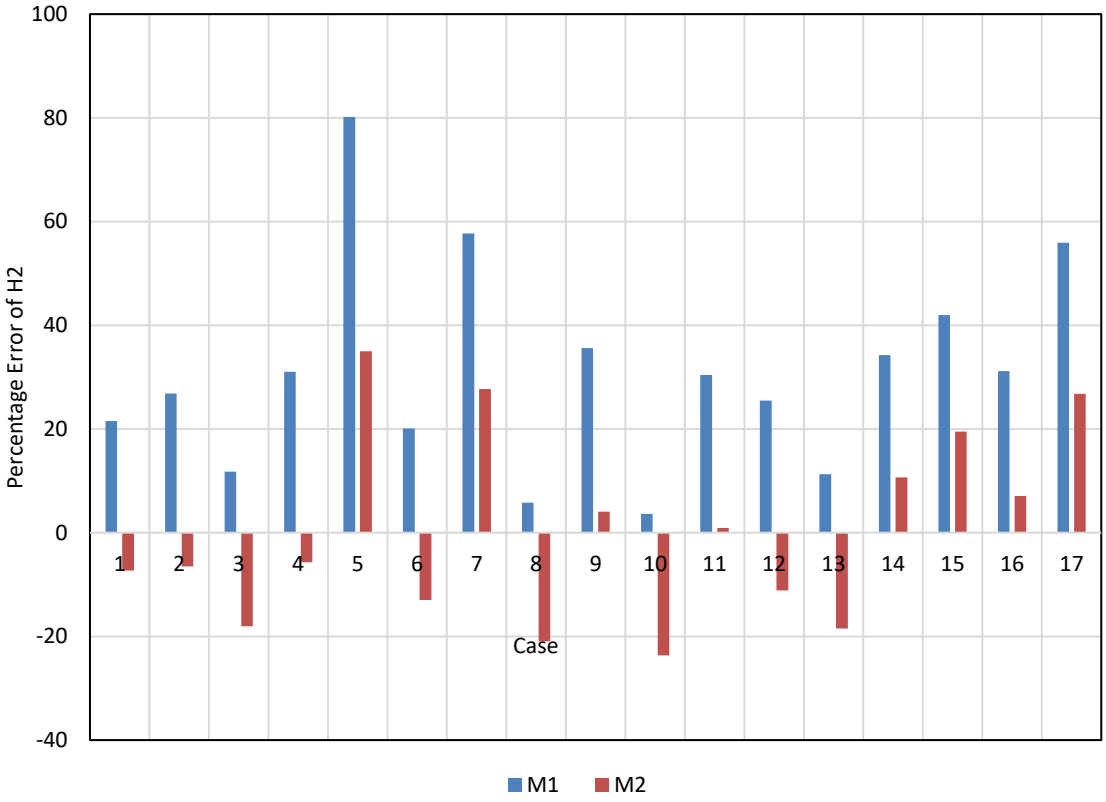

Fig. 16 Comparison of Percentage error of H2

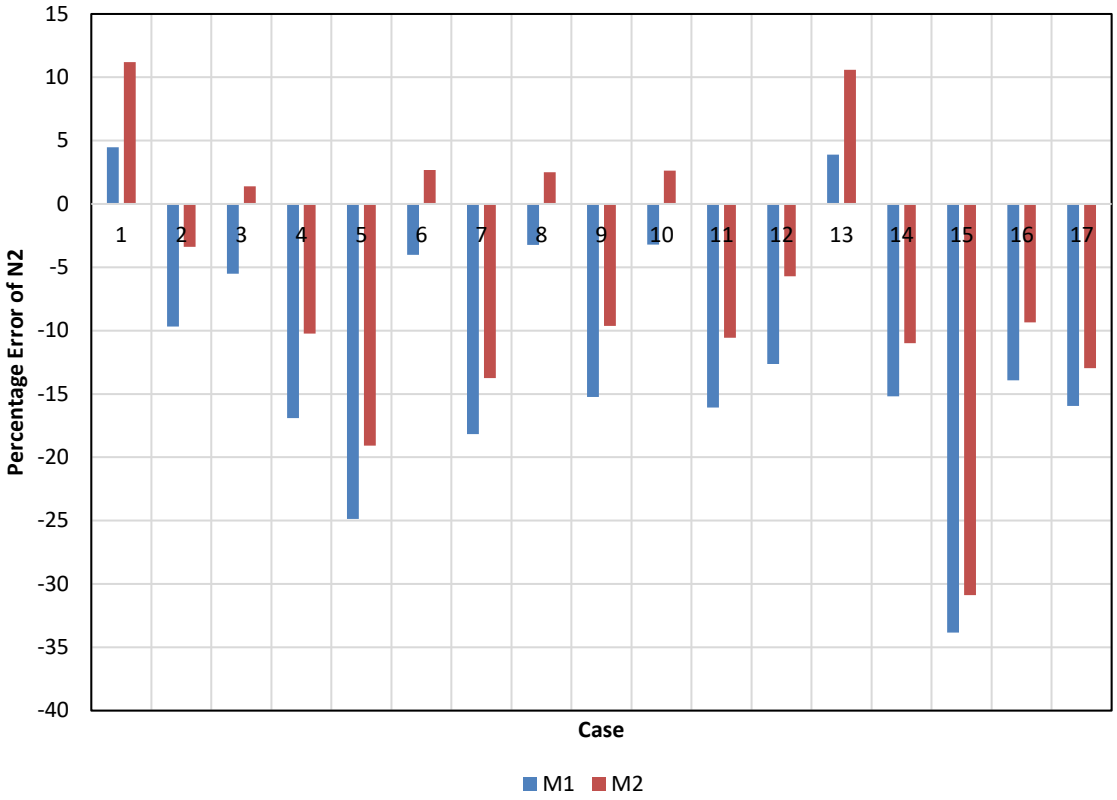

Fig. 17 Comparison of Percentage error of N2

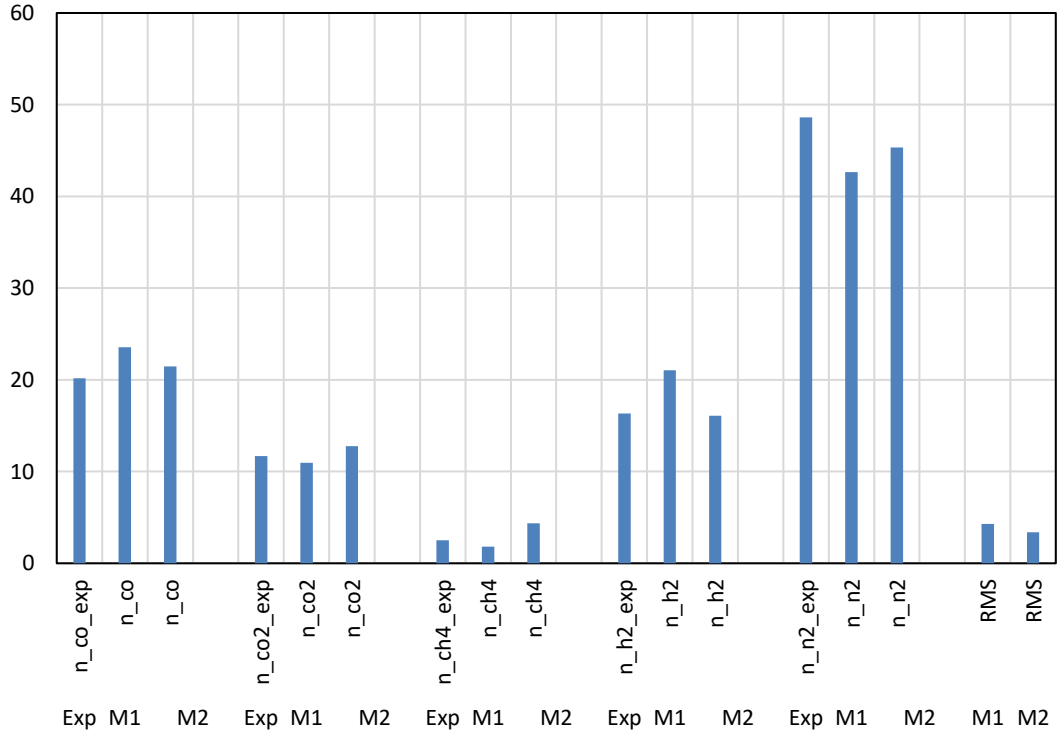

Fig.18 Comparison of all 17 fuels average results

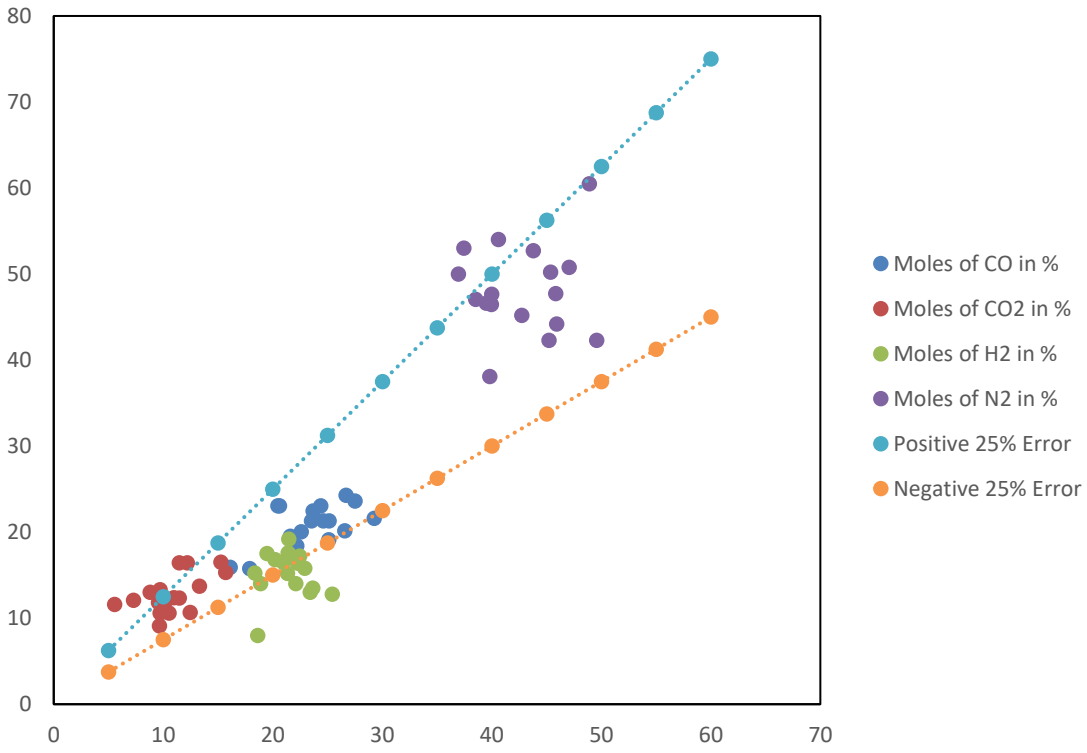

Fig. 19 Parity plot for M1 for comparison

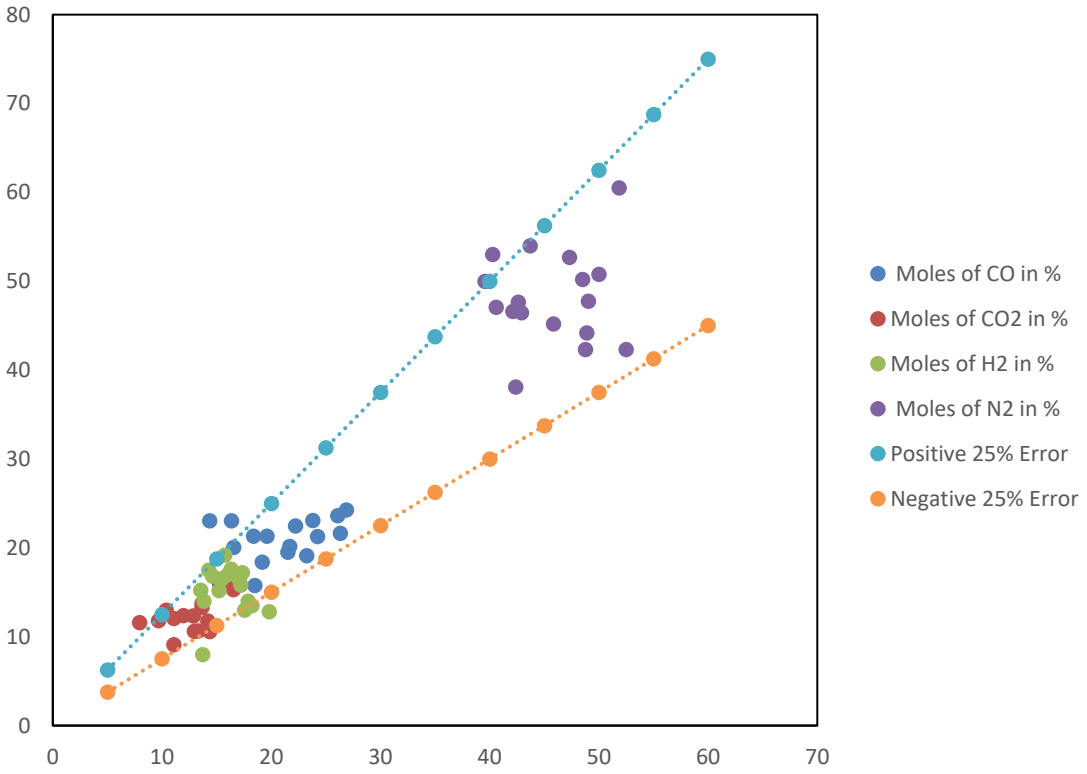

Fig. 20 Parity Plot for M2 for comparison

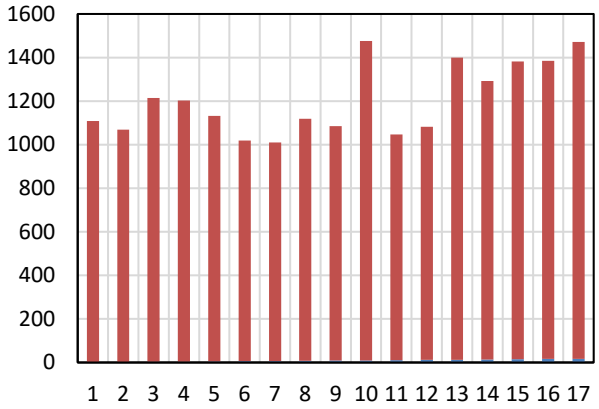

Fig. 21 Gasification temperature for M2

The moles of H2 are estimated at 21.03, surpassing the experimental value of 16.33 by 28.79 %. The revised model M2 yields