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Effect of Modified Equilibrium Constants of Comprehensive Thermodynamic Equilibrium Model on Prediction of Constituents of Producer Gas for Rubber- Wood Biomass

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Abstract — Thermodynamic equilibrium models (TEM) are widely used for predicting producer gas composition in biomass downdraft gasifiers due to their simplicity and computational efficiency. However, conventional TEM often overpredicts hydrogen and carbon monoxide because of the assumption of complete chemical equilibrium. In this work, a Comprehensive Thermodynamic Equilibrium Model (CTEM) incorporating modified equilibrium constants (Kwgs = 1.01 and Km = 0.65) is validated for rubber-wood biomass under varying equivalence ratio (0.274–0.420) and moisture content (0.076–0.185). Mass balance, equilibrium constant formulation, and energy balance equations are solved simultaneously using an iterative approach. Model predictions are evaluated using Mean Percentage Error (MPE) and Root Mean Square Error (RMSE). Results indicate significant reduction in hydrogen prediction error and improved nitrogen estimation compared to conventional TEM. The modified model demonstrates improved robustness across operating ranges and can be used for preparing generalized gasification performance tables.

Keywords: Biomass Gasification; Downdraft Gasifier; Thermodynamic Equilibrium Model; CTEM; Modified Equilibrium Constants; Rubber Wood

I. INTRODUCTION

Biomass gasification is an established thermochemical conversion process that transforms solid biomass into combustible producer gas primarily composed of CO, H_2, CO_2, CH_4 and N_2. Downdraft gasifiers are widely used for decentralized energy generation due to low tar content and operational simplicity. Mathematical modeling plays a crucial role in design optimization and performance prediction of gasifiers.

Thermodynamic equilibrium models (TEM) are attractive because they are independent of reactor geometry and provide quick convergence. However, equilibrium assumptions may not hold under practical gasification conditions due to kinetic limitations. Previous studies indicate overprediction of hydrogen and deviation in CO_2 estimation.

To address this limitation, a Comprehensive Thermodynamic Equilibrium Model (CTEM) was proposed incorporating correction factors for water–gas shift and methane reactions. The present work validates this generalized modification for rubber-wood biomass under wide operating conditions and provides detailed statistical assessment.

Rubberwood, obtained from the plantation species *Hevea brasiliensis*, is an important agro-forestry biomass resource in India. After approximately 25–30 years of latex extraction, rubber trees are felled and replanted, generating substantial quantities of woody biomass. In India, rubber plantations are predominantly located in Kerala, Tamil Nadu, Karnataka, and parts of the North-Eastern region, contributing significantly to lignocellulosic residue availability. Traditionally, rubberwood has been utilized in furniture and plywood industries; however, low-grade stems, branches, and sawmill residues provide a promising feedstock for thermochemical energy conversion [1,2].

Rubberwood exhibits favourable physicochemical properties for gasification applications. On a dry basis, it typically possesses a higher heating value (HHV) in the range of 17–18 MJ/kg, with low sulphur content and moderate ash fraction [3]. Ultimate analysis indicates that rubberwood mainly comprises carbon, hydrogen, and oxygen, with minimal nitrogen and sulphur, making it suitable for clean producer gas generation [4]. During gasification, biomass undergoes partial oxidation at elevated temperatures (800–1000 °C), producing a combustible gas mixture primarily composed of CO, H_2, CH_4, CO_2, and N_2 [5]. The quality and calorific value of the producer gas depend strongly on operating parameters such as equivalence ratio (ER), reactor temperature, and moisture content [6].

To predict the composition of producer gas from rubberwood gasification, the Thermodynamic Equilibrium Model (TEM) is widely employed. TEM is based on the principle that the reacting system reaches thermodynamic equilibrium at a specified temperature and pressure, and the final gas composition is determined by minimizing Gibbs free energy or by applying equilibrium constants of the major gasification reactions [7,8]. The principal reactions considered include carbon oxidation, the Boudouard reaction, the water–gas reaction, the water–gas shift reaction, and methanation [5].

When rubberwood is used as feedstock in TEM analysis, several assumptions are adopted. First, all reactions inside the gasifier are assumed to attain chemical equilibrium. Second, the reactor is considered isothermal with uniform temperature distribution. Third, complete carbon conversion is assumed, neglecting residual char formation. Fourth, gaseous species are treated as ideal gases. Fifth, tar and higher hydrocarbons are neglected or represented by methane for simplification. Finally, the process is assumed to operate under steady-state conditions with elemental balances (C, H, O, N) derived from the ultimate analysis of rubberwood [7–9].

Although real gasifiers may deviate from equilibrium due to kinetic constraints, heat losses, and tar formation, TEM provides a rapid and reliable first-level prediction of producer gas composition, calorific value, and cold gas efficiency. Therefore, rubberwood represents a sustainable and regionally abundant biomass resource in India, and the Thermodynamic Equilibrium Model serves as a robust theoretical framework for evaluating its gasification performance under idealized conditions.

II. FEEDSTOCK CHARACTERISTICS

Rubber wood biomass is selected due to high volatile matter and low ash content. Ultimate and proximate analyses are summarized in Table 1.

C (wt%)	H (wt%)	O (wt%)	N (wt%)	Fixed Carbon (wt%)	Volatile Matter (wt%)	Moisture (wt%)	Ash (wt%)	HHV (MJ/kg)
50.60	6.50	42.00	0.20	19.20	80.10	12.50	0.70	19.60

Table 1: Ultimate and proximate analyses of rubber wood

III. MODEL USED FOR RESULT COMPARISON

The thermodynamic equilibrium model prepared by Jarungthammachote et al. [10] and comprehensive thermodynamic equilibrium model prepared by Parmar DJ et al. [11]is used to predict the result for rubber wood.

The flow chart for TEM is mentioned in below figure[11].

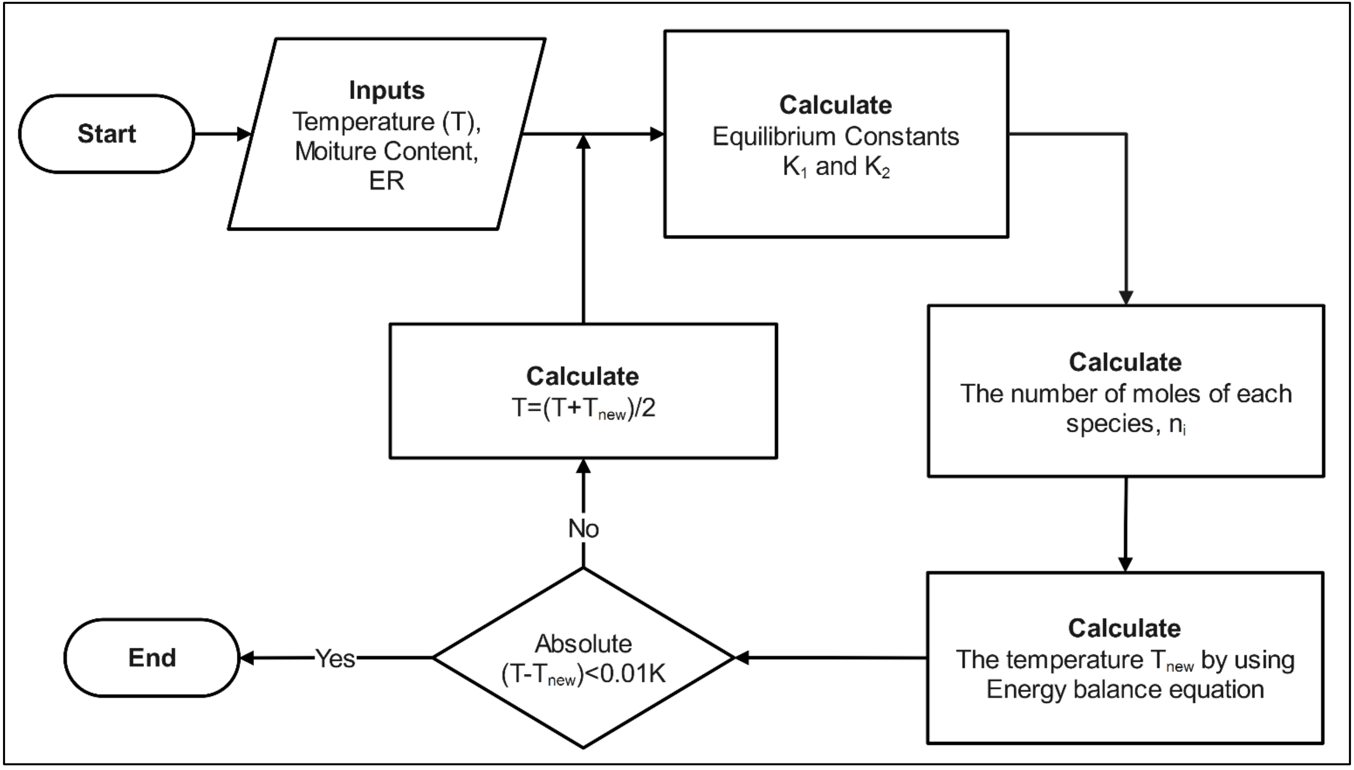

Fig. 1: Flowchart for calculation process of TEM (M1)

This article compares the results obtained by TEM(M1), CTEM(M2) and experimental values available in literature. The modified equilibrium constants adopted in this study are: Kwgs = 1.01 and Km = 0.65. These constants correct hydrogen overprediction and methane deviation observed in TEM. This article uses 20 different cases of rubber wood in which equivalence ratio ranging from 0.274 to 0.420 and moisture content ranging from 0.076 to 0.185. The table 2 shows, 20 different cases.

