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Numerical and Experimental Investigation of Hydrogen Enrichment Effect on the Combustion Characteristics of Biogas

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Abstract- In the present work, the combustion characteristics like adiabatic flame temperature (AFT) and laminar burning velocity (LBV) of methane (CH_4) diluted with carbon dioxide (CO_2), representing biogas, is investigated in detail. The laboratory prepared biogas samples containing CH_4 and CO_2 were also enriched with hydrogen (H_2) to realize the change in their combustion behaviour. The experiments were conducted on flat flame burners based on heat flux method at 1 bar, 298 K and at stoichiometric and off-stoichiometric conditions. The experimental results were also compared with the numerical predictions of ANSYS Chemkin-Pro® with full GRI Mech. 3.0 reaction mechanism. The results revealed that the presence of CO_2 in biogas dominates on richer mixtures, i.e., the CO_2 dilution affects the combustion characteristics of richer biogas mixtures more strongly than for leaner or stoichiometric mixtures. The simulated results of hydrogen-enriched biogas showed that the slope of the laminar burning velocity (LBV) curve for biogas containing the highest percentage of CO_2 sharply rises with about 33% H_2, whereas the slope of the mixture with least CO_2 and more CH_4, sharply changes its nature around 40% H_2-enrichment. This signifies that even with a small amount of H_2 in biogas, may be a suitable option to improve its combustion characteristics. Some preliminary correlations for H_2-enriched biogas were also derived to estimate the effect of H_2 presence in biogas fuels with higher Hydrogen concentrations.

Keywords Alternative fuel, Adiabatic Flame Temperature, Biogas, Hydrogen, Laminar Burning Velocity.

1. Introduction

The clean and green energy approach is the thrust area of all scientists over the globe, due to the exhaustible limited stock of conventional fossil fuels. With renewable energy ramping up at a remarkable pace in the last decade, India's energy sector is witnessing a transition towards renewable energy (RE). India added 11 GW of RE in the financial year 2017, while the country's conventional power raised by 10 GW [1]. The share of renewable energy capacity in India's total installed capacity had increased from 14.2% (2015-16) to 17.5% (2016-17), with a total installed capacity of 330 GW. It is estimated that RE in the total installed capacity of power shall increase to 40% by 2030 [1]. On the other hand, India's energy consumption growth by 4.2% per annum is faster than all major economies in the world.

Biogas, a potential renewable fuel produced by the biochemical decomposition of biomass such as animal dung, agro-wastes [2], poultry waste [3], olive oil [4], cafeteria waste [5], pine needles [6-7] and municipal solid wastes is primarily a mixture of 45-60% CH_4, 40–55% CO_2 along with some traces of H_2S, N_2, CO, O_2, and H_2O [8]. The biggest problem with biogas is its low calorific value of about 17 MJ/kg [9] due to the higher content of CO_2. A portable solution to improve the energy density of biogas like fuels is to enrich them with high calorific value fuels like H_2 having heating value around 120 MJ/kg [10] and burning velocity about 0.275 cm/s [9]. A similar approach has been reported by Mameri et al. [11]. H_2 is also capable of meeting the zero-emission requirements. The only difficulty with H_2 is its generation and storage.

A detailed literature review about the CO_2 presence in biogas and reducing its adverse effect with hydrogen enrichment is presented in the following section.

2. Literature Review

This section presents a summary of available literature on the effect of hydrogen enrichment and CO_2 dilution on biomass derived gaseous fuel mixtures.

2.1. Literature review on the effect of CO_2 dilution

Kishore et al. [8] conducted experiments on heat flux method and reported that the LBV of CH_4 is reduced more by CO_2 dilution compared to N_2 dilution. Also, the peak of LBV shifted towards stoichiometry, when CH_4 was diluted with 20%, 40% or 60% CO_2 by volume. Xie et al. [12-13] observed that the chemical kinetics of the biogas fuels are dependent upon the concentrations of H and OH radicals. Hinton and Stone [14] measured the data for LBV of biogas at various operating temperatures, pressures, and equivalence ratios using constant volume combustion technique and showed that the LBV of biogas increases with temperature and decreases with pressure. Further, the LBV of biogas containing 40% CO_2 was reduced by around 65% compared to pure CH_4 under stoichiometric conditions. Chan et al. [15] reported that the decrease in LBV and temperature is caused due to the dilution, thermal, chemical and radiation effects of CO_2. Liu et al. [16] studied the performance characteristics of biogas MILD oxy-fuel combustion under O_2/H_2O and O_2/CO_2 environment and reported about the high sensitivity of these mixtures to O_2 compared to CO_2 concentration. Nonaka and Pereira [17] performed experiments on heat flux method with 0-50% CO_2 dilution and reported a decrease in LBV and shift in peak towards lean mixture. They further predicted that GRI-Mech. 3.0 was in good agreement with experiments up to 20% CO_2 dilution, while Konnov's mechanism matched well for 30-50% CO_2 dilution. Mohammed et al. [18], Xu et al. [19] and Gascoin et al. [20] reported that when CO_2 replaced N_2, the flame temperature decreases, due to the high specific heat capacity of CO_2. Also, the concentrations of OH and NO decreases. Yang et al. [21] studied the effects of N_2, CO_2 and H_2O dilutions on temperature and concentration of OH in CH_4 on bunsen burner configuration using PLIF thermometry and bi-directional PLIF technology. Their findings revealed that CO_2 dilution affected much on CH_4 flames compared with N_2 and H_2O dilution. Guiberti and Schuller [22] conducted experimental and numerical investigation on premixed conical methane-air flames diluted with CO_2 and N_2 by observing the chemiluminescence signals received through OH, CH, and CO_2. They observed that with increased CO_2 dilution, the chemiluminescence intensity changes and OH/CO_2 ratio decreases. Liu et al. [23] reported that the LBV of biomass derived gaseous fuel mixtures can be correlated to methane as the LBV scales linearly with CH_4 mole fraction.

2.2. Literature review on the effect of H_2 enrichment

As discussed in section 2.1, the high CO_2 content in fuels like biogas can have adverse effects on combustion characteristics leading to a reduction in LBV, energy input per cycle, flammability range, and AFT. Due to this adversity, it is of importance to enrich biogas with small amounts of high-grade fuels (like hydrogen or propane).

