Simulation of Tri-Reforming Reaction Using Flue Gases of Thermal Power Plant (Natural Gas Fired)

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Abstract

This work outlines the modeling aspects of kinetic evaluation for tri-reforming of methane (TRM), by using flue gases of thermal power plant(natural gas fired). The results figure out tri-reforming to be the most synergetic process as being combination of steam reforming, partial oxidation of methane and dry reforming (CO_2 reforming). This not only produces synthesis gas ($CO + H_2$) with desired H_2/CO ratios (1.1–2) but also results in higher values of conversion for methane and carbon dioxide. These two advantages have been demonstrated by tri-reforming of CH_4 in a fixed-bed flow reactor at 1123K with supported nickel catalysts. Over 97% CH_4 conversion and about 67.83 % CO_2 conversion can be achieved in tri-reforming over Ni/Al_2O_3 catalysts. Modeling equations were solved simultaneously using ordinary differential equation solver "ode 45" in MATLAB 9.0. Tri-reforming is more desired for producing syngas with desired H_2/CO ratios of 1.1-2.0 compared to CO_2 reforming, steam reforming and partial oxidation of methane. Moreover, tri-reforming of methane can be achieved successfully with high conversion (>97%) and high CO_2 conversion (>67%) for producing syngas with desired H_2/CO ratios of 1-2 over supported nickel catalyst at 1123 K under atmospheric pressure.

Keywords: tri reforming, syngas production, flue gas

1. INTRODUCTION

Tri-reforming is a new process designed for the direct production of synthesis gas with desirable H_2/CO ratios by reforming methane or natural gas using flue gas from fossil fuel based electric power plants without pre-separation of CO_2.The combination of dry reforming with steam reforming can accomplish two important missions to produce syngas with desired H_2/CO ratios and to mitigate the carbon formation problem that is significant for dry reforming [Chunshan Song and Wei Pan (2004)]. Integrating steam reforming and partial oxidation with CO_2 reforming could dramatically reduce or eliminate carbon formation on reforming catalyst thus increase catalyst life and process efficiency. Therefore, the proposed tri-reforming can solve two important problems that are encountered in individual processing. The incorporation of O_2 in the reaction generates heat in situ that can be used to increase energy efficiency and O_2 also reduces or eliminates the carbon formation on the reforming catalyst.

Wei Pan et. al. (2002) the current major applications of synthesis gas include methanol synthesis and Fischer-Tropsch (F-T) synthesis that require synthesis gas with a H_2/CO ratio close to 2. However, synthesis gas directly produced from CO_2 reforming of methane has H_2/CO ratio close to 1. Hence this kind of synthesis gas (H_2/CO ratio ≤1) requires further treatment in order to be applied in methanol and F-T synthesis. Similarly synthesis gas produced from steam reforming can not be directly applied in methanol or F-T synthesis either since the H_2/CO ratio of synthesis gas produced from steam reforming is usually larger than 3. Although methane partial oxidation produces synthesis gas with a H_2/CO ratio of 2, methane partial oxidation is difficult to control due to its exothermic feature and that is dangerous and expensive due to the handling of pure oxygen. Tri reforming, however, is expected to readily produce synthesis gas with the desired H_2/CO ratios of 1.5 ~ 2 by manipulating tri reforming reactant compositions under relatively mild reaction conditions.

The tri-reforming can thus be achieved with natural gas and flue gases using the 'waste heat' in the power plant and the heat generated in situ from oxidation with the O_2 that is already present in flue gas. Tri-reforming consume more energy than steam or dry reforming. M. Halmann et. al. (2009) thermo-chemical equilibrium calculations along with mass/energy balances indicate that for flue-gas treatment by tri-reforming, CO_2 emission avoidance of up to 59% and fossil fuel savings of up to 75% may be attained when concentrated solar energy is supplied as high-temperature process heat for the calcination step, all relative to conventional H_2 production by coal gasification. If instead fossil fuel would be used to drive the calcination step, the CO_2 emission avoidance and the fuel savings would be only 20% and 67%, respectively.

