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Sensitivity Analysis of CO_2 Diluted and H_2Enriched Methane for StoichiometricCombustion

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ABSTRACT

The biogas and the like fuels having low heating value are abundantly available but are unsuitable for the combustion. These fuelscan be displaced after enhancing its base heating value. In this paper the sensitivity analysis is performed on 40% H_2 enriched methane and 40% CO_2 diluted methane using the ANSYS Chemkin-Pro® with full GRI-Mech 3.0 reaction mechanism. 40% CO_2 diluted methane generally represent the composition of biogases available from different sources. The properties like rate of reaction, rate of production and normalized sensitivity coefficients of aforesaid mixtureswere analyzed.Chemical kinetic analysis revealed that the rate of production of OH radical via $H+O_2 \leftrightarrow O+OH$ (R38) is four times more in magnitude for 40% hydrogen enriched methane compared with 40% CO_2 diluted methane, while the rate of consumption of CO radicals via $OH+CO \leftrightarrow H+CO_2$(R99) is about three times more in magnitude for 40% hydrogen enriched methanecompared to 40% CO_2diluted methane.The predictions of the present work support that the presence of CO_2 in any fuel adversely affects its combustion characteristics. On the other hand, the presence of H_2 in any fuel enhances its combustion quality.

Keywords: Biogas, LBV, Normalized sensitivity coefficient, Rate of production, Rate of reaction.

I- INTRODUCTION:

Biogases generated through biochemical decomposition of animal, garbage and solid wastes are composed of 45-60 % Methane, 40–55 % Carbon dioxide and H_2S, nitrogen, CO, oxygen and water vapor traces[1]. The biogas finds limited use due to their low heating values. However, when enriched with high heating value fuels suitably, may be used in internal combustion engines, house hold applications and gas turbines. In order to find the appropriate composition of the fuel to make them suitable for various applications, their chemical kinetics must be well understood. This can be achieved by predicting the associated chemical reactions and important species responsible for the combustion of low heating value fuels through numerical techniques, as their determination through experimentation may betime consuming and cumbersome task. To analyze the chemical reactions, major and minor species and their corresponding reaction/production rates, the computational simulation through Premix or Chemkin-Pro software is an effective tool. Sensitivity analysis may also be conducted using Chemkin-Pro software, which in turn helps to recognizethe dominant chemical reactions.Sensitivity is a sort of mathematical approach that relates the change in output with the change in input parameter. Sensitivity coefficients correlate the contribution of individual input parameter's uncertainty to overall uncertainty of the model result [2]. In order to compare the sensitivity results, normalized sensitivity coefficients (x_j/y_i) $(\frac{\partial yi}{\partial xj})$ are used. Reactions with positive sensitivity coefficient tendto increase the concentration of highly reactive radical species such as H, O and OH, which contribute in increasing the burning velocity of fuel-air mixtures. Conversely, negative sensitivities are recognized by recombination reactions, in which reactive radicals are transformed into stable species, which in turn reduces the reactive radical concentration and hence the burning rates. In the present approach, it has been tried to correlate the effect of the presence of 40% CO_2 and 40% H_2 in $CH_4$by volume for stoichiometric combustion with air. The mixtures with 40% CO_2mimicthegeneral biogases available in landfill sites.

II- METHODOLOGY ANDCOMPUTATIONAL APPROACH:

The sensitivity analysis was conducted using ANSYS Chemkin-Pro®[3] software using GRI Mech. 3.0 reaction mechanism [4]. GRI Mech. 3.0 reaction mechanism is best suited to methane-air stoichiometric mixtures. The predictions of GRI Mech 3.0 are also suitable for biogas like mixtures. Multi-component transport phenomena were used for better predictions. Soret-effect was also considered for hydrogen enriched methane. The adaptive grid parameters GRAD and CURV were suitably verified and selected in order to get grid-independent results. After verifying grid independency, the predicted results were validated for the results available in literature for methane-air stoichiometric mixtures, which was in closer agreement with the results of other researchers.