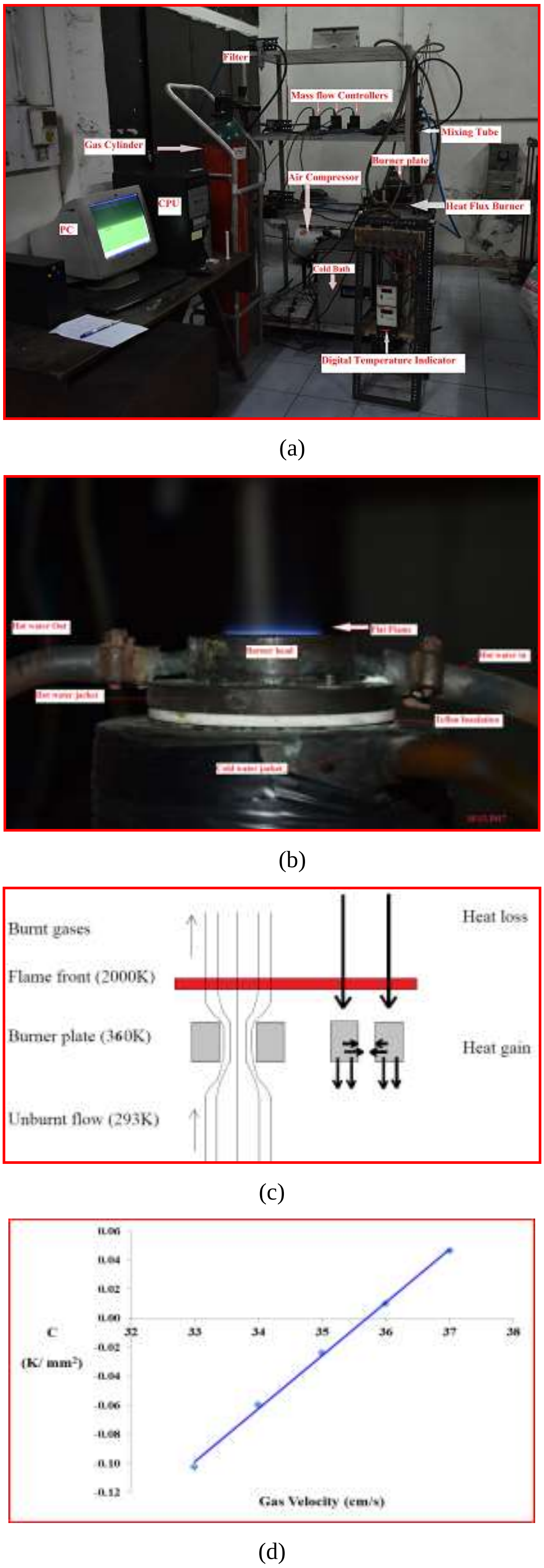
The effect of H_2 enrichment on CH_4, biogas and other C_1-C_4 hydrocarbon fuels were studied by various researchers [24-25, 26-27]. Their findings revealed that with H_2 addition, the flame stability, flame temperature, flammability, heat release rate, reaction energy, and the LBV increases significantly. H_2 addition also increases the concentrations of OH, H, and O. Further, CO emissions are greatly reduced. Wei et al. [28] conducted experiments to determine heat flux with biogas-hydrogen flame jet impinging on a perpendicular flat plate and reported enhancement in the local heat flux with an increase in unburnt gas velocity. Nilsson et al. [29] experimentally measured the LBV's of fuel blends representing natural gas (NG) using heat flux method. They enriched CH_4-C_2H_6 and CH_4-C_3H_8 fuel blends with 0, 10, 35 and 50% H_2 and reported that the addition of H_2 raised the LBV's of fuels with higher hydrocarbon by 20-40% compared to H_2-enriched CH_4 flames. Li et al. [30] studied the effect of H_2 enrichment on the LBV of CH_4, C_2H_6, and C_3H_8 using the counter-flow configuration incorporated with particle image velocimetry (PIV) technique. They observed a linear increase in LBV with increased H_2 concentration. They found CH_4 to be more sensitive to H_2 addition compared to C_2H_6 and C_3H_8. They concluded that the reaction $H+O_2 \Leftrightarrow OH+O$: (R1) is responsible for the increase in flame speed with increased H_2 concentration. From the detailed literature review, it is observed that most of the researchers have focused on the determination of the LBV of the CO_2 diluted CH_4 fuel, representing biogas using various measurement and numerical techniques. However, intense focus on the numerical predictions of AFT of biogas-H_2 is seldom reported. Also, limited literature is available on experimentation on biogas-H_2, especially on heat flux method. In the present work, combustion characteristics of biogas and hydrogen-enriched biogas are dealt in detail.

3. Materials and Methods

The experiments were conducted on the flat flame burner, developed by Maaren [31] and adopted by many research groups with suitable modifications [9, 31-35] which is based on heat flux principle [33]. Heat flux method is chosen for experimentation as it is one of the accurate methods of LBV determination and is based on simple interpolation [17].

3.1. Heat flux method: set up details

The photograph of the experimental setup, indicating major components is shown in Fig. 1a, and the complete design specifications are prescribed in Table 1. In Heat Flux method, the net heat loss from the flame to the burner plate is



(a)

(b)

(c)

(d)

Fig. 1. (a) Experimental setup based on heat flux method. (b) Flat flame photograph from the experiment (c) Principle of heat flux method (d) Interpolation technique.

measured, and the unburned mixture velocity is tuned in such a way that no net heat loss to the burner takes place (attaining adiabatic situation) [33]. A flat, stretch free, nearly one-dimensional adiabatic flame as shown in Fig. 1b, can be developed over the heat flux burner. The burner plate's temperature is maintained around 85ºC to 90ºC using a thermostatic hot bath containing hot water circulation system. The hot bath enables the flame to stabilize by providing the necessary heat to it.