Flue gases from fossil fuel-based electricity-generating units are the major concentrated CO_2 sources. If CO_2 is to be

separated, as much as 100 megawatts of a typical 500 megawatt coal fired power plant would be necessary for today's CO_2 capture processes based on the alkanol amines (Chunshan Song and Wei Pan 2004). Therefore, it would be highly desirable if the flue gas mixtures can be used for CO_2 conversion but without pre-separation of CO_2. CO_2 conversion and utilization should be an integral part of CO_2 management, although the amount of CO_2 that can be used for making industrial chemicals is small compared to the quantity of flue gas. Typical flue gases from coal-fired power plants may contain 13% CO_2, 9% H_2O, 4% O_2, and 74% N_2; typical flue gases from natural gas-fired boilers may contain 9 vol% CO_2, 19 vol% H_2O, 2.5 vol % O_2 and 69.5% N_2. The typical furnace outlet temperature of flue gases is usually around 1200°C which will decreases gradually along the pathway of heat transfer, while the temperature of the flue gases going to stack is around 150 °C. Pollution control technologies can remove the SOx, NOx and particulate matter effectively, but CO_2 and H_2O as well as O_2 remain largely unchanged. The composition of flue gases depends on the types of fossile fuels used in power pants.
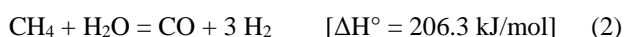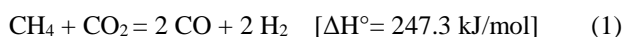
Table 1.2: M Halmann et. al. (2006)

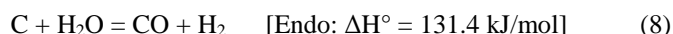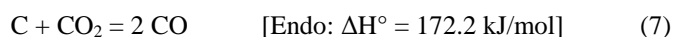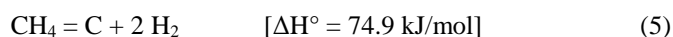| Natural Gas Fired Power Plant (volume)		Coal Fired Power Plant (volume)	
CO_2	9 %	CO_2	13 %
H_2O	19 %	H_2O	9 %
O_2	2.5 %	O_2	4 %
N_2	69.5%	N_2	74%

2. CHEMICAL REACTION

Tri-reforming is a synergetic combination of endothermic CO_2 reforming (eq. 1) and steam reforming (eq. 2) and exothermic partial oxidation of methane (eq. 3, eq. 4). CO_2, H_2O and O_2 in the waste flue gas from fossil-fuel-based power plants will be utilized as co reactants for tri-reforming of natural gas for the production of synthesis gas. The new process is called tri-reforming of methane.

Tri-reforming of Natural Gas

$CH_4 + CO_2 = 2\ CO + 2\ H_2$ [$\Delta H° = 247.3$ kJ/mol]   (1)

$CH_4 + H_2O = CO + 3\ H_2$ [$\Delta H° = 206.3$ kJ/mol]   (2)

$CH_4 + 1/2\ O_2 = CO + 2\ H_2$ [$\Delta H° = -35.6$ kJ/mol]   (3)

$CH_4 + 2\ O_2 = CO2 + 2\ H_2O$ [$\Delta H° = -880$ kJ/mol]   (4)

Reactions for Coke Formation and Destruction

$CH_4 = C + 2\ H_2$ [$\Delta H° = 74.9$ kJ/mol]   (5)

$2CO = C + CO_2$ [Exo: $\Delta H° = -172.2$ kJ/mol]   (6)

$C + CO_2 = 2\ CO$ [Endo: $\Delta H° = 172.2$ kJ/mol]   (7)

$C + H_2O = CO + H_2$ [Endo: $\Delta H° = 131.4$ kJ/mol]   (8)
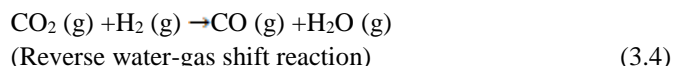
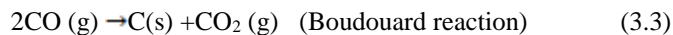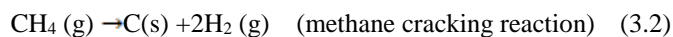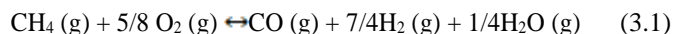$C + O_2 = CO_2$ [Exo: $\Delta H° = -393.7$ kJ/mol]   (9)

