# Computer-Aided Design of a Non-Isothermal Plug Flow Reactor for Non-Catalytic Partial Oxidation of Methane to Synthesis Gas

Dagde, Kenneth, K.[1]    Akpa, Jackson G.[2*]

Department of Chemical/Petrochemical Engineering,Rivers State University of Science and Technology
Port-Harcourt, Rivers State, Nigeria
Email:kenneth_dagde@yahoo.com; jacksonakpa@yahoo.com*

**Abstract**
A computer aided adiabatic, non-isothermal plug flow reactor was designed for the Non-Catalytic Partial Oxidation of methane to Synthesis gas. Design equations for determining the functional dimensions and parameters of the reactor were developed and used to develop the design package for the reactor. The design equations were solved using MathLab and simulated with SimuLink 7.5 to determine optimum values/range of the functional parameters. The optimum values obtained were used to run the design program for a hypothetical reactor processing 600mmscf per day of natural gas. Simulation results showed that the functional parameters: space time and yield of products increases with increase in methane fractional conversion, while space velocity and selectivity decreases. Operating at high pressure (60 -70)bar, increases the selectivity of partial methane oxidation reaction, molar flow rate of synthesis gas (desired product) and space velocity, but decreases space time and reactor length required for high methane fractional conversion (0.95 - 0.99). For optimal functional parameters: feed inlet temperature of 1473K (1200°C), reactor diameter of 0.2m, total pressure of 60bar and methane fractional conversion of 0.95; the design program gave the reactor functional dimensions and parameters as:: Reactor volume = $0.1308m^3$, Reactor length = 9.7734m, Space time = 2.89E-07hr, Space Velocity = $0.2667hr^{-1}$, Yield of synthesis gas = 0.8578, Yield of carbon dioxide = 0.0922, Outlet Temperature = 1762.828 K.
**Keywords**: Partial oxidation, Non-catalytic, Methane, Syngas, Reactor design

## 1.Introduction
Methane, the predominant component of natural gas, has been forecasted to outlast oil by about 70 years (De Smet, 2000). Most studies on the utilization of natural gas concentrate almost exclusively on methane chemical conversion into high-added-value liquid products. These liquid products are obtained through the conversion (oxidation) of methane to synthesis gas: $(CO + H_2)$ and carbon dioxide $(CO_2)$ as an intermediate since direct conversion of methane to hydrocarbon chains with economical selectivity is not yet possible (Enger, et al., 2008). The products particularly synthesis gas is then used in the production of the desired chemical such as methanol, oxo – synthesis and Fischer-Tropsch synthesis (De Groote and Froment, 1996), after removal of carbon monoxide (CO), the hydrogen left is used for ammonia synthesis and hydrogenation (Zhu, 2001). To be effective as a raw material/feed for these processes the composition of the oxidation products, particularly that of syngas: the $H_2/CO$ ratio (mole/mole) required for these processes is critical and very different (Enger, et al., 2008); in the synthesis of methanol: $CO_2$ and CO are both reactants; the required composition of reactants: $(H_2-CO_2)/(CO+CO_2)$ should be close to 2.0; for Fischer Tropsch synthesis Gas to Liquid (GTL) applications: $CO_2$ is not a reactant, the required synthesis gas compositions: $H_2/CO$ ratio is 2.0; for aldehydes productions via olefins hydroformylation: the $H_2/CO$ ratio is 1.0.

Synthesis gas can be produced from methane (Al-Sayari, 2013) via steam reforming: an endothermic reaction in which methane is contacted with steam over a catalyst at high temperature and pressure (Collodi and Wheeler, 2010; Rostrup-Nielsen, et al., 2002); dry or $CO_2$ reforming: combination of methane and CO at high temperatures (Naeem, et al., 2013) and partial oxidation: catalytic: methane is reacted with oxygen or air over a catalyst bed to yield syngas (Kolios, et al., 2000; Biesheuvel and Kramer, 2003; Mitri, et al., 2004; Lyubovsky, et al. 2005; Neumann and Vaser, 2005) or Non catalytic: reaction of methane and oxygen at high temperature and pressure to yield syngas (Pena, et al., 1996; Zhou, et al., 2010; Han, et al., 2010).

The CO content of the synthesis gas produced by steam reforming has been reported by De Groote and Froment, (1996) to be low for methanol synthesis; however, partial oxidation; via a catalytic or non catalytic process (Lyubovsky, et al., 2005) of methane produces synthesis gas with a ratio approximately 2:1 with respect to $H_2/CO$ as required by the Fischer-Tropsch process (Wender, 1996). Thus, Non-Catalytic Partial Oxidation is a better alternative to steam or dry (carbon dioxide) reforming. Extensive research works have been carried out on the production of synthesis gas via non-catalytic partial oxidation of methane which includes: the experimental analysis of non-catalytic partial oxidation of methane over wide temperature range by Zhu *et al.* (2001), Others are Kinetic modeling of non-catalytic partial oxidation of methane using experimental data (Zhu *et al.*, 2001), and several detailed methane partial oxidation reaction mechanisms and performance models (Tsang and Hampson, 1986; Konnov, et al., 2004; Han, et al., 2010; Enger, et al., 2008).

Although, the production of synthesis gas has attracted enormous attention by researchers over the past decades, no work seems to have been done on the development of the design equations of the plug-flow reactor used for the commercial production of Synthesis gas via Non-Catalytic Partial Oxidation of methane for Gas-To-Liquid processing. Thus, the design equations of an adiabatic non-isothermal plug-flow reactor would be developed and used for design and simulation study of the reactor.

## 2.DESIGN MODEL
### 2.1Kinetic Model

Synthesis gas production via the non-catalytic partial oxidation of methane occurs competitively with total methane oxidation as side reaction (York, et al., 2003). The reactions equation and rate expressions for both reactions as given by Tsang and Hampson, (1986) were adapted as follows:

Reaction 1:    Partial Oxidation of Methane to form synthesis gas:

$$CH_4 + 0.5O_2 \xrightarrow{K_1} CO + 2 H_2 \tag{1}$$

$$r_{A_1} = K_1 (C_{CH_4})^{1.5} C_{O_2} \tag{2}$$

$$K_1 = 4.4x10^2 exp\left(\frac{-4530}{T}\right) + 3.2x10^3 exp\left(\frac{-10000}{T}\right) + 2.8x10^3 exp\left(\frac{-8480}{T}\right) \tag{3}$$