Case ID	Biofuel	C %	H %	O %	N %	A %	S %	ER	MC
	Rubber Wood	50.70	6.90	42.40	0.30	0.39	0.00	0.274	0.076
	Rubber Wood	50.70	6.90	42.40	0.30	0.39	0.00	0.274	0.076
	Rubber Wood	50.70	6.90	42.40	0.30	0.39	0.00	0.284	0.076
	Rubber Wood	50.70	6.90	42.40	0.30	0.39	0.00	0.286	0.076
	Rubber Wood	50.70	6.90	42.40	0.30	0.39	0.00	0.292	0.076
	Rubber Wood	50.70	6.90	42.40	0.30	0.39	0.00	0.296	0.076
	Rubber Wood	50.70	6.90	42.40	0.30	0.39	0.00	0.302	0.076
	Rubber Wood	50.70	6.90	42.40	0.30	0.39	0.00	0.322	0.076
	Rubber Wood	50.60	6.50	42.00	0.20	0.70	0.70	0.350	0.125
	Rubber Wood	50.60	6.50	42.00	0.20	0.70	0.70	0.370	0.125
	Rubber Wood	50.60	6.50	42.00	0.20	0.70	0.70	0.380	0.125
	Rubber Wood	50.60	6.50	42.00	0.20	0.70	0.70	0.390	0.125

	Rubber Wood	50.60	6.50	42.00	0.20	0.70	0.70	0.400	0.125
	Rubber Wood	50.60	6.50	42.00	0.20	0.70	0.70	0.420	0.125
	Rubber Wood	50.60	6.50	42.00	0.20	0.70	0.00	0.400	0.185
	Rubber Wood	50.60	6.50	42.00	0.20	0.70	0.00	0.400	0.160
	Rubber Wood	50.60	6.50	42.00	0.20	0.70	0.00	0.400	0.147
	Rubber Wood	50.60	6.50	42.00	0.20	0.70	0.00	0.400	0.152
	Rubber Wood	50.60	6.50	42.00	0.20	0.70	0.00	0.400	0.140
	Rubber Wood	50.60	6.50	42.00	0.20	0.70	0.00	0.400	0.138

Table 2 Rubber wood feedstock with case IDs.

IV. RESULTS AND STATISTICAL ANALYSIS

Model performance is evaluated using Mean Percentage Error (MPE) and Root Mean Square Error (RMSE).

Case ID	Biofuel	CO			CO_2			H_2			N_2		
		Exp	M1	M2	Exp	M1	M2	Exp	M1	M2	Exp	M1	M2
	Rubber Wood	19.10	25.09	23.24	13.00	8.78	10.36	13.00	23.42	17.55	54.00	40.58	43.69
	Rubber Wood	19.10	25.09	23.24	10.13	8.78	10.36	13.00	23.42	17.55	56.49	40.58	43.69
	Rubber Wood	22.10	25.03	22.60	10.00	8.61	10.62	12.70	23.30	17.14	53.82	41.32	44.64
	Rubber Wood	18.90	25.02	22.47	10.25	8.57	10.67	12.50	23.27	17.06	57.07	41.47	44.83
	Rubber Wood	19.40	24.97	22.10	10.56	8.48	10.82	17.20	23.15	16.83	51.66	41.93	45.38
	Rubber Wood	19.40	24.94	21.85	10.13	8.42	10.92	13.20	23.06	16.67	55.89	42.24	45.75
	Rubber Wood	19.70	24.90	21.49	10.56	8.34	11.06	18.30	22.89	16.44	50.26	42.72	46.29
	Rubber Wood	9.60	24.69	20.33	10.25	8.12	11.53	17.20	22.13	15.70	61.47	44.36	48.03
	Rubber Wood	19.10	22.70	18.11	11.40	9.59	13.15	15.50	20.85	14.84	52.90	46.32	49.84
	Rubber Wood	18.40	22.52	17.15	10.60	9.39	13.50	17.00	19.72	14.17	52.70	48.06	51.38
	Rubber Wood	19.60	22.39	16.69	9.90	9.32	13.67	17.20	19.10	13.85	51.90	48.95	52.13
	Rubber Wood	22.10	22.25	16.25	10.50	9.27	13.83	12.70	18.46	13.53	53.40	49.84	52.86
	Rubber Wood	19.70	22.08	15.81	10.80	9.24	13.99	13.20	17.81	13.22	55.00	50.73	53.57
	Rubber Wood	20.20	21.70	14.97	9.70	9.22	14.29	18.30	16.51	12.61	50.70	52.49	54.94
	Rubber Wood	19.63	20.26	14.31	9.90	10.60	15.11	17.20	18.81	13.61	51.90	50.11	53.32
	Rubber Wood	20.20	21.05	14.93	9.70	10.01	14.65	18.30	18.39	13.45	50.70	50.37	53.42
	Rubber Wood	19.40	21.44	15.26	9.70	9.72	14.40	17.20	18.18	13.36	52.60	50.51	53.48
	Rubber Wood	19.70	21.29	15.13	10.80	9.83	14.50	13.20	18.26	13.40	55.00	50.45	53.46
	Rubber Wood	18.90	21.65	15.43	8.50	9.56	14.27	12.50	18.06	13.32	59.10	50.58	53.51
	Rubber Wood	22.10	21.71	15.48	10.50	9.52	14.23	12.70	18.03	13.30	53.40	50.60	53.51
	Average	19.31	23.04	18.34	10.34	09.17	12.80	15.10	20.34	14.88	53.99	46.71	49.88
	Percentage Error		19.26	5.04		11.36	23.72		34.66	1.50		13.50	7.61

Table 3: Mole (%) of different constituents of producer gas

Case ID	Biofuel	PECO _M1	PECO _M2	PECO2 _M1	PECO2 _M2	PEH2 _M1	PEH2 _M2	PEN2 _M1	PEN2 _M2	RMSE _M1	RMSE _M2
	Rubber Wood	31.35	21.66	-32.48	-20.27	80.17	34.98	-24.86	-19.09	8.28	5.50
	Rubber Wood	31.35	21.66	-13.35	2.31	80.17	34.98	-28.17	-22.66	8.94	6.35
	Rubber Wood	13.25	2.24	-13.94	6.22	83.48	34.99	-23.22	-17.06	7.47	4.57
	Rubber Wood	32.36	18.89	-16.35	4.12	86.15	36.51	-27.33	-21.45	8.94	6.06
	Rubber Wood	28.73	13.90	-19.68	2.48	34.60	-2.17	-18.83	-12.15	5.75	3.06
	Rubber Wood	28.58	12.64	-16.84	7.79	74.66	26.30	-24.42	-18.15	7.96	4.93
	Rubber Wood	26.37	9.09	-21.00	4.77	25.08	-10.16	-15.01	-7.90	4.69	2.13
	Rubber Wood	157.22	111.81	-20.77	12.45	28.67	-8.74	-27.83	-21.87	10.48	7.74
	Rubber Wood	18.84	-5.19	-15.90	15.36	34.54	-4.23	-12.43	-5.78	4.20	1.66
	Rubber Wood	22.38	-6.78	-11.43	27.37	16.02	-16.63	-8.80	-2.50	3.08	1.99
	Rubber Wood	14.25	-14.83	-5.85	38.07	11.07	-19.50	-5.69	0.44	2.02	2.61
	Rubber Wood	0.67	-26.49	-11.70	31.73	45.39	6.52	-6.67	-1.02	3.08	3.05
	Rubber Wood	12.10	-19.75	-14.45	29.54	34.95	0.12	-7.76	-2.60	3.09	2.34
	Rubber Wood	7.43	-25.89	-4.92	47.36	-9.80	-31.10	3.53	8.37	1.34	4.45
	Rubber Wood	3.21	-27.08	7.04	52.60	9.37	-20.85	-3.44	2.74	1.16	3.75
	Rubber Wood	4.21	-26.08	3.19	50.98	0.50	-26.50	-0.65	5.37	0.43	4.08
	Rubber Wood	10.53	-21.36	0.17	48.48	5.67	-22.31	-3.98	1.67	1.38	3.31
	Rubber Wood	8.09	-23.19	-9.00	34.22	38.32	1.49	-8.26	-2.81	3.15	2.72

	Rubber Wood	14.55	-18.35	12.50	67.91	44.48	6.53	-14.42	-9.47	4.74	3.93
	Rubber Wood	-1.77	-29.94	-9.35	35.57	41.94	4.75	-5.25	0.21	2.73	3.41
	Average of absolute values	23.36	22.84	13.00	26.98	39.25	17.47	13.53	9.17	4.65	2.74

Table 4: Calculation of PE and RMSE

V. RESULTS

This section compares the results obtained from TEM and CTEM using box–whisker. The results include moles of CO, CO_2, H_2 and N_2. The percentage error of CO, CO_2, H_2 and N_2 and RMSE.