3. MODEL DEVELOPMENT

The conversion of natural gas was carried out via tri-reforming of methane in a fixed bed reactor employing a Ni/γ-Al_2O_3 catalyst. The effects due to water and oxygen addition to the feed of the process were examined in terms of the yields of hydrogen and carbon monoxide.The kinetic model for tri-reforming was developed considering a fixed bed reactor($h_{reactor}$=0.64m, h_{bed}=0.02m, $d_{reactor}$=212μm) under atmospheric pressure and temperature of 1123K on nickel catalyst bed on gamma-aluminum tri-oxide support(Ni/γ-Al_2O_3) .The ratio of mixture of reactants of feed(natural gas,NG) was considered as CH_4:CO_2:H_2O:O_2/1.0:0.49:0.30:0.04 v/v and feed flow rate of 11.67 cm³/s was taken for the reforming processes.

3.1 KINETIC MODEL FOR TRI-REFORMING

Tri-reforming is a synergetic combination of endothermic CO_2 reforming, and steam reforming and exothermic oxidation of methane. With this process concept, CO_2, H_2O, and O_2 in the flue gas from fossil-fuel-based power plants can be utilized as co-reactants for tri-reforming of natural gas for the production of synthesis gas. The set of reactions for the process are given below:

CH_4 (g) + 5/8 O_2 (g) $\leftrightarrow$ CO (g) + 7/4H_2 (g) + 1/4H_2O (g)   (3.1)

CH_4 (g) $\rightarrow$ C(s) +2H_2 (g)   (methane cracking reaction)   (3.2)

$2CO$ (g) $\rightarrow$ C(s) +CO_2 (g)   (Boudouard reaction)   (3.3)

CO_2 (g) +H_2 (g) $\rightarrow$ CO (g) +H_2O (g)
(Reverse water-gas shift reaction)   (3.4)

The kinetic model for the reactions on Ni/γ-Al_2O_3 by following reaction mechanism in which the rate expressions for reactions (1) – (4) are given by:

$$r_1 = \frac{k_1 K_{CH_4} C_{CH_4} K_{O_2} C_{O_2}}{(1 + K_{CH_4} C_{CH_4} + K_{O_2} C_{O_2})}$$ (3.5)

$$r_2 = \frac{k_2 K_{CH_4} C_{CH_4}}{(1 + K_{CH_4} C_{CH_4})}$$ (3.6)

$$r_3 = k_3 C_{CO}^2$$ (3.7)

$$r_4 = \left(C_{H_2} C_{CO_2} - \frac{C_{CO} C_{H_2O}}{K_{eq}} \right)$$ (3.8)

The component relations R_i (i=CH$_4$, CO$_2$, CO, H$_2$), based on rate laws of the four step reaction proposed above, are considered as:

$$R_{CH_4} = -r_1 - r_2 , \quad R_{CO_2} = r_3 - r_4 ,$$

$$R_{H_2} = \frac{7}{4} r_1 - 2r_2 - r_4 , \quad R_{CO} = r_1 - 2r_3 + r_4$$

The mass balances of the components are expressed as $\frac{dC_i}{dt} + R_i = 0$, where t (minutes) is the time.

$$\frac{dC_{CH_4}}{dt} = -\frac{k_1 K_{CH_4} C_{CH_4} K_{O_2} C_{O_2}}{(1+K_{CH_4} C_{CH_4}+K_{O_2} C_{O_2})} - \frac{k_2 K_{CH_4} C_{CH_4}}{(1+K_{CH_4} C_{CH_4})} \qquad (3.9)$$

$$\frac{dC_{CO_2}}{dt} = k_3 C_{CO}^2 - (C_{H_2} C_{CO_2} - \frac{C_{CO} C_{H_2O}}{K_{eq}}) \qquad (3.10)$$

$$\frac{dC_{H_2}}{dt} = \frac{7}{4} \frac{k_1 K_{CH_4} C_{CH_4} K_{O_2} C_{O_2}}{\left(1+K_{CH_4} C_{CH_4}+K_{O_2} C_{O_2}\right)}$$
$$- 2\frac{k_2 K_{CH_4} C_{CH_4}}{(1+K_{CH_4} C_{CH_4})} - (C_{H_2} C_{CO_2} - \frac{C_{CO} C_{H_2O}}{K_{eq}}) \qquad (3.11)$$

$$\frac{dC_{CO}}{dt} = \frac{k_1 K_{CH_4} C_{CH_4} K_{O_2} C_{O_2}}{(1+K_{CH_4} C_{CH_4}+K_{O_2} C_{O_2})}$$
$$- 2k_3 C_{CO}^2 + (C_{H_2} C_{CO_2} - \frac{C_{CO} C_{H_2O}}{K_{eq}}) \qquad (3.12)$$

The mass balances of the components are obtained in terms of reactor length as $\frac{dP_i}{dz} + R_i = 0$, where z (meters) ,is the reactor length.