3.1.1. Principle of heat flux method

The principle of flame stabilization over the heat flux burner is shown in Fig. 1c. The net difference (heat loss – heat gain) is responsible for the temperature distribution that is observed in the burner plate which is measured by attaching thermocouples at various radial locations. The heat flux can be realized by solving the energy equation provided by Maaren [31] in cylindrical coordinates. The burner plate is considered as rotationally symmetric and tangential component is neglected. Under these assumptions, the temperature distribution of the burner plate can be represented by equation 1 [31].

$$T_p\,(r) = T_c - (q\,r^2 / 4.\,K_p.t) \qquad (1)$$

Where T_p (r) is the plate temperature at some radial distance, T_c is the temperature indicated by thermocouple fitted at the center of the burner plate, q is net heat transfer, r is radial distance, K_p is the thermal conductivity of the plate, and't' is the plate thickness. The parameter q / $4.K_p.t$ represent the parabolic coefficient (C) and is expressed in K /mm². It can be observed that the temperature distribution in the burner plate represents a parabola with the center of the burner plate being the symmetry axis. Under adiabatic conditions (net heat loss = net heat gain), the temperature of the plate (T_p) will be identical at each point on the plate to the temperature indicated by the thermocouple fitted at the centre (T_c).

3.1.2. Constructional details of heat flux set up

The heat flux set up used in the present work consists of a circular, honeycomb holed, brass burner plate, having 2 mm thickness and 30 mm diameter to stabilize flat flame over it. The number of holes in the burner plate is approximately 1519 (counted after fabrication) with 0.5 mm diameter and 0.7 mm pitch. The mass flow controllers (Mfg: Alicat Scientific Inc. U.S) are used to control and regulate the mass flow rate of associated gases. K-type Chromel-Alumel thermocouples with a bead size of 0.3 mm are attached at different radius-angle locations in the burner plate to read its temperature. The thermocouples are insulated with Teflon to prevent any heat interaction with the surrounding. The input and output of mass flow controllers can be monitored through a PC (using FLOWVISION Software). . A mixing tube is fitted just before the plenum chamber to prepare a homogeneous mixture of fuel and oxidizer. The plenum chamber is designed in such a way to homogenize the fresh incoming fuel-oxidizer mixture after the mixing tube. The detailed specifications of the setup are provided in Table 1.

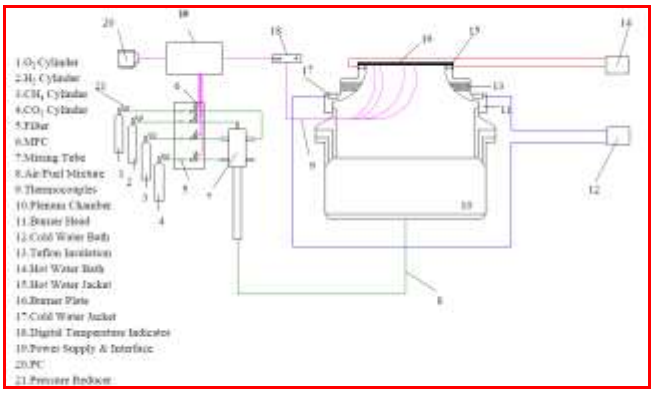


Fig. 2. Schematic of the heat flux setup

3.1.3. Interpolation technique

The adiabatic situation cannot be realized practically because there is no such condition like zero heat flux during experiments. Hence, the parabolic coefficient is determined by using the least square method in the temperature profile expression presented in equation (1) after measuring the temperature of the burner plate using 5-6 thermocouples. Afterwards, the parabolic coefficient at different velocities, varying from negative to positive is plotted in a graph as shown in Fig. 1d. The unstretched adiabatic burning velocity is determined through interpolation [31-35], in the situation where the parabolic coefficient becomes zero.

3.1.4. Working of the heat flux setup

The gas from cylinders (1, 2, 3, or 4) as shown in Fig. 2, is passed through a gas filter (5). The volume flow rate of the gas is metered by mass flow controllers (6) connected through a PC (20) via the RS232 communication port. A homogeneous mixture of fuel and oxidizer is prepared in the mixing tube (7). The premixed fuel-oxidizer mixture then goes to the plenum chamber (10), which stabilizes the flow and finally to the burner plate (16) via burner head (11). After igniting the fuel-oxidizer mixture through ignitor, a burner stabilized flat flame is developed over the burner plate. The hot bath (14) helps to keep the unburnt mixture heated to about 85-90^{o}C as desired by heat flux principle. The cold bath (12) maintains the unburnt mixture temperature when it passes through plenum chamber and burner head.

3.2. Computational details

Numerical computations were done using ANSYS Chemkin-Pro$^®$ [36] with GRI Mech. 3.0 [37] to predict the combustion characteristics of hydrogen-enriched biogas. GRI-Mech. 3.0 reaction mechanism is best suited to understand the chemical kinetics of CH_4 and NG fuels and is inbuilt with NO formation and re-burns chemistry. GRI-Mech. 3.0 has 53 species and 325 elementary chemical reactions along with rate coefficients and thermochemical parameters. The mechanism also takes care of propane and C_2 oxidation products. ANSYS Chemkin-Pro$^®$ software simulates one-dimensional burner stabilized flames under steady-state conditions, relevant to the modeling and simulation of gas-phase chemistry for the conceptual development of various practical combustion systems. During numerical simulations, grid independence test was conducted to check the convergence. Grid points were varied from 800-1300 in steps of 100. The results with 1200 and 1300 grid points were comparable. Hence, for all simulations, 1200 grid points were chosen to get grid-independent solutions. The adaptive grid control based on solution gradient and curvature were set to 0.02 and 0.1 respectively. Similar gradient and curvature values were reported by Kishore et al. [8]. The starting and ending axial positions were set to -2 cm and 10 cm respectively. The initial grid was based on temperature profile estimate. For biogases enriched with hydrogen, thermal diffusion (Soret effect) was also taken into account.

The synthetic biogas for conducting experiments was prepared in the laboratory by diluting CH_4 with CO_2, as these two gases are the main constituents of the biogas. Further few biogases were enriched with 20 or 40 % H_2. The H_2 concentration was limited to 40% due to the limitation of the present heat flux set-up capable of measuring burning velocity in the range of 50-60 cm/s [38]. However, numerical simulations were conducted for higher H_2 concentrations.