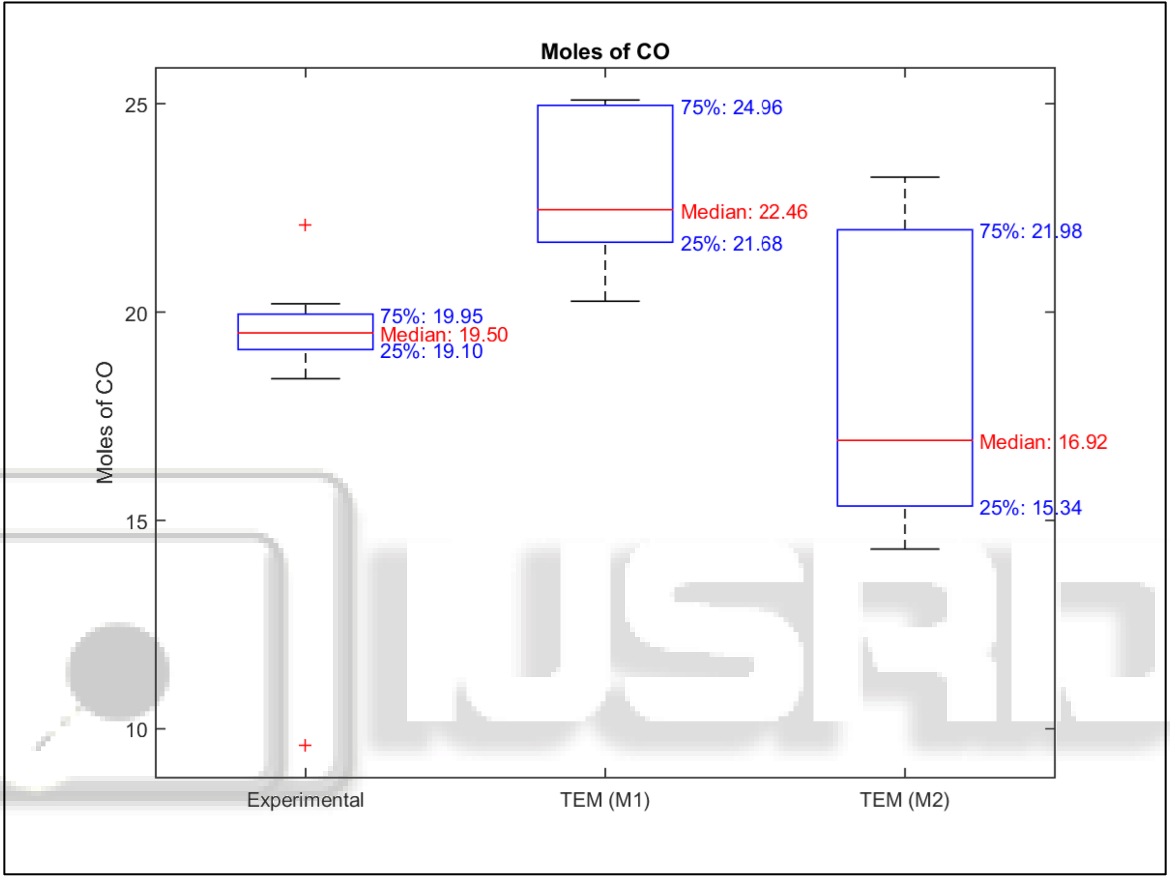

Fig. 2: Mole (%) of CO

The figure presents a box–whisker comparison of carbon monoxide (CO) mole fractions for Experimental data, Conventional Thermodynamic Equilibrium Model (TEM – M1), and the Modified Comprehensive Thermodynamic Equilibrium Model (CTEM – M2). It provides a statistical view of distribution, central tendency, and variability across the investigated operating range of equivalence ratio and moisture content. The experimental CO distribution shows a narrow interquartile range (25% ≈ 19.10, 75% ≈ 19.95) with a median of approximately 19.50, indicating stable and consistent CO production during rubber-wood gasification. The limited spread suggests that under practical downdraft gasifier conditions, CO formation remains relatively uniform across the tested operating range. In contrast, the conventional TEM (M1) significantly overpredicts CO concentration. Its median value (≈ 22.46) is notably higher than the experimental median, and the interquartile range (21.68–24.96) is considerably wider. This larger spread reflects greater sensitivity of the equilibrium model to variations in operating conditions. The overprediction arises from the assumption of complete chemical equilibrium, which favors CO formation through the Boudouard and water–gas reactions at elevated temperatures.

The CTEM (M2) results demonstrate improved stability compared to M1. The median CO value (≈ 16.92) shifts closer toward the experimental range, and the overall dispersion is reduced relative to the conventional model. Although slight underprediction is observed in some conditions, the reduction in extreme values indicates that modification of the equilibrium constants effectively compensates for kinetic limitations present in practical gasifiers. Overall, the figure confirms that CTEM provides a more controlled and realistic prediction of CO mole fraction compared to the conventional equilibrium model.

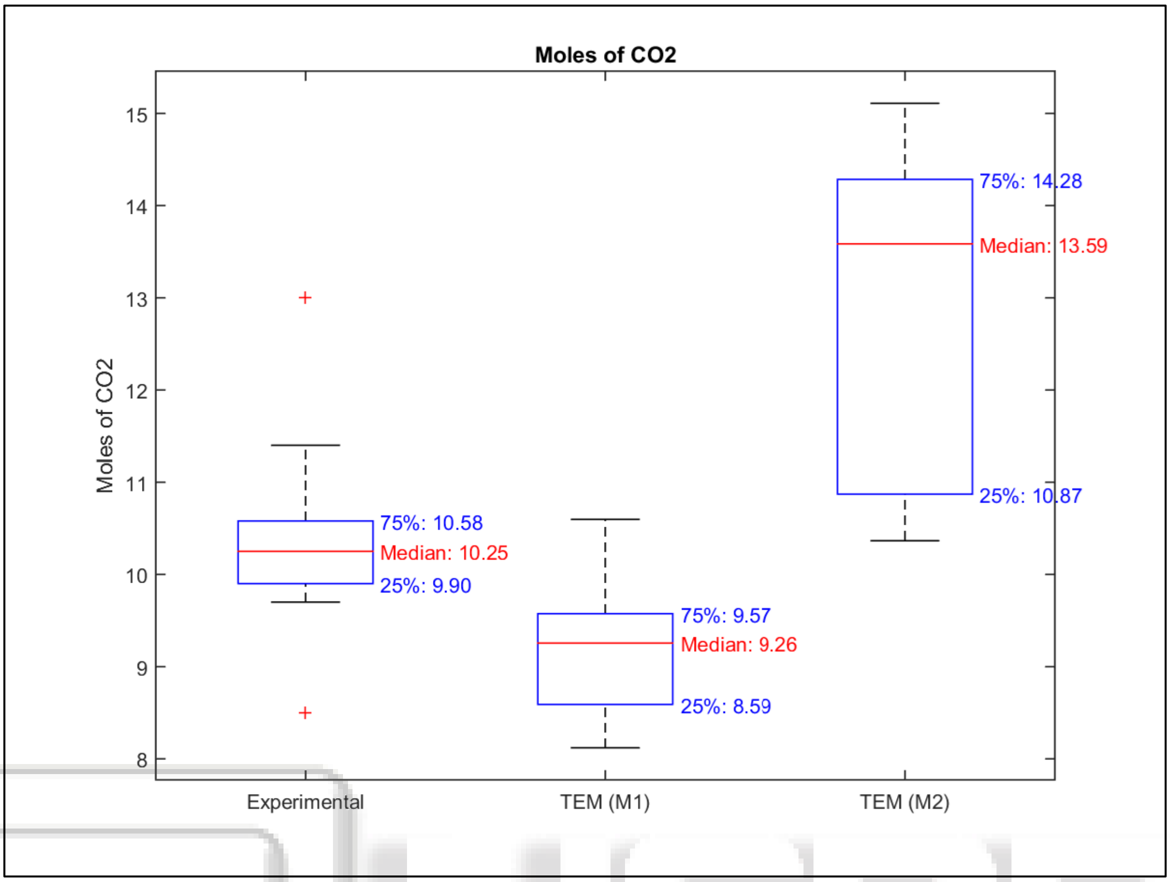

Fig. 3: Mole (%) of CO_2

The figure presents a box–whisker comparison of carbon dioxide (CO_2) mole fractions for Experimental data, Conventional Thermodynamic Equilibrium Model (TEM – M1), and the Modified Comprehensive Thermodynamic Equilibrium Model (CTEM – M2). It illustrates the distribution, central tendency, and variability of CO_2 predictions across the studied equivalence ratio and moisture content range.