$t = \frac{\pi r_1^2 z}{F}$, (3.13) where r_1 = radius of reactor, F is the volumetric flow rate of feed

$$\frac{dC_{CH_4}}{dz} = \left(\frac{F}{\pi r_1^2}\right) \left[-\frac{k_1 K_{CH_4} C_{CH_4} K_{O_2} C_{O_2}}{(1+K_{CH_4} C_{CH_4}+K_{O_2} C_{O_2})} - \frac{k_2 K_{CH_4} C_{CH_4}}{(1+K_{CH_4} C_{CH_4})}\right] \quad (3.14)$$

$$\frac{dC_{CO_2}}{dz} = \left(\frac{F}{\pi r_1^2}\right) \left[k_3 C_{CO}^2 - (C_{H_2} C_{CO_2} - \frac{C_{CO} C_{H_2O}}{K_{eq}})\right] \qquad (3.15)$$

$$\frac{dC_{H_2}}{dz} = \left(\frac{F}{\pi r_1^2}\right) \left[\frac{7}{4} \frac{k_1 K_{CH_4} C_{CH_4} K_{O_2} C_{O_2}}{(1+K_{CH_4} C_{CH_4}+K_{O_2} C_{O_2})}\right.$$
$$\left. -2\frac{k_2 K_{CH_4} C_{CH_4}}{(1+K_{CH_4} C_{CH_4})} - (C_{H_2} C_{CO_2} - \frac{C_{CO} C_{H_2O}}{K_{eq}})\right] \quad (3.16)$$

$$\frac{dC_{CO}}{dz} = \left(\frac{F}{\pi r_1^2}\right) \left[\frac{k_1 K_{CH_4} C_{CH_4} K_{O_2} C_{O_2}}{(1+K_{CH_4} C_{CH_4}+K_{O_2} C_{O_2})} \right.$$
$$\left. - 2k_3 C_{CO}^2 + (C_{H_2} C_{CO_2} - \frac{C_{CO} C_{H_2O}}{K_{eq}})\right] \qquad (3.17)$$

The solutions of the mass balance equations system were obtained with the 4th order Runge–Kutta method with the help of ODE-45 solver from MATLAB toolbox.

3.5 SOLUTION PROCEDURE

Considering the reaction mechanism of the four reaction mechanisms, indicated as the observed reaction steps, expressions of rate laws to the components were derived in order to yield mass balances for the four components namely methane (CH$_4$), carbon dioxide (CO$_2$), carbon monoxide (CO) and hydrogen (H$_2$).the mass balances were derived with respect to time and length of the reactor. The solutions obtained set of mass balance equations for each reforming process were obtained by the help of ordinary differential equations solver "ODE 45" in MATLAB 9.

Model Parameters For Tri-Reforming

Parameters	Pre-exponential factor
k_1	$1.21 \pm 0.06 \times 10^{-1}$ mol/ g$_{cat}$ .s
k_2	$3.91 \pm 0.16 \times 10^{-4}$ mol/ g$_{cat}$ .s
k_3	$7.32 \pm 0.32 \times 10^{-2}$ m^3/ mol.g$_{cat}$.s
k_4	$1.04 \pm 0.05 \times 10^{-4}$ mol/ g$_{cat}$ .s
K_{CH4}	$2.93 \pm 0.11 \times 10^{-3}$ m^3/ mol
K_{O2}	$3.53 \pm 0.15 \times 10^{5}$ m^3/ mol
K_{eq}	$1.07 \pm 0.06 \times 10^{3}$ m^3/ mol

4. SIMULATION RESULTS

The MATLAB programs incorporated four set of following equations framed for each component namely, Methane, Carbon Dioxide, Carbon Monoxide and Hydrogen.