4. Results and Discussions

In this work, the experiments were conducted on perforated flat flame burner operating on heat flux principle, at 1 bar and 298 K, under off-stoichiometric and stoichiometric conditions. The combustion characteristics of biogas-air and hydrogen-enriched biogas-air mixtures were studied in detail. Numerical computations were also done using ANSYS Chemkin-Pro [36] with full GRI Mech. 3.0 [37] to predict the AFT, and the LBV with higher H_2 content.

4.1. Validation

The experimental results were validated by comparing them with results available in the literature (Fig. 3). For validation, a very common CH_4-air mixture was used for which experimental data is abundantly available in the literature. The results were also compared with the computational result of ANSYS Chemkin-Pro$^®$ with GRI Mech. 3.0. The measured results are in good agreement with literature data [35, 39-40] and GRI-Mech. 3.0 predictions, validating the accuracy of the developed set up to conduct experiments.

Table 2 shows the fuel compositions that were prepared in the laboratory for experimental investigation and volume fractions of similar blends were set as input for numerical predictions. The measured and predicted results of methane-air and CO_2 diluted methane-air (representing biogas) are also incorporated in Table 2 for comparison. The measured and computed results exhibit a continuous decrease in LBV when the volume fraction of CO_2 is increased from 10% to 50% in fuel mixture (designated as Bio-fuels BF10 to BF50) respectively. Furthermore, the predicted and experimental results are comparable and exhibit a similar trend of CO_2 dilution effect on stoichiometric methane at 1 bar and 298 K, within the specified uncertainty band of ± 1 cm/s reported in literature [38].

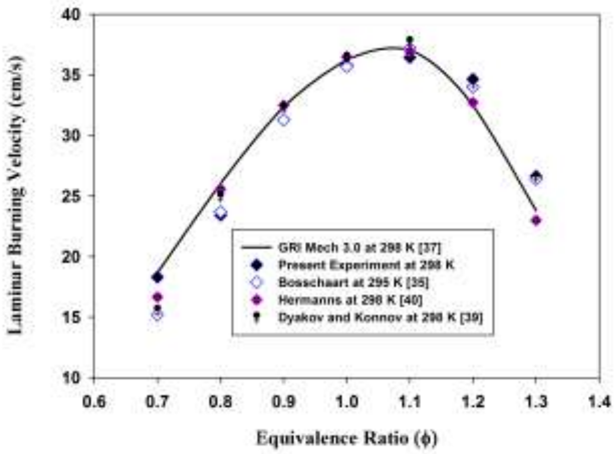


Fig. 3. Validation of measured LBV for CH_4-air at 1 bar 298 ± 1 K

4.2. Experimental Uncertainty

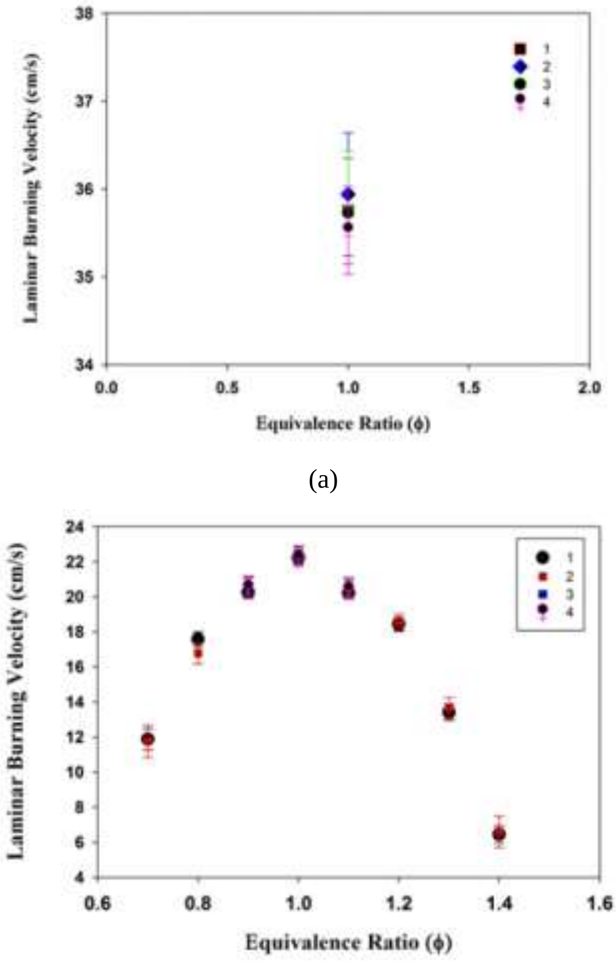
The experimental uncertainties are calculated adopting the technique used by Bosschaart [35]. The uncertainties in LBV, equivalence ratio (ϕ) and temperature measurement for the current work were estimated as ± 0.8 cm/s, 0.02 and ± 1°C respectively. The uncertainties noticed here are better than other techniques of laminar burning velocity measurements [38]. In extremely leaner and extremely richer mixtures, the uncertainty was more due to flame stabilization issue [17] and operation of mass flow controllers to their minimum values. The measured LBV for stoichiometric CH_4-air mixture at 1 bar and 298 K was 35.6 cm/s, which agrees with 36 ± 1 cm/s reported in the literature.

4.3. Experimental repeatability

The repeatability of the measured CH_4-air and biogas BF40-air was also verified by repeating the experiments four times on different days. The results obtained were repeatable and within the specified uncertainty limits, as shown in Fig. 4a for CH_4-air at stoichiometry and Fig. 4b for BF40-air at 1 bar and 298 K under stoichiometric and off-stoichiometric conditions.