III- RESULTS AND DISCUSSIONS:

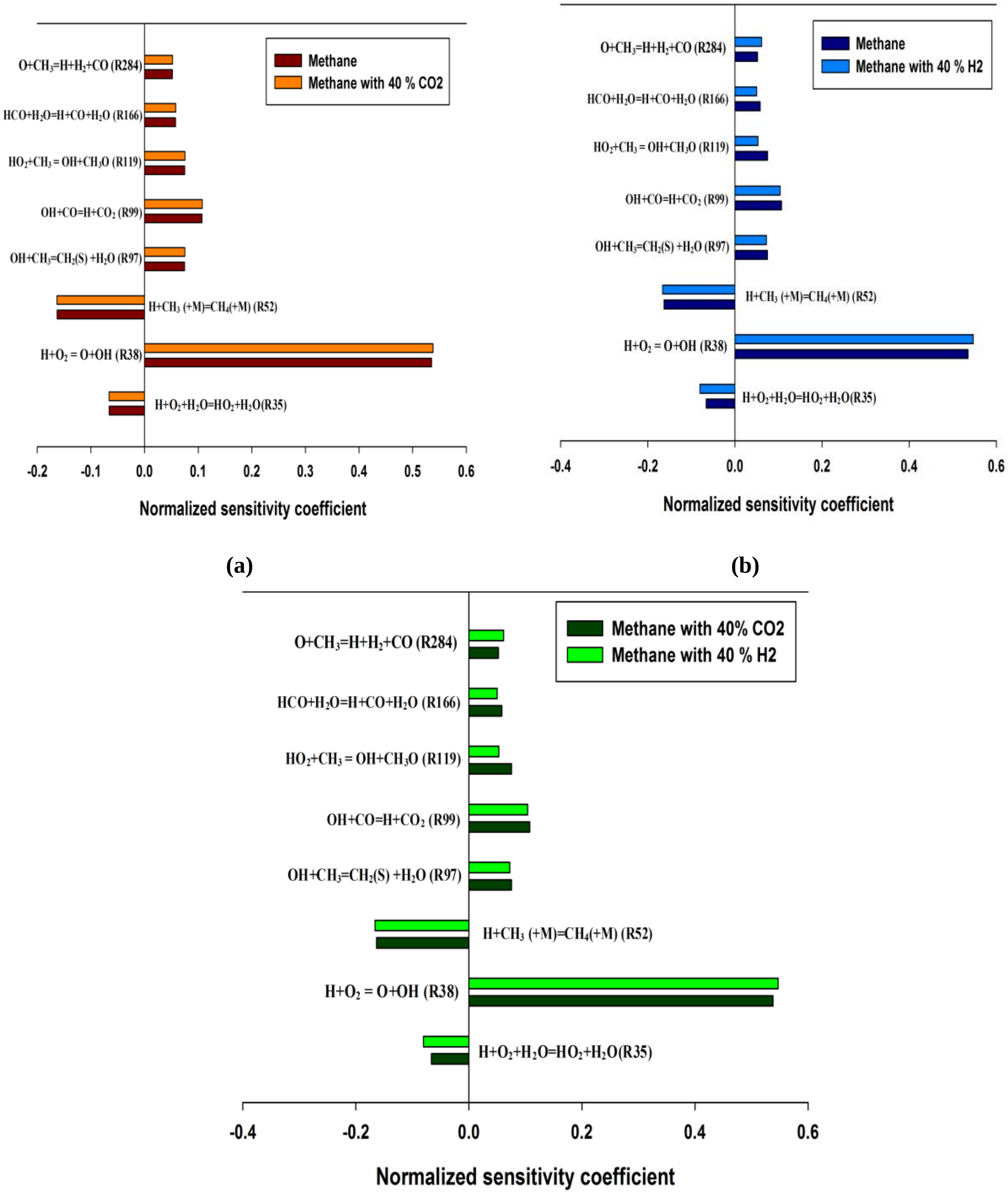
To analyze the chemical effects of CO_2 dilution and H_2 enrichment on CH_4, the behavior of H, O and OH radicals was studied using ANSYS Chemkin-Pro®[3] with a full GRI- Mech. 3.0 reaction mechanism [4]. Though GRI Mech. 3.0 has 325 reversible reactions for simulations, heretop eight most dominant reactions are only considered. The list of reactions common to CH_4, CH_4 with 40% CO_2 and CH_4 with 40% H_2 are shown in Table 1.It was observed that, the chain branching reaction $H+O_2\leftrightarrow O+OH$ (R38) and chain propagating reactions like $HO_2+CH_3\leftrightarrow OH+CH_3O$ (R119) and $OH+CO\leftrightarrow H+CO_2$ (R99) have positive sensitivities for all selected mixtures as shown in Fig. 1(a-c).The reactions with negative sensitivity coefficients are $H+O_2+H_2O\leftrightarrow HO_2+H_2O$ (R35) and $H+CH_3(+M)\leftrightarrow CH_4(+M)$ (R52).It was observed that for methane with 40% CO_2 dilution at stoichiometric condition, the reactions R38, R52 and R35 became more sensitive when compared with stoichiometric CH_4-air mixture. However, reaction $OH+CO\leftrightarrow H+CO_2$ (R99) shows decrement in normalized sensitivity coefficient for 40% CO_2 diluted methane.