- ➤ ODE's for concentration variations with respect to time
- ➤ ODE's for concentration variations with respect to length
- ➤ ODE's for conversion variations with respect to time
- ➤ ODE's for conversion variations with respect to length
- ➤ ODE's for Hydrogen to Methane ratio with respect to length
- ➤ ODE's for Hydrogen to Methane ratio with respect to time
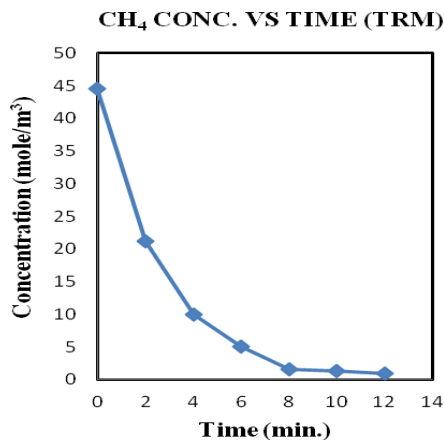
4.1 PLOTS FOR SIMULATED RESULTS

CH$_4$ CONC. VS TIME (TRM)

Fig 4.1 Methane Concentration versus Time Plots

CH$_4$ CONC. VS LENGTH (TRM)

Fig 4.2 Methane Concentration versus Length   Plots

CH$_4$ CONVERSION VS TIME (TRM)

Fig 4.3 Methane Conversion versus Time Plots

CH$_4$ CONVERSION VS LENGTH (TRM)
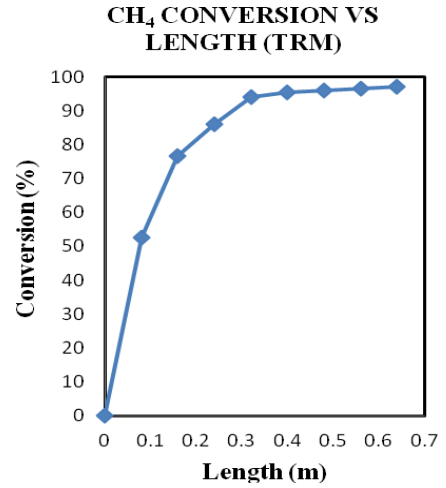
Fig 4.4 Methane Conversion versus Length Plots

CO$_2$ CONC. VS TIME (TRM)
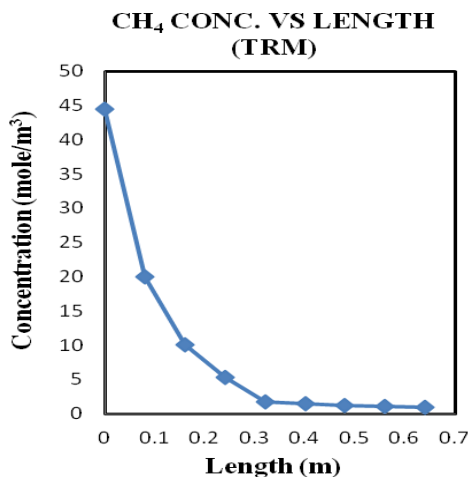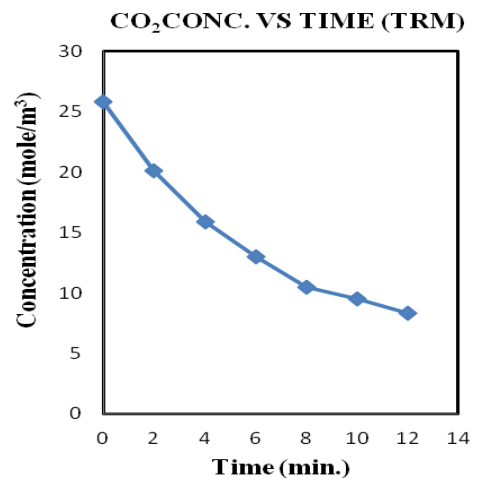
Fig 4.5 Carbon Dioxide Concentration versus Time Plots
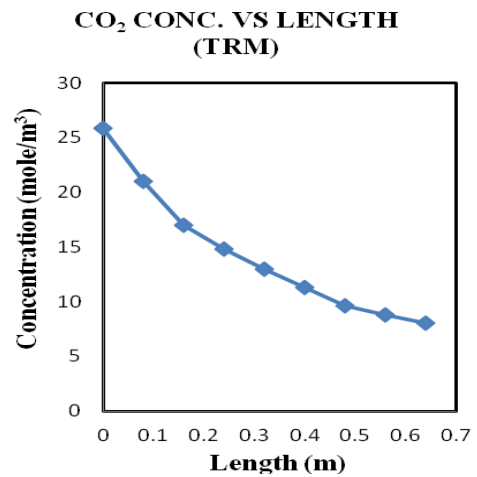
CO$_2$ CONC. VS LENGTH (TRM)
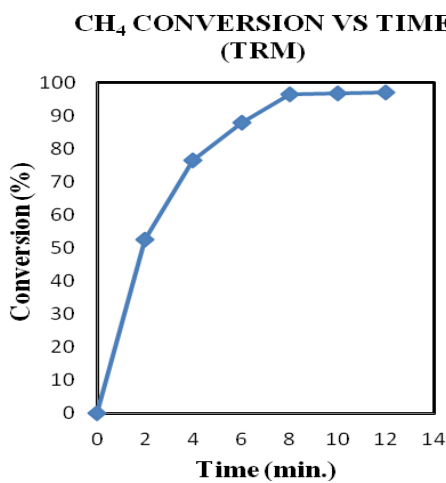
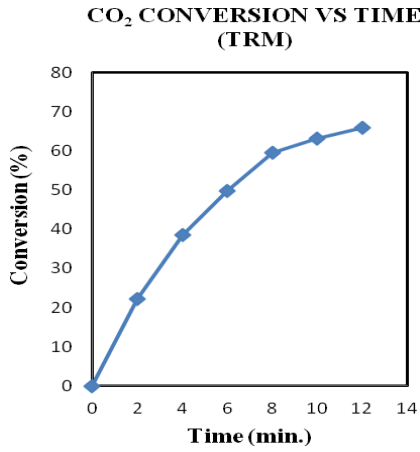Fig 4.6 Carbon Dioxide Concentration versus Length Plots