4.4. Experimental and computational results

When a homogeneous mixture with some initial temperature and concentration is brought to equilibrium through an isobaric adiabatic process, then the final temperature attained is called adiabatic flame temperature (AFT). AFT may be affected by equivalence ratio (ϕ), pressure, temperature and fuel composition. Predominantly equivalence ratio is the main parameter that affects the AFT. The AFT through Arrhenius kinetics affects the LBV of any fuel significantly, since it is controlled by the heat of combustion. The flames having large heat of combustion move faster [41]. In this paper, the AFT of biogas and H_2-enriched biogas fuels were predicted using ANSYS Chemkin-Pro® with GRI Mech. 3.0 reaction mechanism. The effect of CO_2 dilution on the AFT of biogas samples is presented in Fig. 5(a). The variations of predicted adiabatic flame temperature as a function of percentage CO_2 dilution are plotted in Fig 5(b) for CH_4-air at 1 bar, 298 K and $\phi = 1$.



(a)

(b)

Fig. 4. Repeatability of stoichiometric mixtures at 1 bar and 298 K (a) CH_4 (b) BF40

It can be observed from Fig. 5b that, with increased CO_2 dilution, the AFT decreases monotonically. This reduction is due to the presence of CO_2, which captures H through $CO+OH \leftrightarrow CO_2+H$, with $H+O_2 \leftrightarrow O+OH$ as the main branching reaction [42]. This phenomenon of H capturing by CO_2 decreases the overall mixture temperature in the reaction

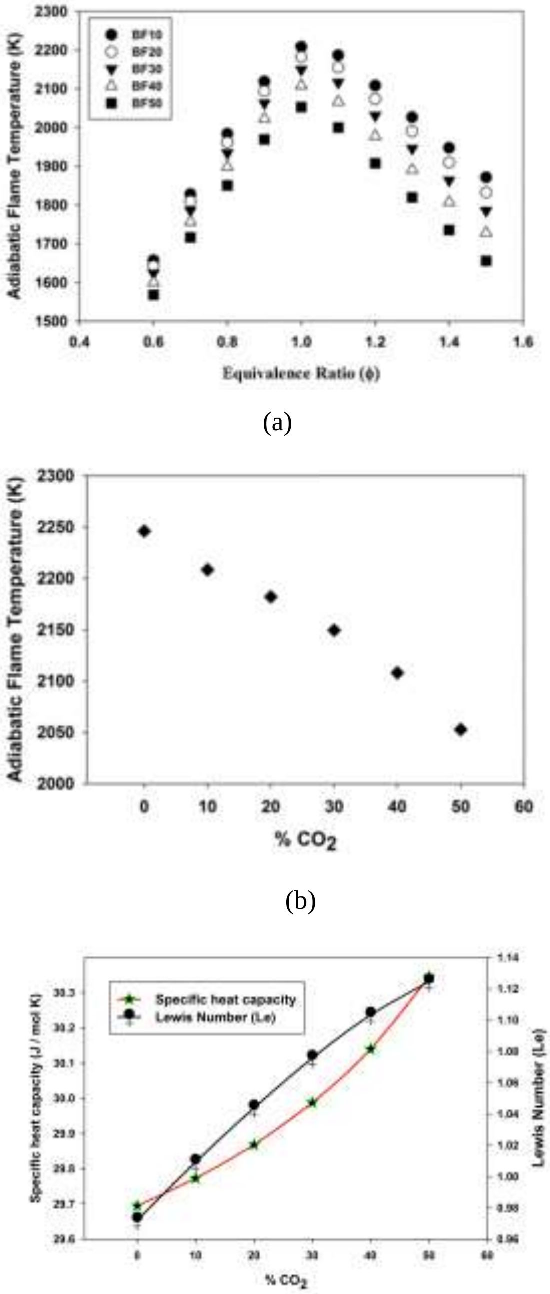
Table 1 – Specifications of major components of the Heat Flux set up

Part Name	Details / Specifications
 **Burner Plate**	**Purpose:** To stabilize the flat flame **Specifications:** **Material:** Brass **Plate thickness:** 2 mm **Plate diameter:** 30 mm **Hole diameter:** 0.5 mm **Perforation pattern:** Honeycomb holes (hexagonal) **Hole center to center distance:** 0.7 mm **No. of holes:** 1519 (approx.) **Mfg. technique:** CNC drilling (25000-50000 spindle speed)
 **Mass Flow Controller**	**Purpose:** To meter and control the mass flow rate of gases **Specifications:** **Mfg.:** Alicat Scientific Inc. USA **No. of MFC's used**: 5 **MFC Range (LPM): 0-1, 0-2, 0-5, 0-10 and 0-20** **Accuracy:** ± 0.4% of reading ± 0.2% of the full scale **Interface:** RS232 communication port (to PC) **No. of gases that can be handled:** 25
 **Thermocouple wires**	**Purpose:** To measure the temperature of the burner plate **Specifications:** **Material:** K-type Chromel-Alumel **Wire diameter:** 0.125 mm (each) **Bead size:** 0.3 mm **Wire insulation:** Teflon **Attachment material:** Silver glue (EPO-TEK H20E)
 **Digital Temperature Indicator (DTI)**	**Purpose:** To display the burner plate temperature **Specifications:** **Make:** Omega DP 462 **No. of channels:** 5 **Temperature Range:** 0-1000^{o}C
 **Gas Filter**	**Purpose:** To remove dirt and moisture from the gas **Specifications:** **Make:** Festo (Model No. 159613 LF 1/4 – D- MINI) **Size:** 40 µm
 **Hot and cold water bath**	**Purpose:** **Hot Bath:** To heat up the burner top (Flame stabilization) **Cold bath:** To maintain the temperature of the incoming gas **Specifications:** **Hot Bath Capacity:** 25 litres (Motor ¼ HP CG) **Cold Bath Capacity:** 5 liter (Motor 0.1 HP)