Reaction 2:   Total Oxidation of Methane a competitive secondary reaction results from excess supply of oxygen to form unwanted products:

$$CH_4 + 2O_2 \xrightarrow{K_2} CO_2 + 2 H_2O \tag{4}$$

$$r_{A_2} = K_2 C_{CH_4} \tag{5}$$

$$K_2 = 4.0x10^8 exp\left(\frac{-28640}{T}\right) \tag{6}$$

where $K_1$ and $K_2$ are the rate constants for partial and total methane oxidation respectively, $C_{CH4}$ and $C_{O2}$ are the concentrations of methane and oxygen respectively, $r_{A1}$ and $r_{A2}$ are the rate of reaction for partial and total methane oxidation respectively, T is reaction temperature, let  $CH_4 = A$,   $O_2 = B$,   $CO = C$,   $H_2 = D$,   $CO_2 = E$, $H_2O = F$

**Overall Rate Expression**: The net rate of reaction for methane oxidation reactions is the sum of the rate of reactions for partial and total methane oxidation:

$$r_A = r_{A_1} + r_{A_2} \tag{7}$$

### 2.2Reactor Model

The design models for the non-isothermal adiabatic plug flow reactor for the production of Synthesis gas (Syngas), via Non-Catalytic Partial Oxidation of methane with pure oxygen were developed with the following assumptions:

**Assumptions:**

The reactor operates adiabatically, non-isothermally and at steady state. The reaction takes place in the gaseous phase with constant density. Pressure drop along the reactor is negligible (the vessel is empty and refractory lined), The reaction mixture is composed of 1.0 mole of methane and 0.5 mole of pure oxygen, and the products are carbon monoxide (CO), Hydrogen ($H_2$) as desired products, carbon dioxide ($CO_2$) and Steam ($H_2O$) as by-product resulting from the side reactions (total oxidation of methane).

With these assumptions, the molar flow rates of the various components and the reactions temperature as a function of the reactor length were obtained by applying the laws of conservation of mass and energy over a differential volume of the reactor as:

$$\frac{dF_A}{dL_R} = -K_1 \left[\left(\frac{C_{A_O}F_A}{\sum_{i=A}^F F_i}\right)\frac{T_O}{T}\right]^{1.5} \left[\left(\frac{C_{B_O}F_B}{\sum_{i=A}^F F_i}\right)\frac{T_O}{T}\right] + K_2 \left[\left(\frac{C_{A_O}F_A}{\sum_{i=A}^F F_i}\right)\frac{T_O}{T}\right]\frac{\pi D_r^2}{4} \tag{8}$$

$$\frac{dF_B}{dL_R} = -0.5K_1 \left[\left(\frac{C_{A_O}F_A}{\sum_{i=A}^F F_i}\right)\frac{T_O}{T}\right]^{1.5} \left[\left(\frac{C_{B_O}F_B}{\sum_{i=A}^F F_i}\right)\frac{T_O}{T}\right] + 2K_2 \left[\left(\frac{C_{A_O}F_A}{\sum_{i=A}^F F_i}\right)\frac{T_O}{T}\right]\frac{\pi D_r^2}{4} \tag{9}$$

$$\frac{dF_C}{dL_R} = K_1 \left[\left(\frac{C_{A_O}F_A}{\sum_{i=A}^F F_i}\right)\frac{T_O}{T}\right]^{1.5} \left[\left(\frac{C_{B_O}F_B}{\sum_{i=A}^F F_i}\right)\frac{T_O}{T}\frac{\pi D_r^2}{4}\right] \tag{10}$$

$$\frac{dF_D}{dL_R} = 2K_1 \left[\left(\frac{C_{A_O}F_A}{\sum_{i=A}^F F_i}\right)\frac{T_O}{T}\right]^{1.5} \left[\left(\frac{C_{B_O}F_B}{\sum_{i=A}^F F_i}\right)\frac{T_O}{T}\frac{\pi D_r^2}{4}\right] \tag{11}$$

$$\frac{dF_E}{dL_R} = K_2 \left[\left(\frac{C_{A_O}F_A}{\sum_{i=A}^F F_i}\right)\frac{T_O}{T}\frac{\pi D_r^2}{4}\right] \tag{12}$$

$$\frac{dF_F}{dL_R} = 2K_2 \left[\left(\frac{C_{A_O} F_A}{\sum_{i=A}^{F} F_i}\right)\frac{T_O}{T}\right]\frac{\pi D_r^2}{4} \tag{13}$$

$$\frac{dT}{dL_R} = \frac{\left(-\Delta H_{R_{A_1}} T\right)\left[K_1\left[\left(\frac{C_{A_O} F_A}{\sum_{i=A}^{F} F_i}\right)\frac{T_O}{T}\right]^{1.5}\left[\left(\frac{C_{B_O} F_B}{\sum_{i=A}^{F} F_i}\right)\frac{T_O}{T}\right]\right] + \left(-\Delta H_{R_{A_2}} T\right)\left[K_2\left[\left(\frac{C_{A_O} F_A}{\sum_{i=A}^{F} F_i}\right)\frac{T_O}{T}\right]\right]}{\sum_{i=A}^{F} F_i C_{P_i}}\frac{\pi D_r^2}{4} \tag{14}$$

where $F_i$ are molar flow rates of component i, i = A,B,C,D,E,F, $D_r$ is reactor diameter, $C_{Ao}$ and $C_{Bo}$ are initial concentration methane and oxygen respectively, $Cp_i$ is specific heat capacity of component i, $T_o$ feed inlet temperature, $\Delta H_{RxA1}(T)$ and $\Delta H_{RxA2}(T)$ are heat of reaction at temperature T for partial and total methane oxidation respectively.

## 2.3 Determination of Reactor Functional Parameters

**Reactor Volume ($V_r$):** The material balance on a differential element of the reactor was rearranged to give an expression for the volume of the reactor:

$$V_R = F_{A_O}\int_0^{X_A} \frac{dX_A}{K_1\left(\frac{C_{A_O}(1-X_A)T_O}{(1+\varepsilon_A X_A)T}\right)^{1.5}\left(\frac{(C_{B_O}-C_{A_O}X_A)T_O}{(1+\varepsilon_A X_A)T}\right) + K_2\left(\frac{C_{A_O}(1-X_A)T_O}{(1+\varepsilon_A X_A)T}\right)} \tag{15}$$

**Reactor Length ($L_r$):** The reactor volume (eqn. 15) expressed in terms of cross sectional area and length was rearranged to obtain:

$$L_R = \frac{4F_{A_O}}{\pi D_r^2}\int_0^{X_A} \frac{dX_A}{K_1\left(\frac{C_{A_O}(1-X_A)T_O}{(1+\varepsilon_A X_A)T}\right)^{1.5}\left(\frac{(C_{B_O}-C_{A_O}X_A)T_O}{(1+\varepsilon_A X_A)T}\right) + K_2\left(\frac{C_{A_O}(1-X_A)T_O}{(1+\varepsilon_A X_A)T}\right)} \tag{16}$$