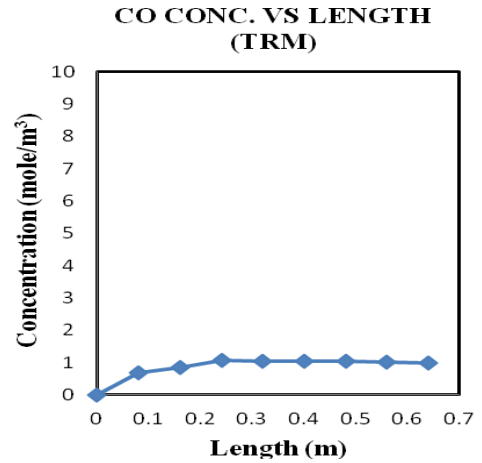**Fig 4.7 Carbon Dioxide Conversion versus Time Plots**

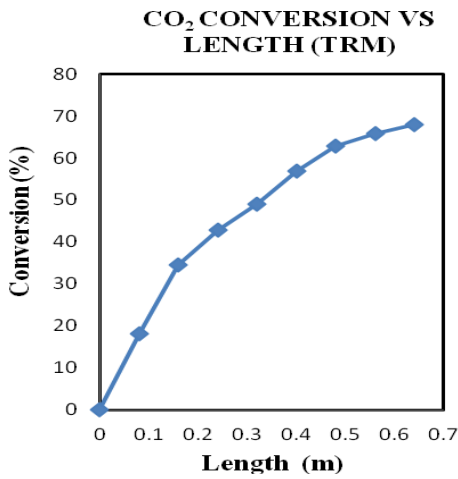**Fig 4.10 Carbon Monoxide Concentration versus Length Plots**

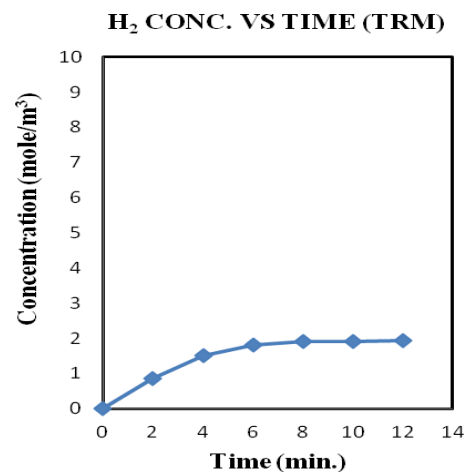**Fig 4.8 Carbon Dioxide Conversion versus Length Plots**
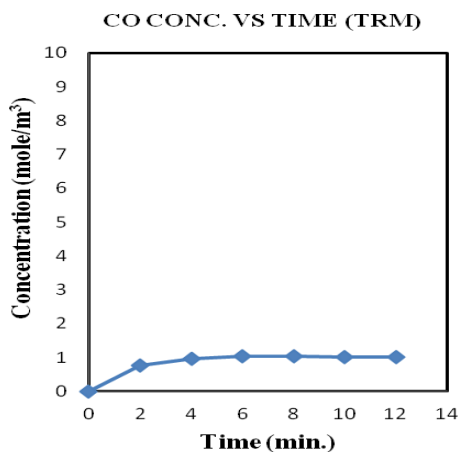