zone, as reported by many researchers [42-46]. When CO_2 dilution is increased from 10 to 50%, AFT decreased by 6.5%, 7% and 10% for lean ($\phi = 0.8$), stoichiometric ($\phi = 1$) and rich ($\phi = 1.2$) mixtures respectively. The AFT of BF50 under stoichiometric conditions decreased by about 200 K compared to the CH_4-air mixture under similar operating conditions. The reason for the decrease in AFT with increased CO_2 dilution in CH_4 is the dilution, thermal and kinetic effects as reported by Lee et al. [47] and Hu et al. [48]. The mixture's specific heat capacity increases with increased CO_2 dilution as shown in Fig. 5c. This increase in specific heat makes the thermal effect more dominant compared to dilution and chemical effect, as reported by Khan et al. [49] in context to LBV of CO_2 diluted CH_4. As LBV and AFT can be directly correlated, especially for CH_4-air mixture [41], the reduction in AFT with CO_2 dilution will also result in LBV reduction, similar to Khan et al. [49]. Furthermore, the AFT of rich CO_2 diluted mixtures was more affected compared to lean and stoichiometric ones as can be seen from Fig. 5a. This can also be realized through Lewis Number (Le) plot shown in Fig. 5c. It is well known that for rich mixtures, there is less O_2 and more fuel. Hence, the total number of moles of H_2 and CO in rich fuels, representing species of excess fuel, are more compared to original species H_2O and CO_2 due to which the specific heat is larger for H_2 and CO [41], affecting the AFT much in a rich mixture. When Le = 1, the flame temperature corresponds to AFT. However, with Le > 1, the heat loss is more than the heat gain in deficient species concentration, in that case, flame temperature is less than AFT. Conversely, when Le < 1, the flame temperature is higher than AFT [41]. Fig. 5c depicts that, with increased CO_2 dilution, the Lewis Number increases monotonically, and for all CO_2 diluted mixtures, it is more than unity. As Le > 1, the heat loss is more than the heat gain in deficient species, thus lowering the AFT and ultimately the LBV of such fuels.

4.5. Hydrogen enrichment effect on the AFT of biogas

Fig. 6a-d represents the predicted results of the AFT of some biogas fuels on which experiments were performed with 20 or 40% H_2 enrichment. The H_2 is enriched in multiples of 20% to realize the significant change in properties and to reduce the cost of experimentation. The fuel compositions listed in Table 3 were used for studying the effect of H_2 enrichment. All biogas mixtures exhibited an increase in AFT with 20 or 40% H_2 enrichment. Further, the peak of the AFT shifted towards the richer mixture side with increased H_2-concentration. The shift in peak AFT is due to increased kinetic effect and reactivity of the fuels after H_2 addition due to abundance of H radical in the radical pool under insufficient Oxygen environment. The OH and O radicals are readily formed due to dominance of $H+O_2 \Leftrightarrow OH+O$ reaction, with increased H_2 concentration [24-25,28, 30]. Fig. 6a-d also depicts that H_2 addition affects more in rich fuel mixtures due to increased production of H, OH and O radicals, resulting in higher rise in AFT of rich mixture compared to leaner and stoichiometric ones.



(a)

(b)

(c)

Fig. 5. (a) Effect of CO_2 dilution on the AFT of Stoichiometric CH_4 fuel (b) Decrease in AFT with 5 to 50% CO_2 dilution (c) Effect of CO_2 dilution on the specific heat capacity of the mixture and Lewis Number: All computations conducted at 1 bar and 298 K.

A similar effect of H_2 presence on fuels with low calorific values was reported by Pizzuti et al. [10]. For fuel BG1:1 and BG4:1, the CH_4 to CO_2 ratio raised from 1:1 to 4:1 and the percentage increase in AFT and LBV was 2.2% and 11.4 % respectively with 20% H_2-enrichment at stoichiometry. However, with 40% H_2 enrichment, the percentage increase in AFT and LBV was 1.6% and 7% respectively.

Table 2 - CO_2 dilution effect on LBV of stoichiometric CH_4 at 1 bar and 298 K.

CO_2 (%)	Fuel Nomenclature	Computational LBV (cm/s)	Experimental LBV (cm/s) (± 0.8)
0	CH_4-air	36.5	35.6
10	BF10	34.4	32.2
20	BF20	31.9	29.8
30	BF30	28.2	27.5
40	BF40	24.5	23.9
50	BF50	19.2	18.8

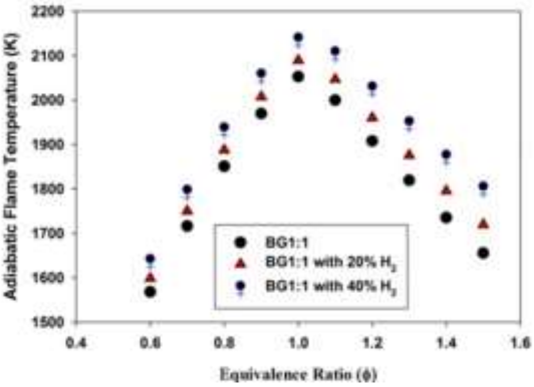
Table 3 - Fuels for AFT study with H_2 enrichment

CH_4 / CO_2	Designation	Fuel composition (% by volume)	
		CH_4	CO_2
1:1	BG1:1	50	50
1.5:1	BG1.5:1	60	40
2.3:1	BG2.3:1	70	30
4:1	BG4:1	80	20

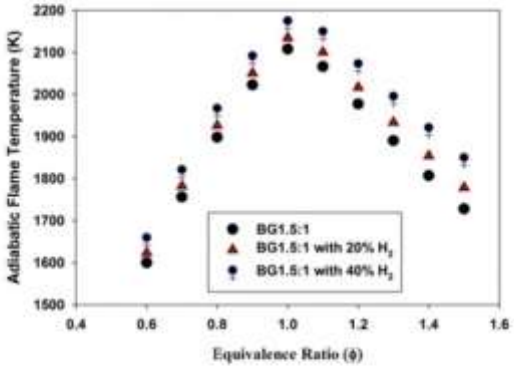
Note:- The ratio of CH_4 and CO_2 with H_2 enrichment are designated as BG1:1 to BG4:1 for better description ahead

Table 4 - Fuel designation and numerical correlations for H_2 enriched biogases.