**Space – Time ($S_T$):** This is the time necessary to process one reactor volume of fluid is estimated using the reactor volume expression as:

$$S_T = \frac{F_{A_O}\int_0^{X_A} \frac{dX_A}{K_1\left(\frac{C_{A_O}(1-X_A)T_O}{(1+\varepsilon_A X_A)T}\right)^{1.5}\left(\frac{(C_{B_O}-C_{A_O}X_A)T_O}{(1+\varepsilon_A X_A)T}\right) + K_2\left(\frac{C_{A_O}(1-X_A)T_O}{(1+\varepsilon_A X_A)T}\right)}}{V_O} \tag{17}$$

**Space – Velocity ($S_v$):** This is the number of reactor volumes of feed treated in a unit time and is obtained as the inverse of the space time (eqn. 17) as:

$$S_V = \frac{V_O}{F_{A_O}\int_0^{X_A} \frac{dX_A}{K_1\left(\frac{C_{A_O}(1-X_A)T_O}{(1+\varepsilon_A X_A)T}\right)^{1.5}\left(\frac{(C_{B_O}-C_{A_O}X_A)T_O}{(1+\varepsilon_A X_A)T}\right) + K_2\left(\frac{C_{A_O}(1-X_A)T_O}{(1+\varepsilon_A X_A)T}\right)}} \tag{18}$$

where $X_A$ is the fractional conversion of methane, $V_o$ is the initial volumetric flow rate, and $\square_A$ is the voidage.

## Selectivity

The selectivity parameter enables the prediction of the product produced from the reaction and was introduced in other to determine reaction conditions that minimize the unwanted products ($CO_2$ and $H_2O$) from the complete oxidation reaction. The selectivity of thereaction product was obtained using the expression given by Fogler, (1999); Coulson & Richardson, (1991):

$$S_{CO} = \frac{Moles\ of\ Methane\ Transformed\ to\ CO\ and\ H_2}{Moles\ of\ Methane\ Transformed\ to\ CO_2\ and\ H_2O} = \frac{r_{A_1}}{r_{A_2}} \tag{19}$$

Substituting the rate expressions ($r_{A1}$) and ($r_{A2}$), expressed by equation (1) and (3) respectively, yields:

$$S_{CO} = \frac{K_1}{K_2}\left(\frac{C_{A_O}(1-X_A)T_O}{(1+\varepsilon_A X_A)T}\right)^{0.5}\left(\frac{(C_{B_O}-C_{A_O}X_A)T_O}{(1+\varepsilon_A X_A)T}\right) \tag{20}$$

## Yield (Y)

The product distribution as reaction proceeds in each reaction was obtained using the expression for relative or instantaneous yield (Coulson & Richardson, 1991; Fogler, 1999):

$$Y_S = \frac{Moles\ of\ reactant\ transformed\ to\ product}{Total\ moles\ of\ reactant\ which\ have\ reacted} \tag{21}$$

The yield of each reaction path was obtained by substituting the appropriate terms into this equation to give:

$$Y_{S_1} = \frac{r_{A_1}}{r_{A_2}} = \frac{K_1\left(\frac{C_{A_O}(1-X_A)T_O}{(1+\varepsilon_A X_A)T}\right)^{1.5}\left(\frac{(C_{B_O}-C_{A_O}X_A)T_O}{(1+\varepsilon_A X_A)T}\right)}{\left[K_1\left(\frac{C_{A_O}(1-X_A)T_O}{(1+\varepsilon_A X_A)T}\right)^{1.5}\left(\frac{(C_{B_O}-C_{A_O}X_A)T_O}{(1+\varepsilon_A X_A)T}\right)\right] + \left[K_2\left(\frac{C_{A_O}(1-X_A)T_O}{(1+\varepsilon_A X_A)T}\right)\right]} \tag{22}$$

$$Y_{S_2} = \frac{r_{A_2}}{r_{A_1}} = \frac{K_2\left(\frac{C_{A_O}(1-X_A)T_O}{(1+\varepsilon_A X_A)T}\right)}{\left[K_1\left(\frac{C_{A_O}(1-X_A)T_O}{(1+\varepsilon_A X_A)T}\right)^{1.5}\left(\frac{(C_{B_O}-C_{A_O}X_A)T_O}{(1+\varepsilon_A X_A)T}\right)\right]+\left[K_2\left(\frac{C_{A_O}(1-X_A)T_O}{(1+\varepsilon_A X_A)T}\right)\right]} \tag{23}$$

**2.4 Operating Parameter and Constants Estimation**

The flow rates of the reactants and the feed concentrations were calculated using physical and thermodynamic parameters obtained from Perry *et al.* (1999) and Smith *et al.* (2001) and are presented in Table 1. The feed concentrations were calculated using the ideal gas law and Dalton's law at feed inlet temperature of 1474K, pressure range of 12 to 70 Bar. The deviation from ideality by the reacting gaseous mixture as a result of high pressure was accounted for by the introduction of compressibility factor (Z) into the calculations of operating design parameters. The reactor was designed to process 600 million Standard Cubic Feet (mmscf) of methane per day (196.53m$^3$/s or 140.91kg/s).

**Table 1: Flow Rates of Reactants**

| | |
|---|---|
| **Volumetric Flow Rate of Methane (CH$_4$) : V$_{AO}$** | 196.53 m$^3$/sec |
| **Volumetric Flow Rate of Oxygen (O$_2$) : V$_{Bo}$** | 98.34 m$^3$/sec |
| **Molar Flow Rate of Methane (CH$_4$) : F$_{Ao}$** | 8783.82 mol/sec |
| **Molar Flow Rate of Oxygen (O$_2$) : F$_{Bo}$** | 4391.73 mol/sec |
| **Total Pressure** | 12 -70 bar |
| **Partial Pressure** | 6 – 25 bar |
| **Feed Inlet Temperature** | 1473 K |
| **Reactor Diameter** | 0.2m |

**Calculating Feed Concentration from Partial Pressures of Reactants**

The feed concentration of methane and oxygen were calculated from the partial pressures of reactants using equations obtained from Smith *et al.* (2001).

$$P_i = Z_i C_{i_O} R T_O \tag{23}$$

$$C_{i_O} = \frac{P_i}{Z_i R T_O} \tag{24}$$

**Total Reaction Pressure (P$_T$):** The total pressure was obtained using Dalton's law:

$$P_T = P_A + P_B \tag{25}$$

The compressibility factors were calculated using equations and data obtained from Perry *et al.*, (1999) is given as:

$$Z_i = 1 + \frac{Pr_i}{Tr_i}(B_i^0 + \omega_i B_i^1) \tag{26}$$

$$B_i^0 = 0.083 - \frac{0.422}{T_{r_i}^{1.6}} \tag{27}$$

$$B_i^1 = 0.139 - \frac{0.422}{T_{r_i}^{4.2}} \tag{28}$$

$$P_{r_i} = \frac{P_i}{P_c} \tag{29}$$

$$T_{r_i} = \frac{T_i}{T_c} \tag{30}$$

where $\omega_i$ is Acentric Factor of Component $i$, $Pr_i$ is the Reduced Pressure of Component $i$, $Tr_i$ is the Reduced temperature of Component $i$, $P_{Ci}$ is the Critical Pressure of Component $i$, $T_{Ci}$ is the Critical Temperature of Component $i$, $P_i$ is Partial Pressure of Component $i$. These expressions were used to compute the feed inlet concentrations