The experimental CO_2 values show a relatively narrow distribution, with a median of approximately 10.25 and an interquartile range (25% ≈ 9.90, 75% ≈ 10.58). This indicates stable CO_2 production under practical downdraft gasifier conditions. Although a few outliers are visible, the majority of experimental values are tightly clustered, suggesting limited variation in carbon dioxide formation across operating conditions.

In the case of the conventional TEM (M1), the median CO_2 value decreases to approximately 9.26, indicating underprediction compared to experimental results. The interquartile range (8.59–9.57) is also relatively narrow, but the entire distribution is shifted downward. This underestimation arises from the complete equilibrium assumption, which tends to favour CO formation over CO_2 at higher temperatures through the Boudouard reaction and related equilibrium pathways.

The CTEM (M2), however, shows a significant upward shift in CO_2 prediction, with a median of approximately 13.59 and a wider interquartile range (10.87–14.28). This indicates that modification of the equilibrium constants strongly influences carbon redistribution between CO and CO_2. While CTEM corrects hydrogen and CO overprediction observed in TEM, it results in comparatively higher CO_2 estimation. The increased spread suggests greater sensitivity of CO_2 prediction to operating parameters when modified constants are applied.

Overall, the figure demonstrates that conventional TEM underpredicts CO_2, whereas CTEM shifts the carbon balance toward higher CO_2 formation. The modification of equilibrium constants therefore significantly affects carbon distribution, highlighting the interdependence between CO and CO_2 predictions in thermodynamic modeling of biomass gasification.

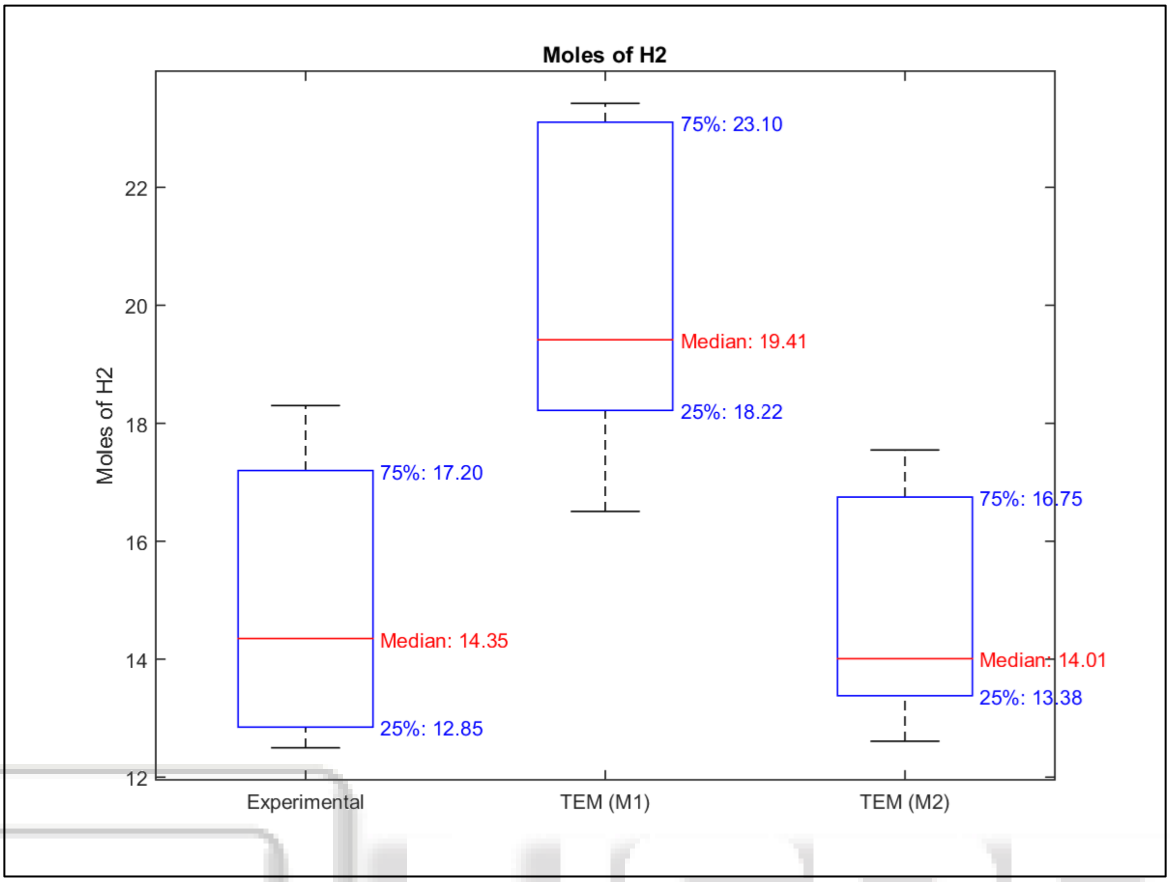

Fig. 4: Mole (%) of H_2

The figure presents a box–whisker comparison of hydrogen (H_2) mole fractions for Experimental data, Conventional Thermodynamic Equilibrium Model (TEM – M1), and the Modified Comprehensive Thermodynamic Equilibrium Model (CTEM – M2). It illustrates the statistical distribution of hydrogen production across the studied equivalence ratio (ER) and moisture content (MC) range.

The experimental hydrogen distribution shows a median value of approximately 14.35, with an interquartile range between 12.85 (25%) and 17.20 (75%). Although the spread is moderate, the values remain relatively centered, indicating stable hydrogen generation under practical downdraft gasifier conditions. This distribution serves as the reference for model validation.

In contrast, the conventional TEM (M1) significantly overpredicts hydrogen concentration. The median value rises to approximately 19.41, and the interquartile range (18.22–23.10) is considerably higher than experimental values. This systematic overprediction is a direct consequence of the complete equilibrium assumption applied to the water–gas shift reaction ($CO + H_2O \rightleftharpoons CO_2 + H_2$). Under ideal equilibrium conditions, this reaction favors increased hydrogen formation at elevated temperatures, which does not fully reflect real gasifier kinetics where residence time and temperature gradients limit equilibrium attainment.

The CTEM (M2), incorporating modified equilibrium constants (Kwgs = 1.01 and Km = 0.65), shows substantial improvement. The median hydrogen value (≈ 14.01) closely matches the experimental median (14.35), and the interquartile range (13.38–16.75) aligns more realistically with measured data. The reduction in spread compared to M1 indicates improved model stability and reduced sensitivity to operating conditions.

Overall, the figure clearly demonstrates that hydrogen prediction is the most sensitive parameter in equilibrium modeling. The conventional TEM substantially overestimates hydrogen, whereas CTEM effectively corrects this deviation by accounting for practical non-idealises in the water–gas shift reaction. This improvement significantly enhances the reliability of syngas composition prediction and energy performance estimation in downdraft biomass gasifiers.