more precise findings. For CO, the value is 21.45 compared to 20.18; for CO_2, it is 12.76 compared to 11.68; and for H_2, it is 16.08 compared to 16.33. Figure 3 compares the prediction of moles of CO for all 17 fuels for M1 and M2. Figure 4 shows the average value of 17 fuels' moles of CO. Same way, Figure 5 to 12 compares for different species. Figure 13 compares RMSE in case of M1 and M2, which clearly indicates the decrement is RMSE. Figure 14 to 18 compares individual percentage error of CO, CO_2, CH_4, H_2, and N_2 of 17 fuels. It is found that M2 decreases the RMSE and individual percentage error too. Except two fuels the individual percentage error is within +/- 25 %.

Looking at the graphs, it's clear that M2 has better prediction accuracy than M1. Displayed in Figures 19 and 20, the moles of different species in percentage, the parity plot makes it quite evident that both the RMSE and individual percentage errors diminish. Figure 21 shows the gasification temperature in Kelvin for all fuels.

5. Conclusion

The aim of this work is to determine two modified equilibrium constants for the water-gas shift reaction and the methane reaction, therefore rendering this model generic for application to other fuels and feedstocks. The optimization approach was used to determine the modified equilibrium constants K_{wgs} and K_m. The modified equilibrium constants of 1.01 and 0.65 for the water-gas shift reaction and methane reaction, respectively, provide optimal predictions of syngas compositions, exhibiting minimal RMSE and individual percentage errors. The average RMSE value for all 17 fuels is 3.40. The fuel, a blend of lignite and wood, has a distinct composition relative to other fuels and biomass, resulting in somewhat varied prediction outcomes. For such fuels, modified equilibrium constants 0.25 and 0.64 gives the more accurate results.

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