**Heat of Reaction (ΔH$_{RX}$)**

The heats of reactions were calculated using the expressions obtained from (Smith *et al.,* 2001) given as:

$$\Delta H_{R_{A1}}T = \Delta H_{R_{A1}}^0 + R\left[\Delta A1(\tau-1)T_r + \frac{\Delta B1}{2}(\tau^2-1)T_r^2 + \frac{\Delta C1}{3}(\tau^3-1)T_r^3 + \frac{\Delta D1}{T_r}\left(\frac{\tau-1}{\tau}\right)\right] \tag{31}$$

$$\Delta H_{R_{A2}}T = \Delta H_{R_{A2}}^0 + R\left[\Delta A2(\tau-1)T_r + \frac{\Delta B2}{2}(\tau^2-1)T_r^2 + \frac{\Delta C2}{3}(\tau^3-1)T_r^3 + \frac{\Delta D2}{T_r}\left(\frac{\tau-1}{\tau}\right)\right] \tag{32}$$

where $\tau = T/T_r$, $\Delta H^o{}_{A1}$ and $\Delta H_{A2}^o$ is the Standard heat of reaction for partial and total methane oxidation at a reference temperature (Tr), A, B, C & D are constant and can be found in Table 2.

Table 2: Required Constants (Smith *et al.,* 2001).

| | |
|---|---|
| Standard Heat of Reaction for Partial Methane Oxidation $(\Delta H^o{}_{A1})$ | -36 KJ/mol |
| Standard Heat of Reaction for Partial Methane Oxidation $(\Delta H^o{}_{A2})$ | -802.625 KJ/mol |
| Universal Gas Constant (R) | 8.314 J mol$^{-1}$ k$^{-1}$ |
| Pi (П) | 3.142 |
| Reference Temperature (Tr) | 298.15 K |

The specific heat capacities of the various components of each reaction were obtained using the expressions below and constants given in Table 3.

$$C_{P_i} = R(A + BT + CT^2 + DT^{-2}) \tag{33}$$

$$\Delta A1 = A3 + 2(A4) - [A1 + 0.5(A2)] \qquad \Delta A2 = A5 + 2(A6) - [A1 + 2(A2)]$$
$$\Delta B1 = B3 + 2(B4) - [B1 + 0.5(B2)] \qquad \Delta B2 = B5 + 2(B6) - [B1 + 2(B2)]$$
$$\Delta C1 = C3 + 2(C4) - [C1 + 0.5(C2)] \qquad \Delta C2 = C5 + 2(C6) - [C1 + 2(C2)]$$
$$\Delta D1 = D3 + 2(D4) - [D1 + 0.5(D2)] \qquad \Delta D2 = D5 + 2(D6) - [D1 + 2(D2)]$$

Table 3: Heat Capacity Constants (Smith *et al.,* 2001).

| S/NO | Species | A | B x 10$^3$ | C x 10$^6$ | D x10$^{-5}$ |
|---|---|---|---|---|---|
| 1 | $CH_4$ | 1.702 | 9.081 | -2.164 | 0 |
| 2. | $O_2$ | 3.639 | 0.506 | 0 | -0.227 |
| 3 | CO | 3.376 | 0.557 | 0 | -0.031 |
| 4 | $H_2$ | 3.249 | 0.422 | 0 | 0.083 |
| 5 | $CO_2$ | 5.457 | 1.045 | 0 | -1.157 |
| 6 | $H_2O$ | 3.470 | 1.450 | 0 | 0.121 |

## 2.6 Solution Techniques

The model equations were used to develop a design algorithm which was followed to develop the design program that determines the functional parameters of the reactor. Various methods and simulation packages/software were used in solving the specific design equations viz: the temperature dependence of the reaction rate constants was simulated using Simulink, the differential model equations for the reactants and products flow rate and temperature progression along the reactor were solved using ode 4.5 of MathLab 7.5, the reactor volume, reactor length, space time and space velocity model equations were integrated numerically using Simpson's function in MathLab 7.5; while the selectivity and yield parameters were simulated using Simulink.

## 3. DISCUSSION OF RESULTS
### 3.1 Determination of Optimum Temperature Range

From the expressions of selectivity derived (eqns 19 and 20), the reaction path (between partial or complete oxidation) which is favored/product formed is dependent on the rate constant of the two reaction paths. Therefore the effective reaction rate constant defined as K = K1 – K2 and the individual rate constant expressions for both partial and total oxidation were simulated at temperatures (0 – 2000)K as shown in Figure 1 and 2 to determine the optimum operating temperature range to operate the reactor.
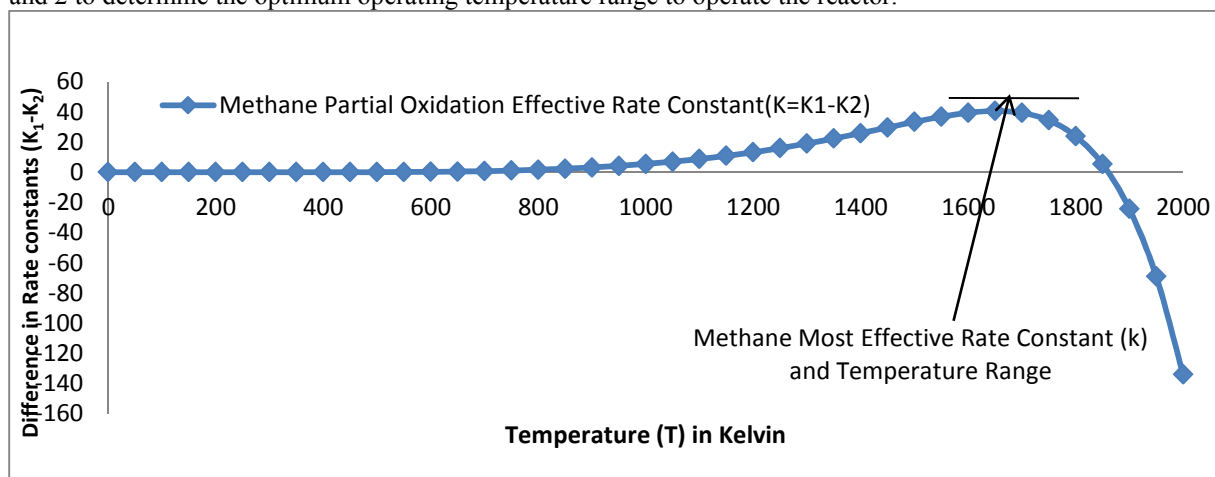