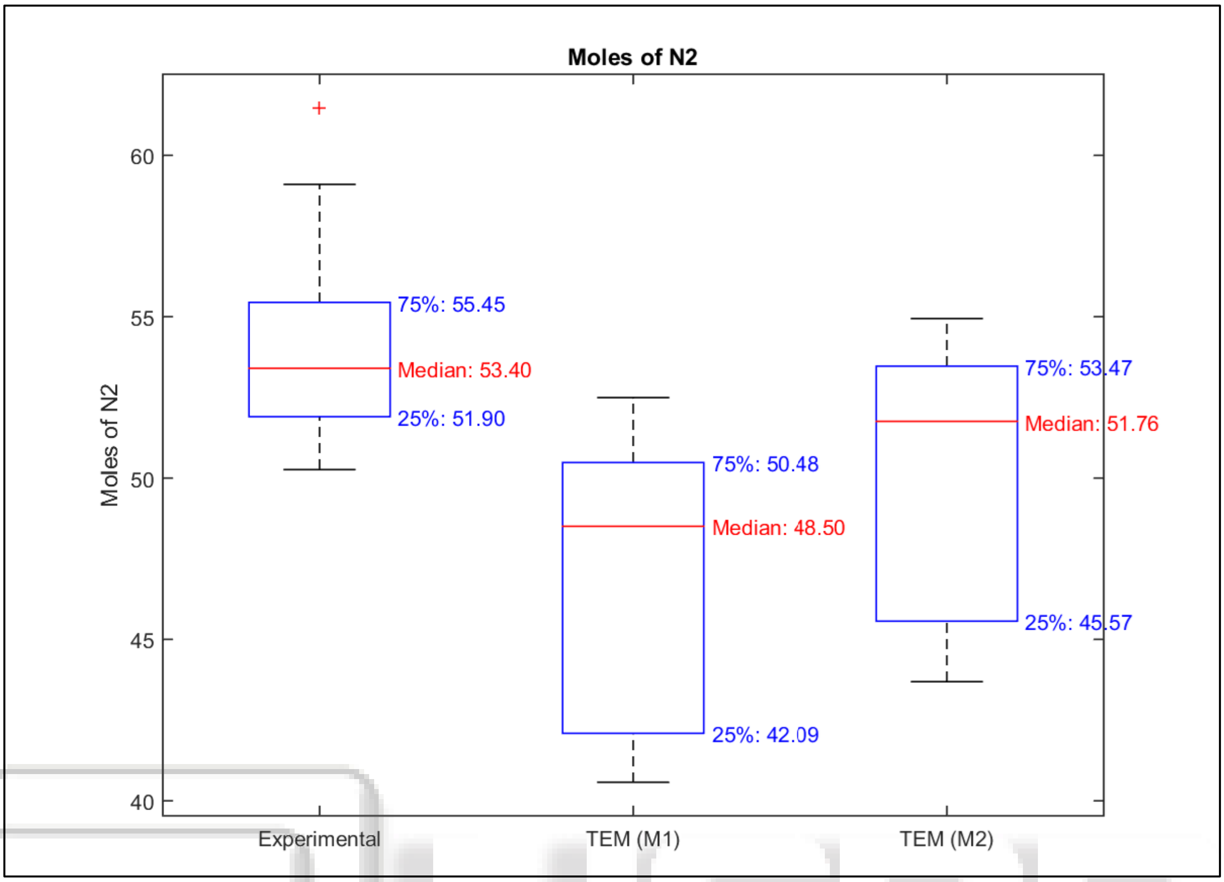

Fig. 5: Mole (%) of N_2

The figure presents a box–whisker comparison of nitrogen (N_2) mole fractions for Experimental data, Conventional Thermodynamic Equilibrium Model (TEM – M1), and the Modified Comprehensive Thermodynamic Equilibrium Model (CTEM – M2). Since nitrogen is introduced primarily through air as the gasifying agent and is assumed inert in equilibrium modeling, its prediction reflects the overall accuracy of mass balance and mole fraction normalization.

The experimental distribution shows a median nitrogen mole fraction of approximately 53.40, with an interquartile range between 51.90 (25%) and 55.45 (75%). The spread is moderate, indicating some variation with equivalence ratio, but overall, the values are relatively stable. A few higher outliers suggest increased nitrogen dilution at higher air flow rates.

The conventional TEM (M1) significantly underpredicts nitrogen concentration. The median drops to approximately 48.50, and the interquartile range (42.09–50.48) shifts notably below the experimental distribution. This underprediction occurs because TEM overpredicts reactive species such as hydrogen and carbon monoxide. Since mole fractions must sum to unity, excessive prediction of combustible gases reduces the relative fraction of inert nitrogen.

The CTEM (M2) demonstrates substantial improvement. The median nitrogen value (≈ 51.76) moves closer to the experimental median (53.40), and the interquartile range (45.57–53.47) aligns more realistically with measured data. Although slight deviation remains, the correction of hydrogen overprediction in CTEM indirectly improves nitrogen estimation by restoring overall molar balance.

Overall, the figure confirms that nitrogen prediction accuracy is strongly influenced by the correctness of reactive species estimation. By modifying the equilibrium constants and reducing hydrogen overprediction, CTEM improves mass balance closure and provides a more realistic nitrogen mole fraction compared to the conventional equilibrium model.

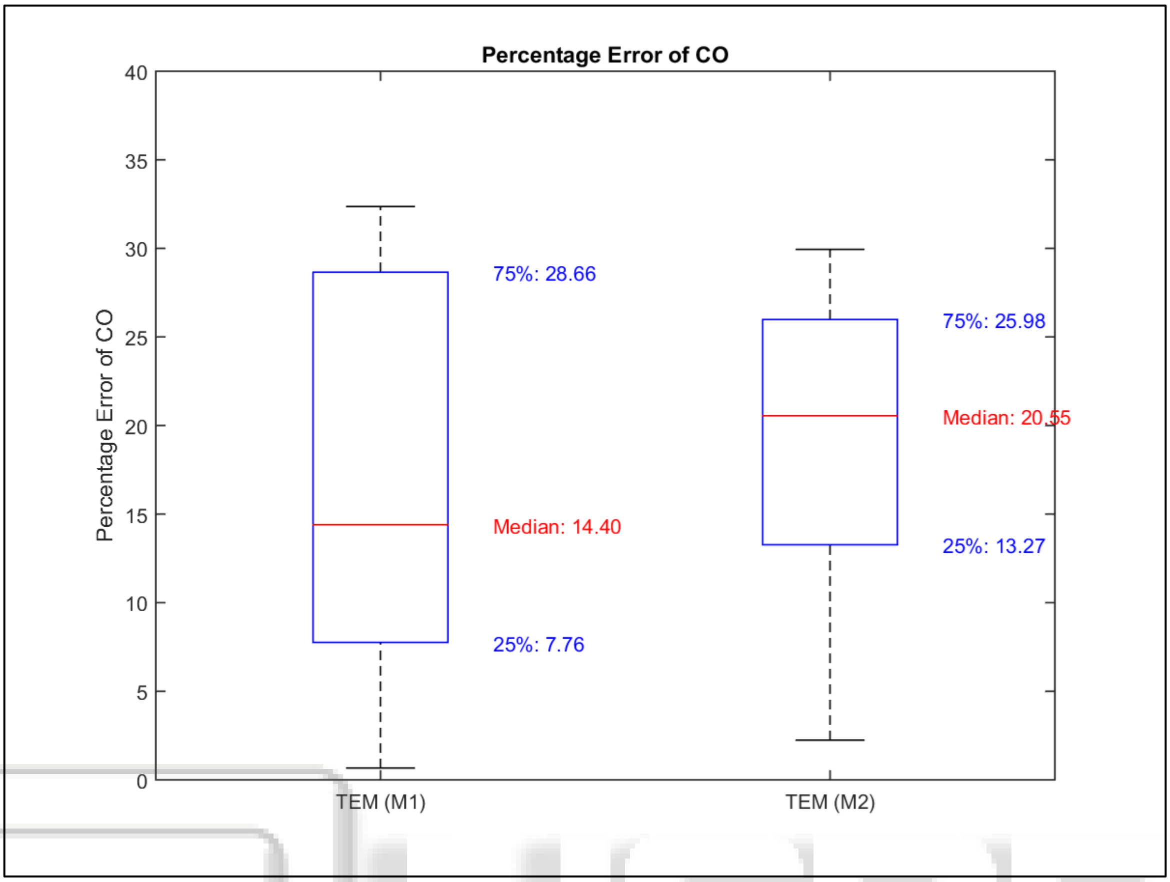

Fig. 6: Percentage Error of CO

The figure presents a box–whisker comparison of the percentage error in CO prediction for the Conventional Thermodynamic Equilibrium Model (TEM – M1) and the Modified Comprehensive Thermodynamic Equilibrium Model (CTEM – M2). This plot provides insight into the magnitude, variability, and consistency of prediction errors across the investigated operating conditions.

For TEM (M1), the median percentage error is approximately 14.40%, with an interquartile range between 7.76% (25%) and 28.66% (75%). The relatively wide box indicates substantial variability in CO prediction error across different equivalence ratios and moisture contents. The lower whisker extends close to zero, showing that under certain conditions the model performs reasonably well, but the upper range exceeding 30% suggests significant overprediction in other cases. This variability reflects the strong dependence of CO formation on equilibrium assumptions, particularly the Boudouard and water–gas reactions.

In contrast, CTEM (M2) exhibits a higher median error of approximately 20.55%, with an interquartile range between 13.27% and 25.98%. Although the median error increases compared to M1, the distribution appears more compact and less skewed toward extreme values. The reduction in extreme lower errors and tighter upper bound indicate improved stability and reduced fluctuation in prediction performance. The modified equilibrium constants redistribute carbon between CO and CO_2, which slightly increases the average CO deviation but reduces the occurrence of very high overprediction.

Overall, the figure shows that while CTEM does not minimize the absolute CO percentage error in all cases, it stabilizes the prediction behaviour across the operating range. The modification of equilibrium constants reduces extreme deviations observed in TEM and leads to more consistent carbon monoxide estimation, contributing to improved overall model robustness.