Fig 4.11 Hydrogen Concentration versus Time Plots
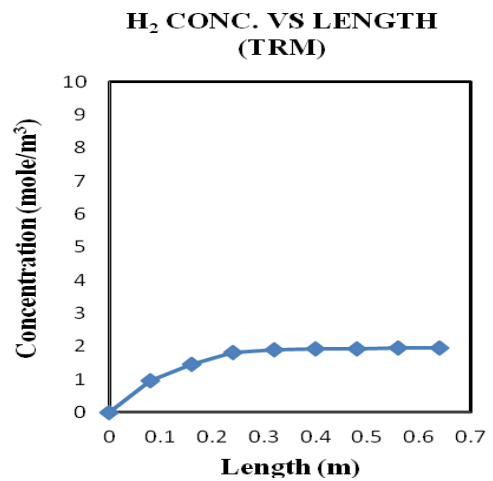

Fig 4.9 Carbon Monoxide Concentration versus Time Plots
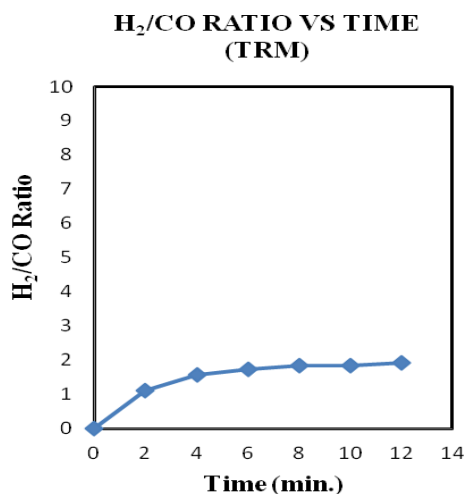

Fig 4.12 Hydrogen Concentration versus Length Plot

H₂/CO RATIO VS TIME (TRM)

Fig 4.13 Hydrogen to Carbon Monoxide Ratio versus Time Plots
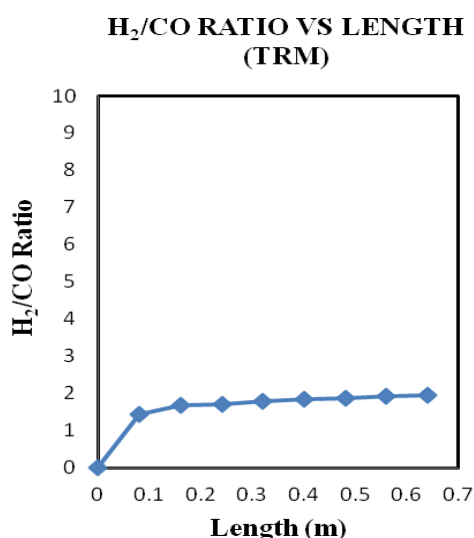
H₂/CO RATIO VS LENGTH (TRM)

Fig 4.14 Hydrogen to Carbon Monoxide Ratio versus Length Plots

4.2 DISCUSSION

A modeling study of kinetics of processes of steam reforming, dry reforming, partial oxidation of methane and tri-reforming of methane has been done. The various results and discussions are being enlisted in following sections.