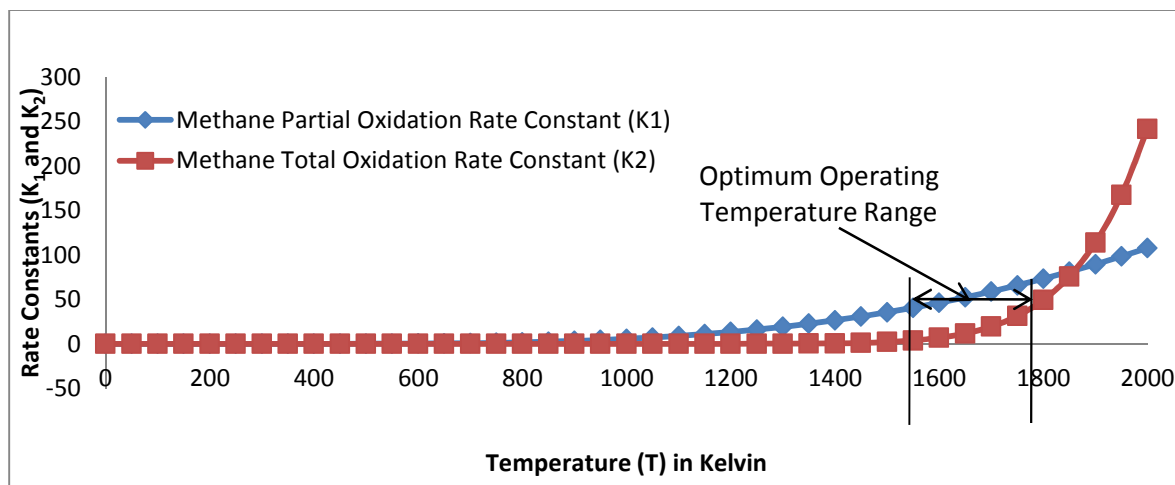Figure 1: Profile of the Variation in Effective Rate constant (k) With Temperature.

Figure 2: Profile of the Variation in Rate Constants ($K_1$ and $K_2$) With Temperature.

Figure 1 shows that an optimum effective rate constant occurs at a temperature range between 1550 – 1750 K; above this range, the effective reaction rate begins to drop. Figure 2 shows that the rates of reaction increase for both reaction paths with temperature, the partial oxidation path had higher rates at operating temperatures of 1200 – 1800K; the total oxidation path had higher rates above this temperature range. Comparing Figures 1 and 2, the optimum temperature for selectivity of partial oxidation path leading to the formation of desired products is 1550 – 1750K. This temperature range is in agreement with the temperature range of Shell Gasification process as reported by Wender, (1996); above this range, Figure 2 predicts a sharp increase in K2 (complete oxidation) leading to the formation of unwanted products compared to K1 (partial oxidation) which leads to the formation of desired products.

**3.2 Flow Rates of Reactants, Products and Temperature Progression across Reactor Length**
The molar flow rates of the reactants, products, and temperature progression along the reactor length at various operating pressures 12bar: Figures 3 and 4; 30bar: Figures 5 and 6.
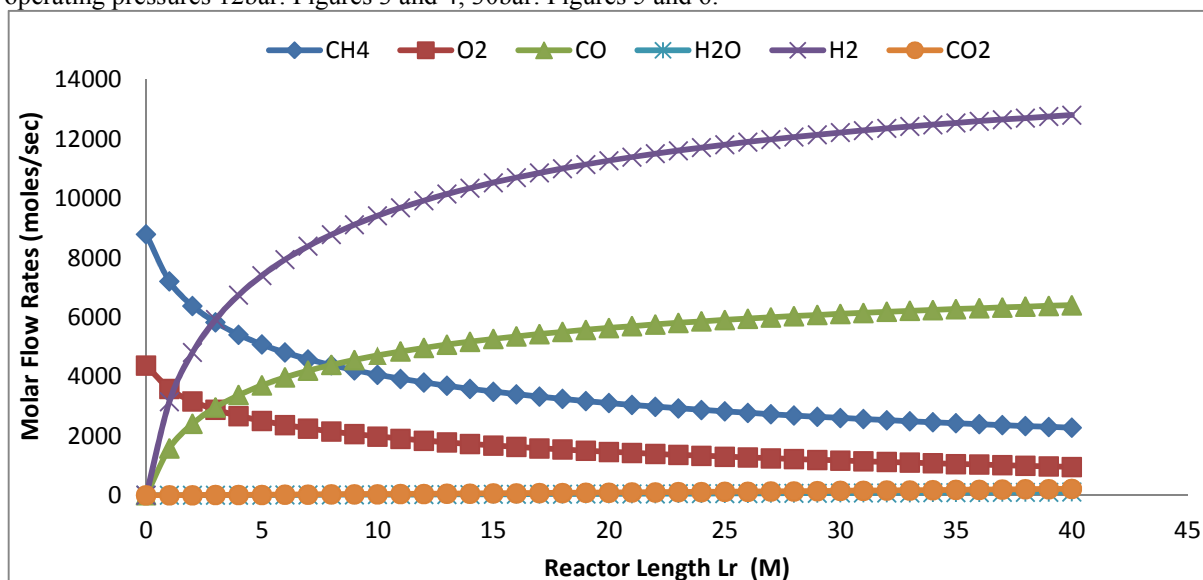