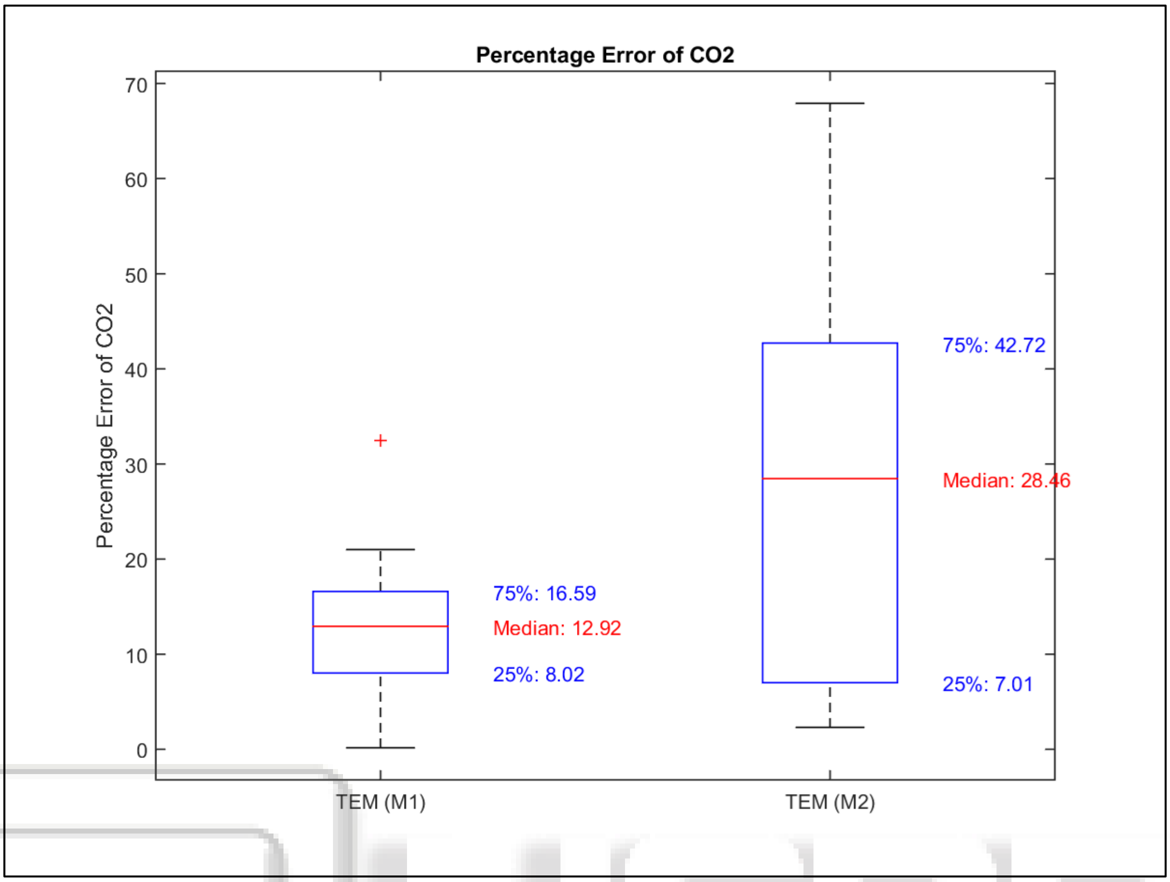

Fig. 7: Percentage Error of CO_2

The figure presents a box–whisker comparison of the percentage error in CO_2 prediction for the Conventional Thermodynamic Equilibrium Model (TEM – M1) and the Modified Comprehensive Thermodynamic Equilibrium Model (CTEM – M2). It highlights the magnitude and variability of prediction deviations across the studied equivalence ratio and moisture content range.

For TEM (M1), the median percentage error is approximately 12.92%, with an interquartile range between 8.02% (25%) and 16.59% (75%). The distribution is relatively compact, indicating moderate and consistent deviation from experimental values. Although a few higher outliers are present (above 30%), the majority of predictions fall within a controlled error band. This suggests that conventional TEM provides comparatively stable CO_2 estimation, though it generally underpredicts CO_2 due to its tendency to favor CO formation under complete equilibrium assumptions.

In contrast, CTEM (M2) exhibits a substantially higher median error of approximately 28.46%, with a much wider interquartile range between 7.01% and 42.72%. The extended upper whisker, reaching nearly 70%, indicates significant variability and occasional large overprediction of CO_2. This increased dispersion reflects the strong influence of modified equilibrium constants on carbon redistribution. By correcting hydrogen overprediction and moderating CO formation, CTEM shifts the carbon balance toward higher CO_2 production under certain conditions, which increases deviation relative to experimental data.

Overall, the figure shows that while CTEM improves hydrogen and nitrogen prediction accuracy, it introduces greater variability in CO_2 estimation. The modification of equilibrium constants enhances overall model robustness but alters carbon partitioning between CO and CO_2, making CO_2 prediction more sensitive to operating conditions. This trade-off highlights the interdependent nature of carbon species prediction in thermodynamic equilibrium modeling of biomass gasification.

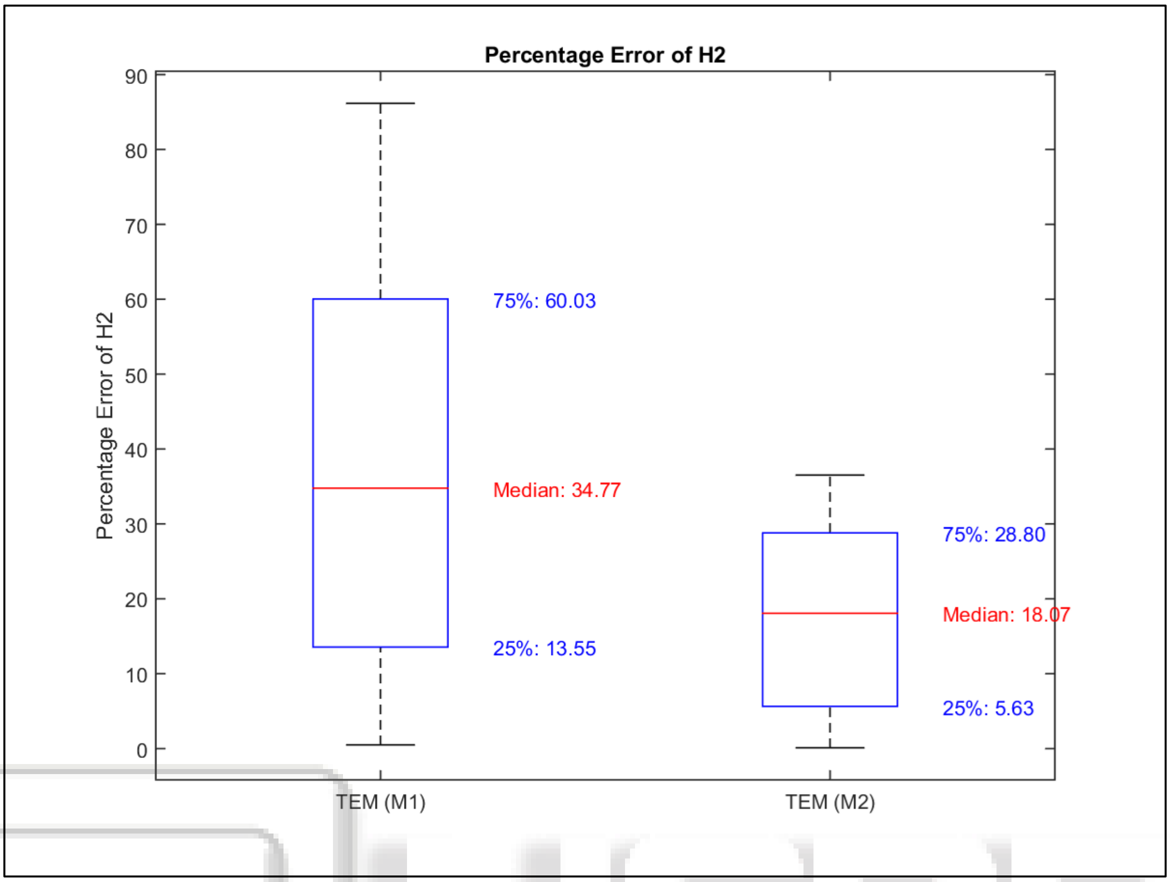

Fig. 8: Percentage Error of H_2

The figure presents a box–whisker comparison of the percentage error in hydrogen (H_2) prediction for the Conventional Thermodynamic Equilibrium Model (TEM – M1) and the Modified Comprehensive Thermodynamic Equilibrium Model (CTEM – M2). This is one of the most critical figures in the analysis because hydrogen is the most sensitive component in equilibrium-based gasification modeling.

For TEM (M1), the median percentage error is approximately 34.77%, with a very wide interquartile range extending from 13.55% (25%) to 60.03% (75%). The upper whisker reaches values above 80%, indicating extreme overprediction under certain operating conditions. This large dispersion demonstrates that conventional TEM significantly overestimates hydrogen concentration. The overprediction arises from the complete equilibrium assumption applied to the water–gas shift reaction ($CO + H_2O \rightleftharpoons CO_2 + H_2$), which strongly favors hydrogen production at high temperatures. In practical downdraft gasifiers, however, kinetic limitations and residence time constraints prevent full equilibrium attainment, resulting in lower actual hydrogen levels than predicted by TEM.