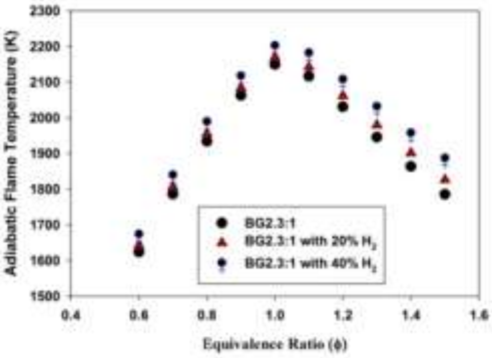
CH_4 / CO_2	Designation	LBV Correlation	Type	Equation
1:1	BG1:1	$LBV = 0.011\chi^2 + 0.099\chi + 20.00$	Exp.	3a
		$LBV = 0.008\chi^2 + 0.234\chi + 18.86$	GRI 3.0	3b
1.5:1	BG1.5:1	$LBV = 0.011\chi^2 + 0.039\chi + 25.12$	Exp.	4a
		$LBV = 0.009\chi^2 + 0.127\chi + 23.2$	GRI 3.0	4b
2.3:1	BG2.3:1	$LBV = 0.009\chi^2 + 0.077\chi + 28.81$	Exp.	5a
		$LBV = 0.008\chi^2 + 0.122\chi + 27.1$	GRI 3.0	5b
4:1	BG4:1	$LBV = 0.008\chi^2 + 0.070\chi + 32.62$	Exp.	6a
		$LBV = 0.005\chi^2 + 0.181\chi + 29.5$	GRI 3.0	6b



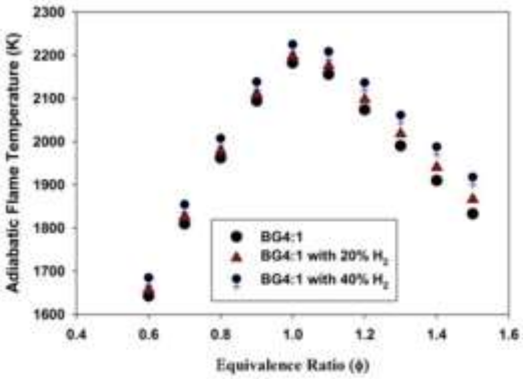
(a) BG1:1



(b) BG1.5:1



(c) BG2.3:1



(d) BG4:1

Fig. 6. Predicted AFT results after H_2 enrichment with GRI Mech. 3.0 at 1 bar and 298 K.

Figure 6a depicts that the mixture with a higher percentage of CO_2, when enriched with a small amount of H_2, undergoes a significant rise in the AFT under stoichiometric and off-stoichiometric conditions. It can also be observed that the AFT of BG1:1 fuel containing a maximum fraction of CO_2, compared to other blends (Fig. 6b-d), has become comparable to the AFT of pure CH_4-air at stoichiometry with 40% H_2 enrichment. This ensures that the LBV of BG1:1 mixture has become comparable to the CH_4-air mixture. Thus, the BG1:1 biogas with 40% H_2 concentration may prove to be a good substitute for practical applications where the CH_4-air mixture is desired.

Figure 7a-d represents the predicted results of 10-60% H_2-enriched biogas fuels. It is observed that the experimental results are in line with the predictions of ANSYS Chemkin-Pro® with GRI Mech. 3.0. As expected, a monotonic rise in the LBV with H_2-enrichment was detected, neglecting the adverse effect of CO_2 presence in the fuel mixtures. This indicates that the presence of CO_2 not only dilutes CH_4 but also participates in the chemical reactions when enriched with high-grade fuels like H_2. A best fitting curve is drawn among the predicted LBV results of H_2-enriched biogas fuel blends. The curve shows that the slope for fuel BG1:1 containing the highest percentage of CO_2 is steeper compared to BG4:1. This signifies that the rise in LBV is sharper for fuel with maximum CO_2 when enriched with a same H_2 percentage.

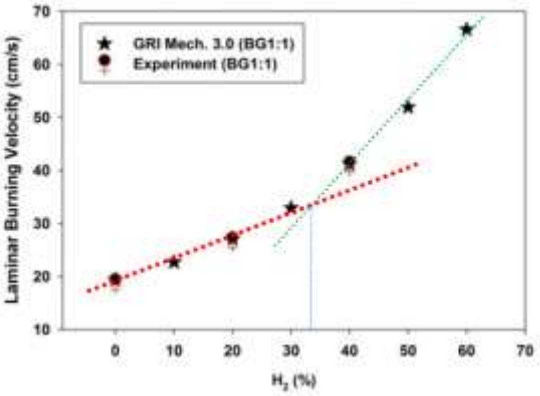
Another important observation from Fig. 7a-d is the change in slope at some distinguished locations. Two regimes have been identified for H_2-enriched biogas fuels. The rise in LBV is consistent for both the regimes. However, the slope of the straight line fitted is steeper in second regime containing higher H_2 concentration compared to the first one with lower H_2 concentration. This shifting in slope has been demarcated by fitting two straight lines following the trend of the results. The intersection of these two lines when extended to the abscissa, will provide an approximate H_2 percentage, at which the LBV of biogas is sharply raised due to H_2 enrichment. Interestingly, the slope of the LBV curve for biogas containing the highest percentage of CO_2 (i.e., BG1:1) suddenly changes with approximately 33% H_2 enrichment, whereas the mixture with least CO_2 content and more CH_4 (i.e., BG4:1) changes its nature at around 40% H_2. This signifies that even a small amount (say about 33%) of hydrogen in LCV fuels like biogas may be a suitable option to raise their AFT leading to improvement in chemical reactions rates and consequently their LBV. It must be noted here that the distinguished locations marked here represents approximate values. However, practical enrichment limits may be accurately determined by conducting experiments on combustors and engines. It is expected that the improvement in thermo-chemical properties of base biogas fuels after H_2-enrichment enables them to become a suitable substitute for conventional fuels by emitting less pollution. The present work suggests that the biogas extracted from landfills can be used for practical applications after being suitably enriched with H_2.