Figure 3: Profile of Molar Flow Rates of Reactants and Products across Reactor Length.
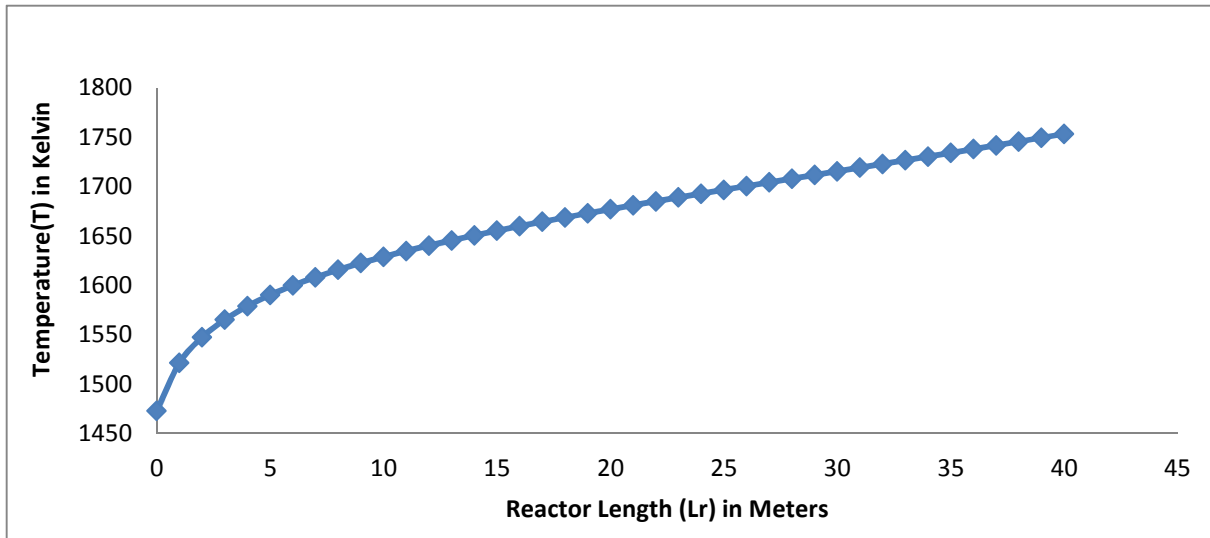
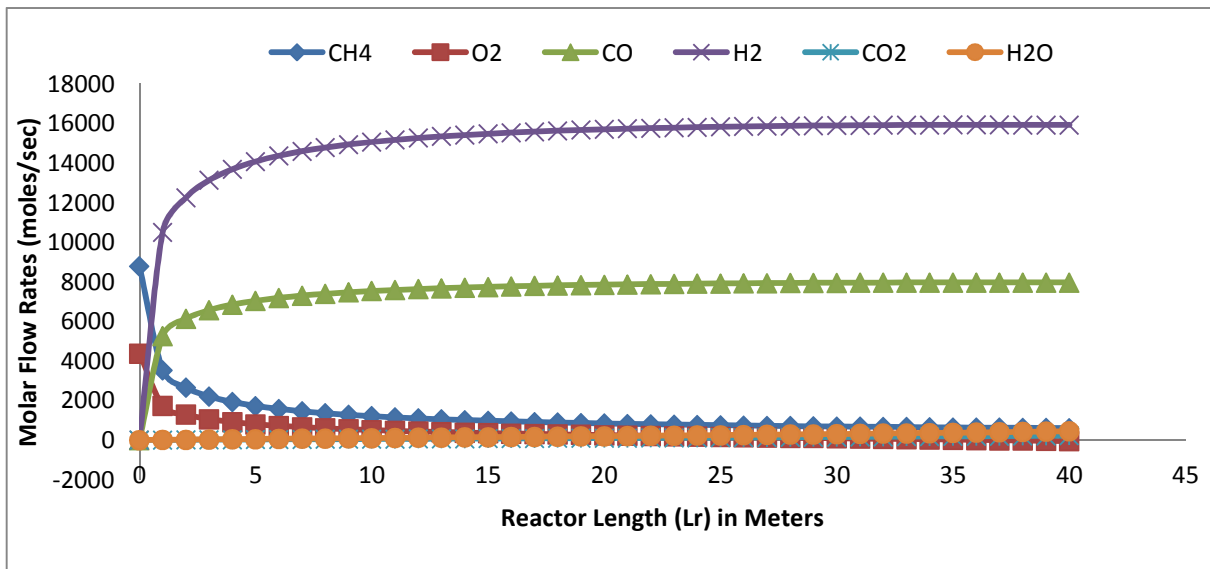Figure 4: Profile of Temperature Variation across Reactor length.



Figure 5: Profile of Molar Flow Rates of Reactants and Products across Reactor Length.
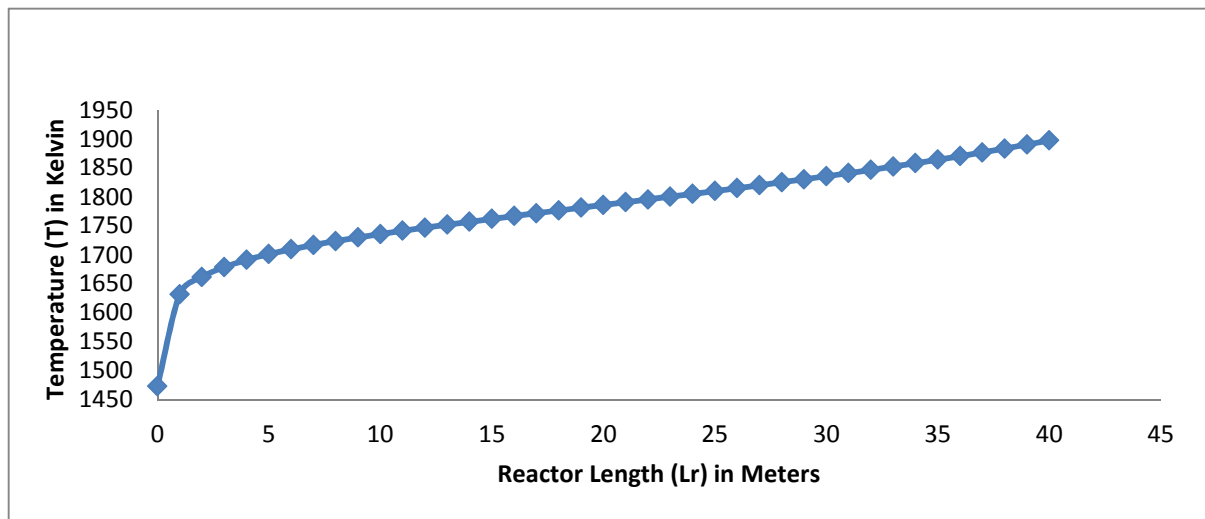
Figure 6: Profile of Temperature Variation across Reactor length.

Figures 3 and 5 shows an increase in flow rates of the desired products (CO and $H_2$) (more of the desired products are produced) and a decrease in that of the unwanted products along the reactor length at each pressure value; Also, an increase in pressure results in an increase in flow rate of the desired product and a sharp decrease in that of the unwanted products. That is, increase in pressure favors the partial oxidation reaction leading to the production of more synthesis gas (desired product).

The temperature profiles along the reactor length: figures 4 and 6 show increase in temperature along the reactor length at both operating pressures, however, operating at 30 bar results in the reaction temperature rising (1850K and above) above the optimum temperature range (1550 – 1750) from a reactor length of 37meters. This rise in temperature above the optimum range favors the total oxidation reaction path leading to the production of unwanted products as predicted by Figure 2. This was evident in the sharp reduction in the flow rate of the reactant oxygen in Figure 5 as more of this reactant is used up for the production of the unwanted products ($CO_2$ and $H_2O$)..