Table 1: Reactions for enriched and diluted methane for stoichiometric combustion

Sl. No.	Reaction No.	Reactions
1	R35	$H+O_2+H_2O \leftrightarrow HO_2+H_2O$
2	R38	$H+O_2 \leftrightarrow O+OH$
3	R52	$H+CH_3\ (+M) \leftrightarrow CH_4(+M)$
4	R97	$OH+CH_3 \leftrightarrow CH_2(S)\ +H_2O$
5	R99	$OH+CO \leftrightarrow H+CO_2$
6	R119	$HO_2+CH_3 \leftrightarrow OH+CH_3O$
7	R166	$HCO+H_2O \leftrightarrow H+CO+H_2O$
8	R284	$O+CH_3 \leftrightarrow H+H_2+CO$

This is attributed to the fact that, due to the presence of CO_2, H radicals are captured [5-8], resulting in its decreased production, which results in decreased normalized sensitivity coefficient of R99. Here high third body efficiency of CO_2 is also responsible for the degradation of flame properties. Qiao et al [9] and Xie et al [10] also reported about the dependency of laminar burning velocity on H and OH radical concentration in the reaction zone where laminar burning velocity of any mixture increases due to the presence of these active radicals. Burke et al [14] and Qiao et al [15] also discussed about the enhancement of third-body efficiency due to CO_2 dilution. In order to understand the effect of CO_2 dilution and H_2 enrichment on the reaction rate of CH_4, the rate of reaction of all the associated reactions in forward and reverse direction were computed. Fig. 2 shows the rate of reaction magnitudes of R38 only in forward and reverse direction for CH_4 and CH_4 diluted with 40% CO_2. However it was found that for remaining reactions too, the rate of reaction in forward direction was more compared to rate of reaction in reverse direction. Also it can be observed from figure 1c, that the sensitivity coefficient of reaction for CH_4-air mixtures via reaction R38 is more with 40% H_2 enrichment compared to 40% CO_2 dilution. This indicates that with increased H_2 concentration, the mole fractions of reactive radicals like O and OH is increased, leading to increase in laminar burning velocity. Hence, by H_2 enrichment, H radical concentration improves considerably, which in turn suppresses the capturing of H by CO_2 via reaction R99, leading to decrease in its normalized sensitivity coefficient compared to its respective base fuel.

In order to broaden the insight of associated chemical reactions, detailed analysis of the rate of production and mole fractions of radicals produced/consumed for top eight reactions was conducted. Fig. 3 indicates that the rate of production of OH radical via R38 is approximately four times more in magnitude for 40% H2enriched CH4 than CH4 diluted with 40% CO2. This is due to the higher reactivity and thermal diffusivity of the H2, which enhances the burning characteristics of H2 enriched mixtures.