4.6. Numerical Correlations for H_2 enriched biogas for LBV prediction.

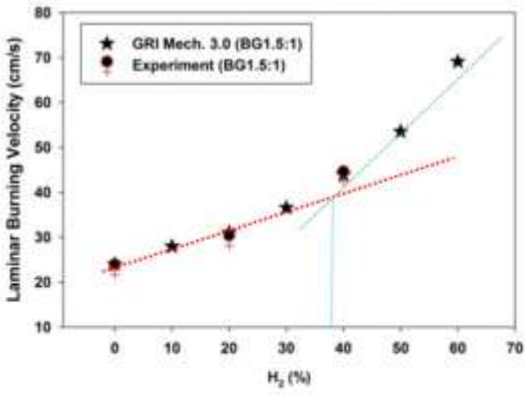
The LBV of H_2-enriched biogas may be predicted by using the correlations derived by fitting the obtained results using the least square method. The parameter χ is calculated as:

$$\chi = \frac{\text{Volume fraction of } H_2}{\text{Volume fraction of } (CH_4 + CO_2 + H_2)} \qquad (2)$$

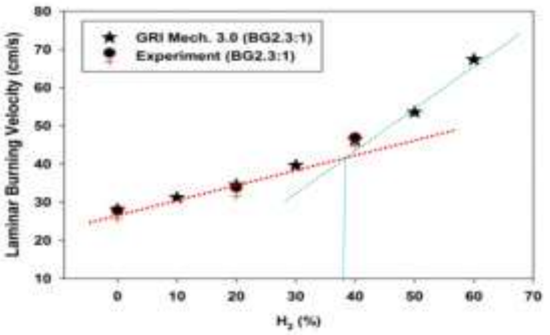
The LBV correlations derived for biogas fuels enriched with H_2 are listed in Table 4. Equation 3a, 4a, 5a, and 6a represent the correlations for experimental results whereas; equations 3b, 4b, 5b and 6b refer the correlations obtained by fitting predicted results. Fig. 7a-d reveals that the curves are of the second-degree parabola in which coefficients are closely related to each other. This ensures that the experimental and computed values are in good agreement as can be verified from the equations written in Table 4. In all cases, the values of correlation coefficients are closely approaching unity. This ensures strong adherence between the experimental and computational parameters. Hence, the derived correlations may prove to be useful in determining the LBV of H_2-enriched biogas fuels without conducting detailed experimentation for all compositions. This will save time and associated cost involved in conducting the experiments.



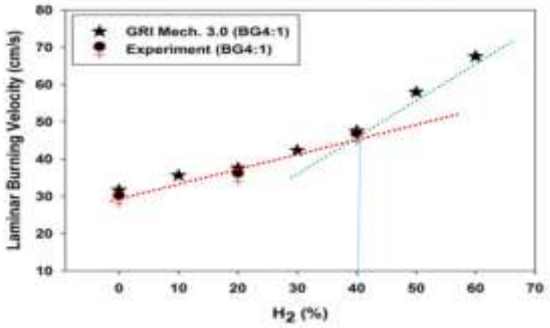
(a) Fuel BG1:1



(b) BG1.5:1



(c) Fuel BG2.3:1



(d) Fuel BG4:1

Fig. 7. Effect of H_2 enrichment on LBV of Biogas at 1 bar and 298 K.

5. Conclusions

In this work, experiments were conducted to investigate the LBV of LCV fuels like biogas. The effect of CO_2 presence in LCVG's was analyzed experimentally on the heat flux setup and computationally using the ANSYS Chemkin-Pro® with full GRI Mech. 3.0 reaction mechanism. The effect of H_2 enrichment on the properties of biogases were also analyzed. For experimental study, the biogas was enriched up to 40% hydrogen. However, numerical studies were performed for biogases with 60% hydrogen enrichment. Some empirical correlations were derived to predict the H_2 enrichment effect on the biogas fuels. The results could be summarized as follows:

1. With increased CO_2 dilution, the AFT decreases monotonically. This reduction is due to the presence of CO_2, which decreases the temperature in the reaction zone, resulting in degradation of the combustion characteristics of base fuels. Conversely, a monotonic rise in the AFT and LBV with H_2 addition was observed overcoming the adverse effects of CO_2 in the fuel mixtures.

2. The presence of CO_2 in LCVG's like biogas dominates on richer biogas-air mixtures, i.e., the CO_2 dilution effect reduces the AFT for richer mixtures more strongly than for leaner or stoichiometric mixtures. This is because, with increased CO_2 dilution, the mixture specific heat and Lewis Number increases monotonically. For all CO_2 diluted methane-air mixtures, the Lewis Number was more than unity, signifying the heat loss to be greater than the heat gain

in deficient species thereby decreasing the flame temperature.

3. Numerical results revealed that the slope of the LBV curve for biogas containing the highest percentage of CO_2 (i.e., BG1:1) suddenly changes with approximately 33% H_2 enrichment, whereas the mixture with least CO_2 content and more CH_4 (i.e., BG4:1) rises sharply at around 40% H_2 concentration. This signifies that even a small amount of H_2 in biogas containing more CO_2 may be a suitable option to raise their AFT leading to improvement in chemical reactions rates and consequently the LBV of the biogas.

4. Some correlations were derived for H_2-enriched biogas and may be used as baseline expression for determining their LBV. This will facilitate in realizing the LBV of H_2-enriched biogas without conducting detailed experimentation for all compositions, saving the time and cost required for experimentation.

The biogas and other LCV fuels derived from biomass after suitable enrichment with H_2 could be a viable option for conventional fuels used in combustors, gas turbines, and internal combustion engines. The obtained results are relevant in understanding the maximum temperature that can be attained for mixtures with lower energy density, at equilibrium. Especially, industrial furnaces working with LCV's like biogas require the temperature information for the safe design of the components, so that the temperature can be controlled effectively. The blends of H_2-enriched biogas, used in the current work provide the fundamental properties of the fuels that are renewable in nature. Further, CH_4 and CO_2 are the notorious gases causing global warming. If CH_4 present in biogas producing sites (like landfills) remain unused, may lead to Global warming. Hence, their effective utilization will help in controlling the global temperature. A major outcome of the current work is that, biogas with 33 % hydrogen, shows similar combustion characteristics as that of conventional CH_4-air mixture. This may help the researchers working in the field of internal combustion engines to conduct practical experiments with 33.5% CH_4 + 33.5% CO_2 + 33% H_2 and test the actual performance and emissions of their engines. The authors expect to get good performance results with reduced emissions.

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