### 3.3 Dependence of Fractional Conversion ($X_A$) on Reactor Length (Lr)
Figure 7 is a plot of fractional conversion ($X_A$) along the reactor length at various operating pressures: 12, 30, 60bar and feed inlet temperature of 1473 K (1200ºC).
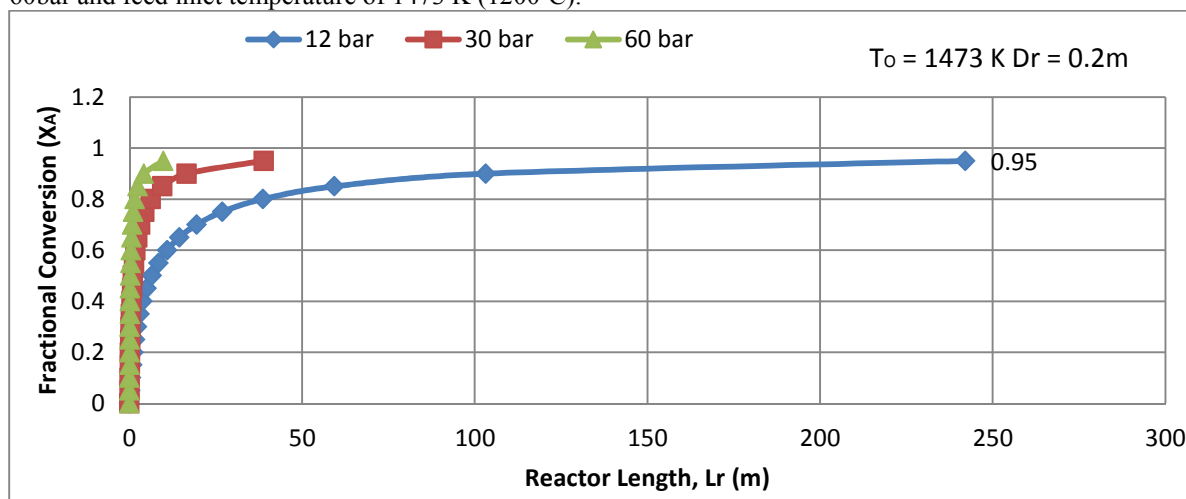


Figure 7: Profile Showing Methane Fractional Conversion versus Reactor Length.

Figure 7 shows that fractional conversion ($X_A$) increases with reactor length at all pressures. Fractional conversion also increases with increase in pressure. Increasing pressure also results in reduced length of reactor for a particular fixed fractional conversion.

### 3.4 Reactor Space Time ($S_T$)

The dependence of space time on fractional conversion ($X_A$) is depicted by Figure 8.
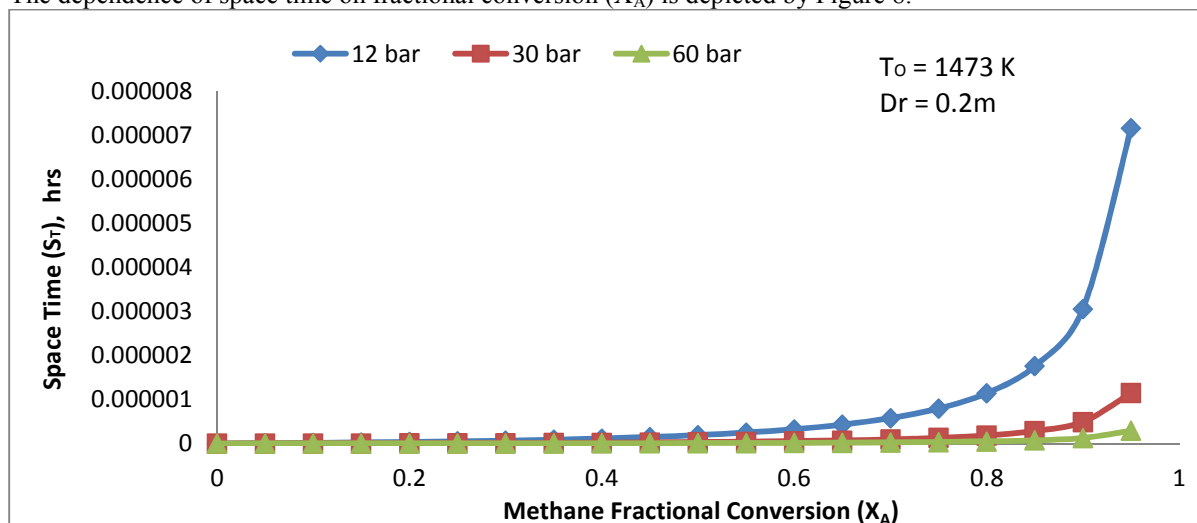


Figure 8: Profile Showing Space Time versus Methane Fractional Conversion.

Space time of a reactor is the time necessary to process one reactor volume of fluid based on entrance conditions (holding time or mean residence time). This should increase with fractional conversion. The profile in Figure 8 shows that space time ($S_T$) increases approximately directly proportional to fractional conversion between $X_A$ = 0 and $X_A$ = 0.65. Above this range ($X_A$ = 0.65 to 0.99), space time ($S_T$) increases sharply with small increment in fractional conversion. This plot, also reveals that increase in reactor pressure (12, 30 and 60) bar, greatly decreases the space time ($S_T$) of the reactor especially at high fractional conversions.

### 3.5 Reactor Space Velocity ($S_v$)

The relationship between the reactor volumes of feed (space velocity) with fractional conversion is shown in Figure 9. The space velocity of a reactor is the number of reactor volumes of feed that is treated in a unit time. This is supposed to decrease with fractional conversion.
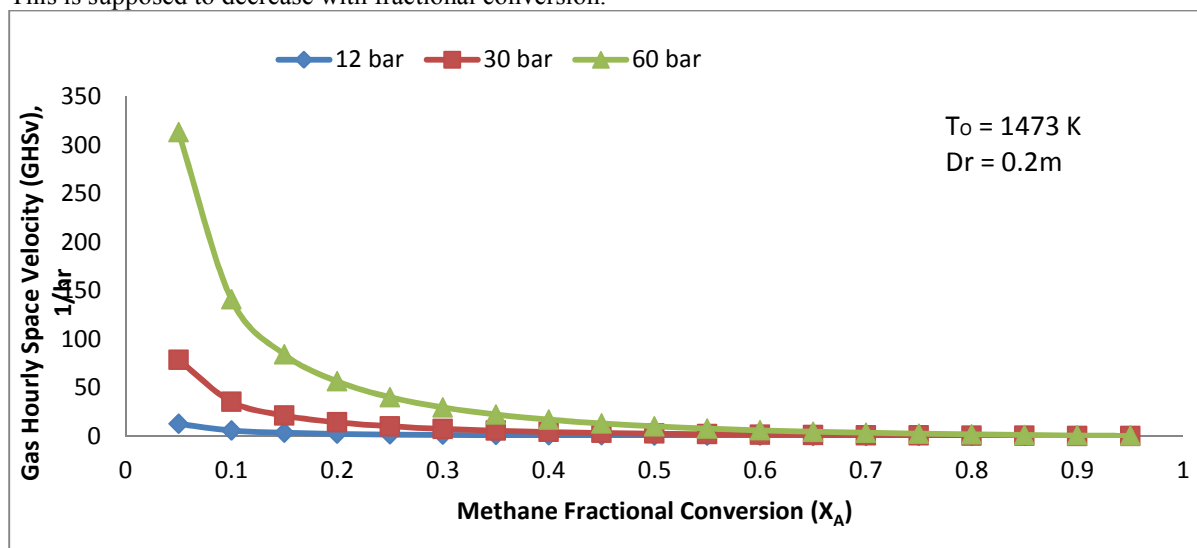


Figure 9: Profile Showing Space Velocity versus Methane Fractional Conversion.