(a) **(b)**

(c)

Fig. 1: Normalized sensitivity coefficient for Stoichiometric at 1 bar and 298 K

Fig. 4 shows the rate of production/consumption of CO for simulated mixtures. It was predicted that with OH+CO↔H+CO2(R99), the consumption rate of CO radicals is about three times more in magnitude for 40% H2 enriched CH4 than CH4 diluted with 40% CO2. Hence, from Fig.3 and Fig.4, it can be concluded that due to the presence of H2 in CH4, the rate of production of OH and the rate of consumption of CO (another reactant) increases, leading to the overall increase in the thermal properties and combustion characteristics of CH4. This is in line with the results of Pizzuti et al. [11], Cardona et al. [12] and Mameri et al. [13], who reported that by enriching fuel having low heating value (like biogas) with fuel having higher heating value like hydrogen, propane or natural gas, the base fuel's reactivity, radical concentration, heating value, flame temperature and laminar burning velocity improves considerably.

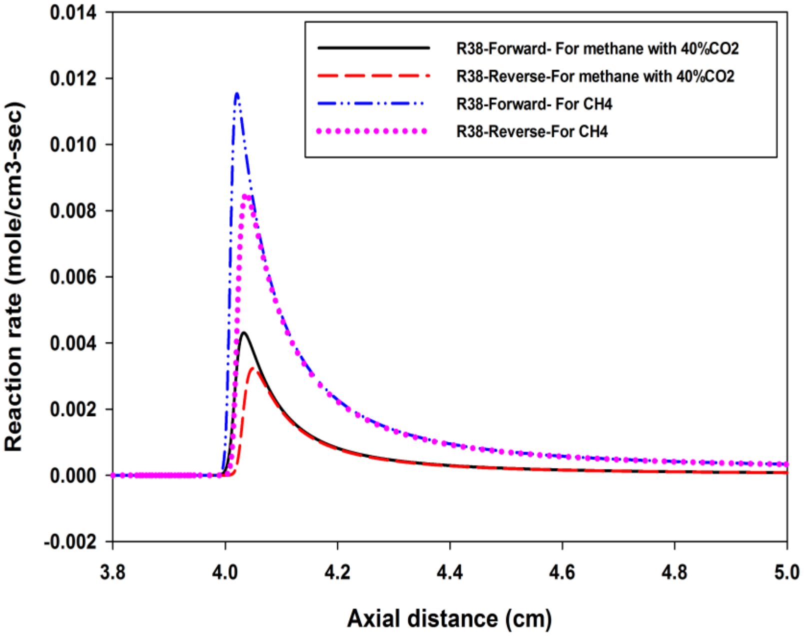


Fig. 2:Variation of Reaction rate Vs.Axial distance

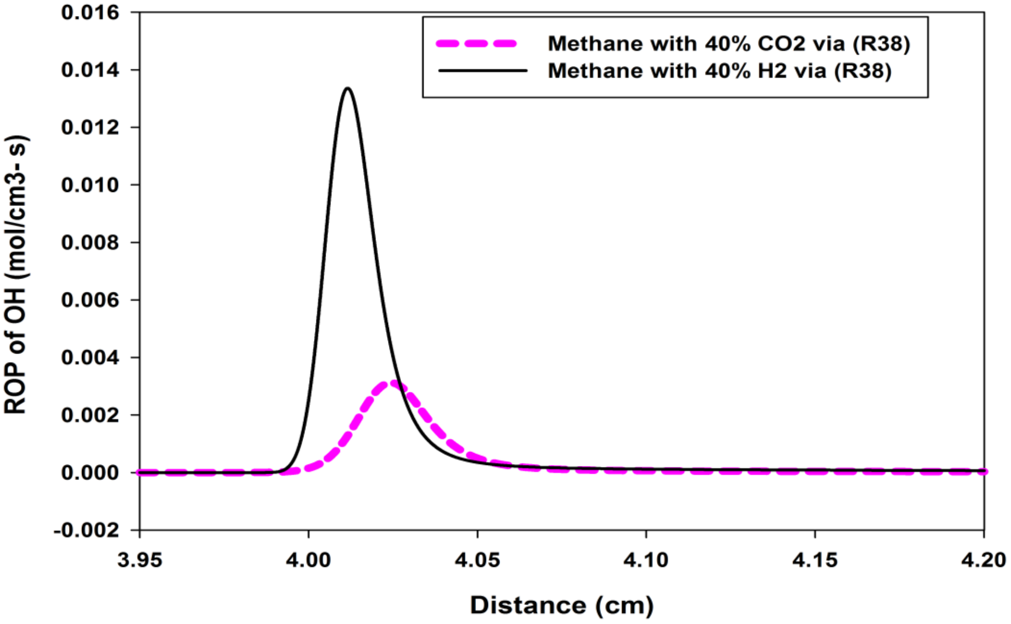


Figure3:Variation of ROP of OH radicals Versus Distance at 1 bar and 298K

The detailed analysis revealed that when CH_4 was diluted with diluents like CO_2, the normalized sensitivity coefficient of R38 increases, while enriching same CH_4 with hydrogen resulted in decreased normalized sensitivity coefficient. However, the normalized sensitivity coefficient of reaction R99 decreases with increased CO_2 dilution and have higher value for H_2 enriched CH_4. The present analysis provides an idea of the important chemical reactions of pure CH_4, biogas and H_2 enriched CH_4. The study also supports the fact that in order to enhance the characteristics of low-calorific-valued fuel like biogas, they may be enriched with metered quantity of high calorific valued fuels like H_2.