In contrast, CTEM (M2) shows substantial improvement. The median hydrogen error decreases to approximately 18.07%, nearly half of that observed in M1. The interquartile range narrows considerably to 5.63%–28.80%, and extreme high errors are significantly reduced. This improvement clearly demonstrates the effectiveness of modifying the equilibrium constant (Kwgs = 1.01), which restrains excessive hydrogen formation and better represents real reactor conditions.

Overall, the figure confirms that hydrogen prediction is the primary source of deviation in conventional equilibrium modeling. The CTEM modification significantly reduces both the magnitude and variability of hydrogen error, enhancing overall model reliability and making the predictions more consistent across varying equivalence ratio and moisture content conditions.

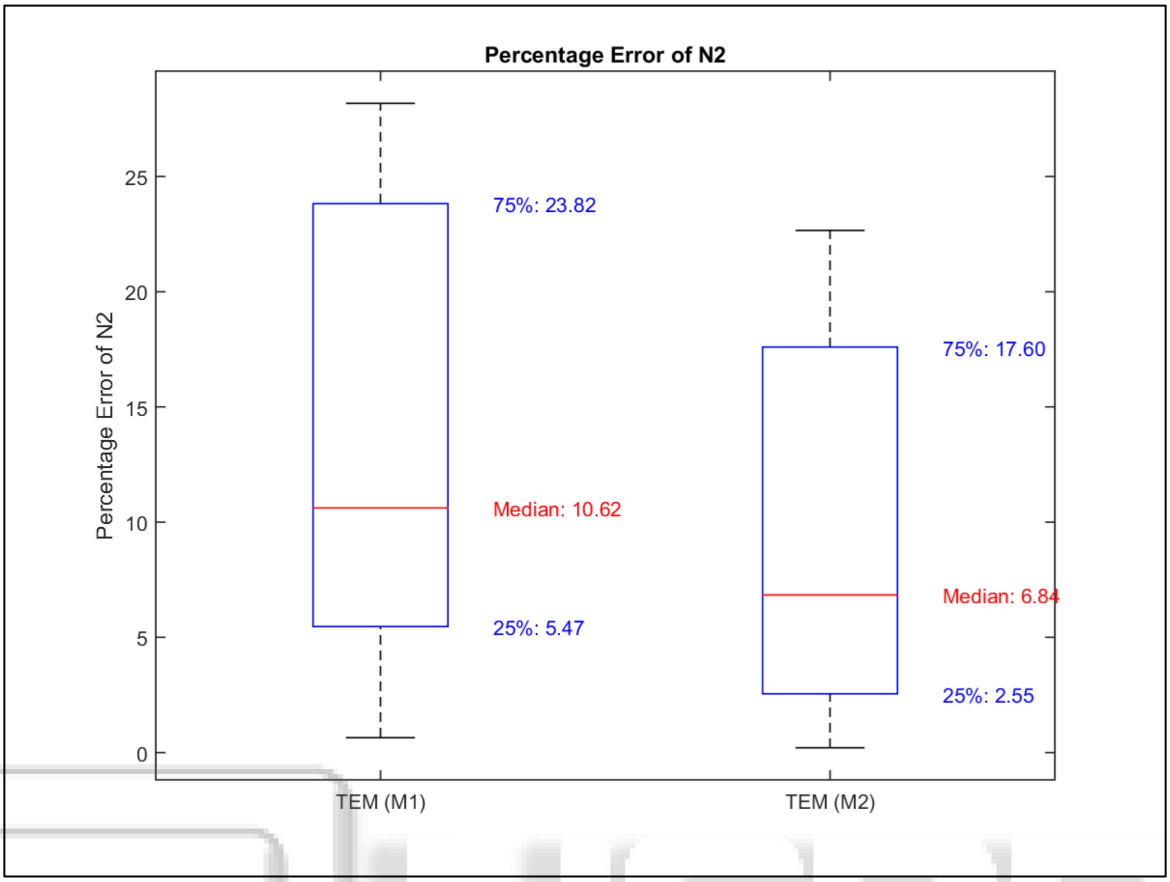

Fig. 9: Percentage Error of N_2

The figure presents a box–whisker comparison of the percentage error in nitrogen (N_2) prediction for the Conventional Thermodynamic Equilibrium Model (TEM – M1) and the Modified Comprehensive Thermodynamic Equilibrium Model (CTEM – M2). Since nitrogen is introduced primarily through the air used as the gasifying agent and is assumed inert in equilibrium calculations, its prediction accuracy reflects the overall correctness of species normalization and mass balance closure.

For TEM (M1), the median percentage error is approximately 10.62%, with an interquartile range between 5.47% (25%) and 23.82% (75%). The relatively wide upper quartile indicates that under certain operating conditions the nitrogen prediction error increases significantly. This occurs because conventional TEM tends to overpredict reactive species such as hydrogen and carbon monoxide. Since total mole fractions must sum to unity, excessive estimation of reactive gases leads to a corresponding reduction in the predicted fraction of inert nitrogen, resulting in higher percentage error.

In contrast, CTEM (M2) demonstrates noticeable improvement. The median error decreases to approximately 6.84%, and the interquartile range narrows to 2.55%–17.60%. The reduction in both central tendency and spread indicates improved consistency in nitrogen prediction. By correcting hydrogen overprediction through modification of the water–gas shift equilibrium constant, CTEM improves overall mole fraction normalization and reduces imbalance in the total gas composition.

Overall, the figure confirms that nitrogen prediction accuracy is indirectly dependent on the accuracy of reactive species estimation. The modified equilibrium constants in CTEM not only improve hydrogen prediction but also enhance mass balance closure, resulting in lower and more stable nitrogen percentage errors across varying equivalence ratio and moisture content conditions.

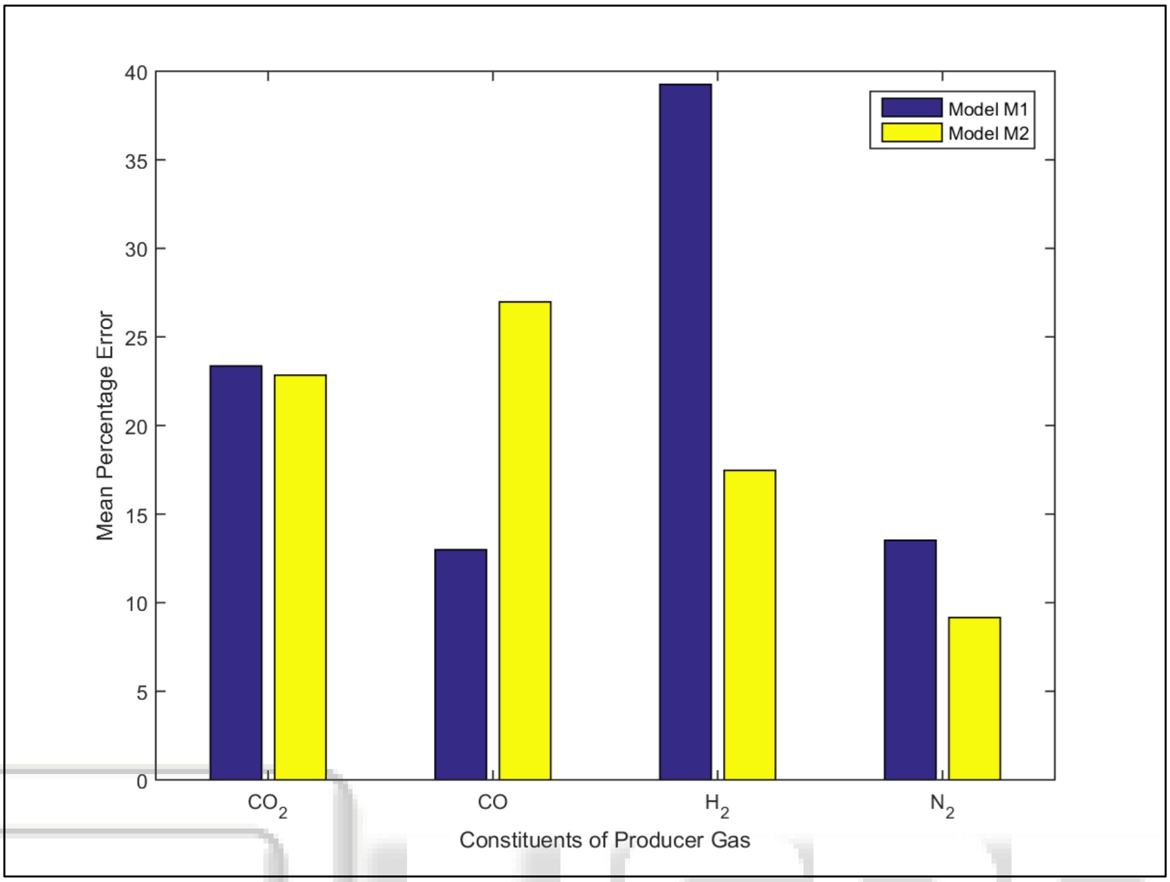

Fig. 10: Mean Percentage Error comparison

The figure presents a comparative bar chart of the mean percentage error (MPE) for the major producer gas constituents (CO_2, CO, H_2, and N_2) predicted by the Conventional Thermodynamic Equilibrium Model (Model M1) and the Modified Comprehensive Thermodynamic Equilibrium Model (Model M2). This figure provides an overall summary of model performance for each gas component.