CH₄ Concentration Variations With Respect To Time And Length

Methane being one of the major reactant, in reforming processes **follows a decreasing trend in concentration with respect to time & length (fig 4.1, fig 4.2). Methane concentration profile cab be explained by the backward equilibrium shift of t**he reaction since, tri-reforming of methane is slightly exothermic in nature. hence, results in a decreasing trend in concentration of methane with respect to time and length of the reactor. But the decrease in

concentration of methane during steam reforming can be explained in terms of forward equilibrium shift since the process is endothermic in nature(ΔH=206.3kJ/mol),the equilibrium shifts in forward direction resulting in falling trend in concentration profile with respect to time and length of the reactor. A similar argument can be stated in favor of dry reforming i.e. due to endothermic nature of reaction (ΔH=247.3kJ/mol) the reaction equilibrium shifts towards forward direction and hence, results in a decreasing trend in concentration profile. While the decrease in concentration of methane during partial oxidation of methane can be explained in terms of the exothermic nature of reaction favors the backward shift of reaction equilibrium, hence, results in a decreasing trend in concentration of methane with respect to time and length of the reactor.

CO₂ Concentration Variations With Respect To Time And Length

Carbon Dioxide follows a decreasing trend in terms of concentration with respect to time and length as it is one of the reactant in reforming processes (fig 4.5, fig 4.6). Tri-reforming of methane can be explained by the backward equilibrium shift of the reaction hence results CO_2 concentration decreasing trends with respect to time and length of the reactor. But the concentration of Carbon Dioxide during steam reforming can be explained in terms of the equilibrium shifts in forward direction resulting in decreasing trend in concentration profile with respect to time and length of the reactor.

H₂ and CO Concentration Variations With Respect To Time And Length

The concentration of hydrogen and carbon monoxide follows an increasing trend as these are the major products of reforming processes (fig 4.9, fig 4.10) and (fig 4.11, fig 4.3.12). From the plots it can be seen that the H_2 and CO concentration are increasing with time and length with respect to methane conversion. This increasing trend can be explained on exothermic nature of try reforming and partial oxidation of methane reforming which shifts the reaction in backward direction.

CO₂ Conversion: The CO_2 Conversion with respect to time is found to be 67.83% in case of Tri-reforming. Also, the percentage conversion of CO_2 via plots of conversion versus reactor length is found to be 69.97%, It indicates that maximum CO_2 conversion is obtained in Tri-reforming process which is much higher than the other reforming processes.The H_2: CO Ratio is found to be in range of 1.1-1.97 for Tri-reforming of methane while dry reforming of methane the shows a trend of H_2: CO ratios lower then 1.the

range for partial oxidation varies from1.1-1.7 as reported in literature. It should be pointed out that the H_2: CO ratio in synthesis gas is important since synthesis gas with different H_2: CO ratios have different applications in industry.

5. CONCLUSIONS

The Tri reforming of methane was studied from modeling and simulation point of view in a fixed bed reactor using nickel/γ-Al_2O_3 catalyst to convert natural gas into syngas. An alternative reforming process of natural gas and flue gases based on the methane conversion was studied combining steam and dry reforming and partial oxidations of methane. The kinetic evaluation of the process indicated that the methane decomposition produced carbon deposition and hydrogen. . They were solved simultaneously using ordinary differential equation solver "ode 45" in MATLAB 9.0 .

Moreover, tri-reforming of methane can be achieved successfully with high conversion (>97%) and high CO_2 conversion (>67%) for producing syngas with desired H_2/CO ratios of 1-2 over supported nickel catalyst at 1123 K under atmospheric pressure. The tri-reforming of methane is a challenging technology and requires more research work like energy management, effective conversion of CO_2, fuel savings, CO_2 emissions and integration of the new process for industrial scale applications.

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NOMENCLATURE:

k_i (i=1,2,3...n)-Kinetic parameters of the step reactions of reforming process

K_i (i=1, 2, 3...n)-Equilibrium parameters of the step reactions of reforming process

r_j (j=1,2,3..n)-Rate laws for reaction steps

R_j (j=1,2,3..n)-Mass balance equations for the components

X_i (i=1,2,3..n)-Conversion of components

P_i (i=1,2,3..n)-Partial Pressure of components

P= Total Pressure of the System

C_i (i=1,2,3..n)-Concentration of components

F_i (i=1,2,3..n)-Molar Flow Rate of components

F-Total Flow Rate of Feed

r -Radius of the reactor

z- Length of the reactor

t= time

CO   - Carbon Monoxide

CO_2 - Carbon Dioxide

H_2 - Hydrogen

H_2O - Water

CH_4 - Methane

O_2 - Oxygen

TRM   - Tri-reforming of methane

SRM   - Steam-reforming of methane

DRM   - Dry-reforming of methane

POM - Partial oxidation of methane