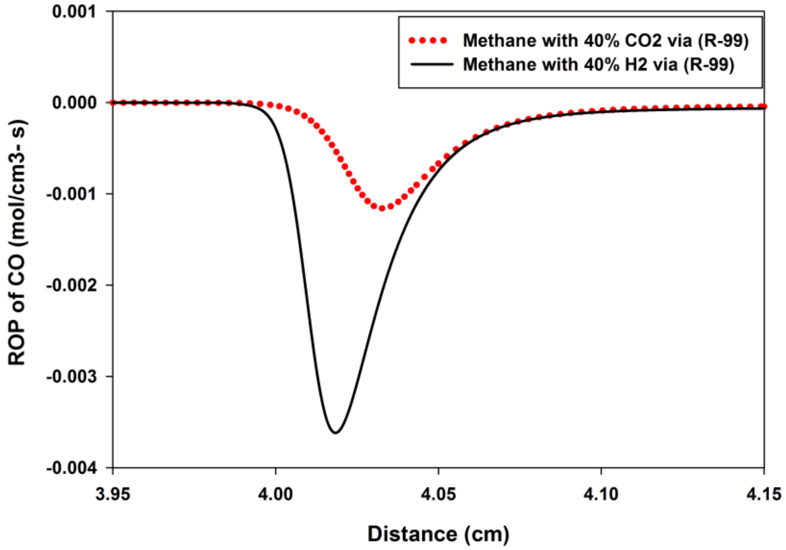


Figure 4:Variation of ROP of COVersus Distance at 1 bar and 298K

IV- CONCLUSION

The analysis was carried out for stoichiometric mixtures at 1 bar and 298K with the help of ANSYS Chemkin-Pro$^{®}$software with a full GRI-Mech. 3.0 reaction mechanism and the following conclusions weredrawn:

(i) The chain branching reaction R38 ($H+O_2 \leftrightarrow O+OH$) and chain propagating reactions like R99 ($OH+CO \leftrightarrow H+CO_2$) with positive sensitivity coefficients and R35 ($H+O_2+H_2O \leftrightarrow HO_2+H_2O$) and R52 ($H+CH_3(+M) \leftrightarrow CH_4(+M)$) with negative sensitivity coefficients are top two reactions respectively, amongst eight reactions for CH_4-air, CH_4-CO_2-air and CH_4-H_2-air mixtures.

(ii) The rate of production of OH radical via R38 is four times more in magnitude for 40% H_2 enriched CH_4 compared to 40% CO_2 diluted CH_4. The rate of consumption of CO is about three times more in magnitude for 40% H_2 enriched CH_4 compared to 40% CO_2diluted CH_4.

(iii) Theanalysis is quite relevant to understand the chemical kinetics associated with combustion of stoichiometricCH_4-air,CH_4-H_2-air and CH_4-CO_2-air (representing biogas).The predictions of the analysis supports that the presence of CO_2 in any fuel adversely affects its combustion characteristics.On the other hand, the presence of hydrogen in any fuel enhances its combustion characteristics.

The outcomes of the present work justifies the addition of hydrogen in low calorific fuels in order to enhance their combustion characteristics and make them suitable to be used with combustors, internal combustion engines and gas turbines.

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