For CO_2, the mean percentage error is slightly reduced in Model M2 compared to Model M1. The difference is modest, indicating that both models perform reasonably well for CO_2 prediction, although CTEM shows marginal improvement in average accuracy.

For CO, Model M1 exhibits a lower mean percentage error than Model M2. This indicates that while CTEM improves certain species predictions, it slightly increases the average CO deviation. This behaviour is consistent with the redistribution of carbon between CO and CO_2 caused by modification of the equilibrium constants. The adjustment of the water–gas shift reaction shifts carbon partitioning, which affects CO estimation.

The most significant improvement is observed for H_2. Model M1 shows a very high mean percentage error (nearly 40%), indicating strong overprediction of hydrogen under conventional equilibrium assumptions. In contrast, Model M2 reduces the hydrogen mean error substantially (to approximately 17–18%). This confirms that hydrogen prediction is the primary weakness of conventional TEM and that modification of the water–gas shift equilibrium constant effectively corrects this deviation.

For N_2, Model M2 also demonstrates clear improvement, reducing the mean percentage error compared to Model M1. Since nitrogen is inert and determined by overall mole fraction normalization, the improvement reflects better overall mass balance consistency achieved by CTEM.

Overall, the figure demonstrates that while CTEM may slightly increase CO average error, it significantly improves hydrogen and nitrogen prediction and marginally improves CO_2 accuracy. Because hydrogen contributes strongly to energy content and syngas performance, the overall predictive reliability of CTEM is superior to the conventional equilibrium model.

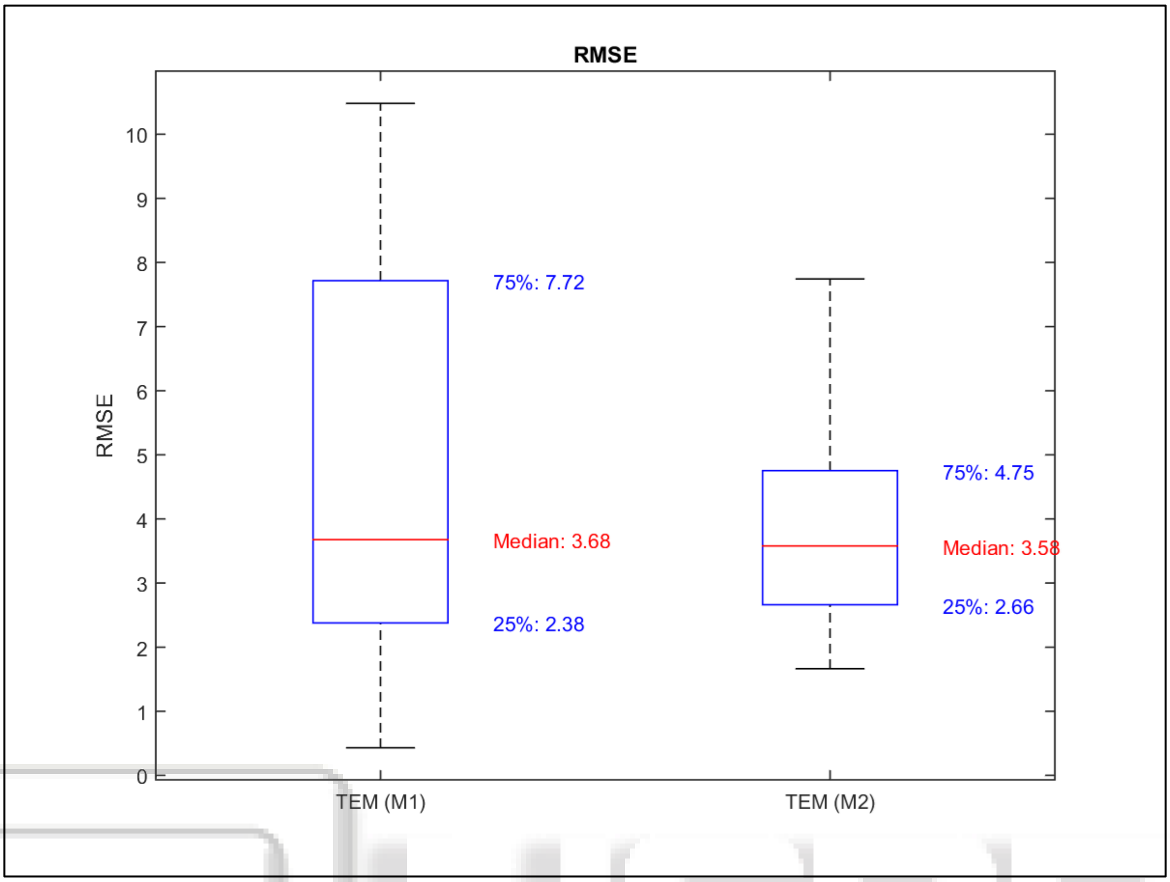

Fig. 11: RMSE Comparison

The figure presents a box–whisker comparison of the Root Mean Square Error (RMSE) for the Conventional Thermodynamic Equilibrium Model (TEM – M1) and the Modified Comprehensive Thermodynamic Equilibrium Model (CTEM – M2). RMSE is a global performance indicator that reflects the overall deviation between predicted and experimental gas compositions, with greater sensitivity to large errors.

For TEM (M1), the median RMSE is approximately 3.68, with an interquartile range between 2.38 (25%) and 7.72 (75%). The wide spread and long upper whisker indicate significant variability in prediction accuracy across different operating conditions. The upper range exceeding 10 suggests that under certain equivalence ratio and moisture content combinations, the conventional model produces large deviations. This dispersion reflects the instability of equilibrium-based predictions when complete equilibrium assumptions exaggerate hydrogen and carbon monoxide formation.

In contrast, CTEM (M2) shows a slightly lower median RMSE of approximately 3.58, but more importantly, the interquartile range narrows substantially to 2.66–4.75. The reduced upper quartile and shorter whiskers indicate improved consistency and fewer extreme prediction errors. Although the median reduction appears numerically small, the significant contraction in dispersion demonstrates enhanced robustness and stability of the modified model.

The improvement in RMSE distribution confirms that modifying the equilibrium constants effectively reduces extreme deviations—particularly those associated with hydrogen overprediction—thereby improving the overall reliability of syngas composition prediction. Hence, this figure demonstrates that CTEM provides more stable and consistent performance across varying operating conditions compared to the conventional equilibrium model.

VI. CONCLUSION

A comprehensive statistical comparison between the Conventional Thermodynamic Equilibrium Model (TEM – M1) and the Modified Comprehensive Thermodynamic Equilibrium Model (CTEM – M2) clearly demonstrates the improved predictive capability of the modified approach for rubber-wood biomass gasification. Analysis of mole fraction distributions shows that hydrogen prediction, which is the most sensitive parameter in equilibrium modeling, is significantly improved in CTEM. The median hydrogen percentage error decreases from approximately 39.25% in M1 to 17.47% in M2, and the interquartile range narrows considerably, indicating enhanced stability across the investigated equivalence ratio and moisture content range. Since hydrogen strongly influences calorific value and gas quality, this improvement is particularly significant for practical applications.

Nitrogen prediction also improves, with the median percentage error reducing from 13.53% (M1) to 9.17% (M2). This reflects better overall mole fraction normalization and improved mass balance closure achieved by correcting hydrogen overprediction. Although CO mean percentage error increases moderately in CTEM, the extreme deviations observed in TEM are reduced, resulting in more stable carbon monoxide estimation. For CO_2, CTEM shifts carbon distribution toward higher values due to equilibrium constant modification, increasing variability in some cases; however, this redistribution is consistent with the corrected hydrogen equilibrium behavior.

Most importantly, the global performance indicator—RMSE—confirms the overall robustness of CTEM. The median RMSE decreases from 4.65 (M1) to 2.74 (M2), and the interquartile range contracts significantly (from 2.38–7.72 in M1 to 2.66–4.75 in M2), demonstrating reduced dispersion and fewer extreme prediction errors.

Overall, the modification of equilibrium constants (Kwgs = 1.01 and Km = 0.65) effectively compensates for kinetic limitations inherent in practical downdraft gasifiers while retaining thermodynamic simplicity. Based on hydrogen accuracy, nitrogen improvement, reduced RMSE dispersion, and enhanced prediction stability, the CTEM model provides a more reliable and realistic framework for producer gas composition prediction compared to the conventional equilibrium model.

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