Figure 9 depicts that space velocity decreases with fractional conversion; decreasing with a steep gradient at low fractional conversions ($X_A$ = 0.05 to 0.25) and with a mild gradient above $X_A$ = 0.25. Figure 6 also shows that increase in operating pressures increases the reactor space velocity ($S_V$) especially at low fractional conversion.

### 3.6 Selectivity ($S_{co}$) and Fractional Conversional ($X_A$)

The relationship between selectivity of partial oxidation reaction leading to the production of the desired product and fractional conversion is shown in Figure 10. Figure 10 shows that selectivity increases with increase in

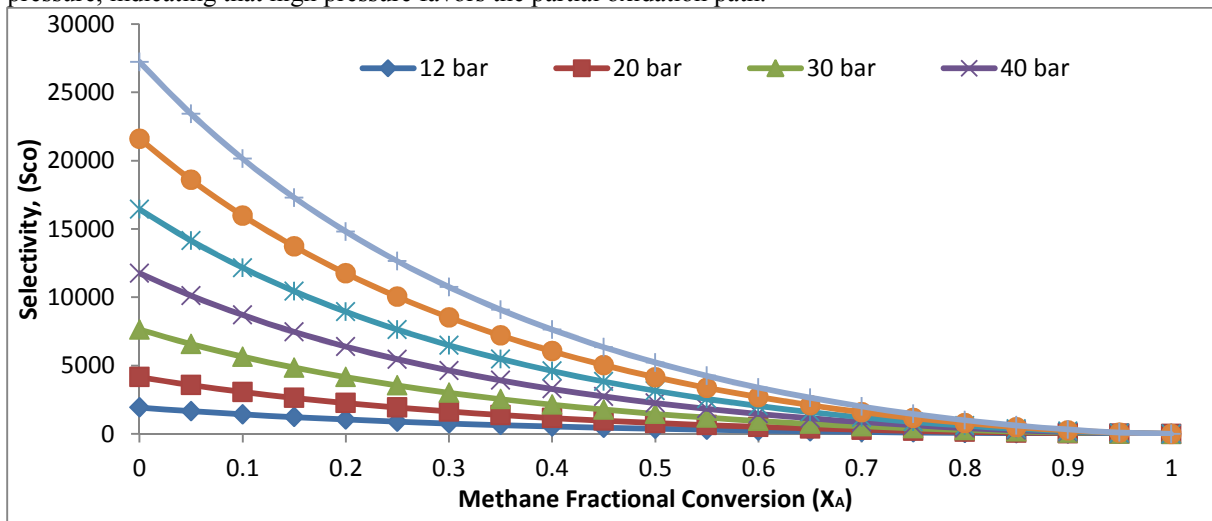pressure, indicating that high pressure favors the partial oxidation path.



Figure 10: Effect of Fractional Conversion and Pressure on Synthesis Gas Selectivity.
It also shows that selectivity decreases with fractional conversion of methane at all pressures.

### 3.7 Yeild Analysis of Synthesis Gas ($Y_s$) and Carbon Dioxide ($Y_{CO2}$)

The yields of synthesis gas ($Y_s$) from partial methane oxidation reaction and yield of carbon dioxide, ($Y_{co_2}$) from total methane oxidation reaction with fractional conversion of methane ($X_a$) are shown in Figure 11.
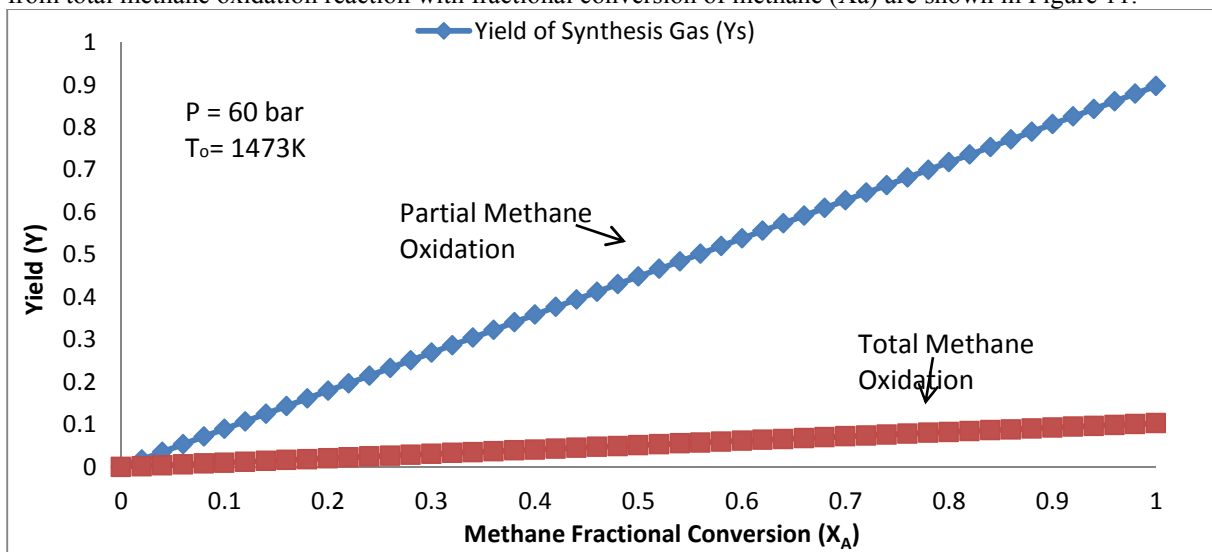


Figure 11: Profile of Products Yield versus Methane Fractional Conversion

Figure 11 shows that the yields of partial and total methane oxidation are proportional to fractional conversion. The yields both increase with increase in methane fractional conversion, however the yields of partial oxidation increased much higher with a steeper gradient than that of total oxidation.

### 4. Conclusion

A computer aided hypothetical plug-flow reactor was designed for the non-catalytic partial oxidation of methane to synthesis gas. The reactor was designed to process 600mmscf of natural gas per day (196.53 $m^3$/s), operates adiabatically at a feed (gas) inlet temperature of 1473 K (1200ºC) and a pressure of 60 bar. After the simulation of the various operating parameters, an optimum set of Design operating parameters were obtained for the plug flow reactor. The optimal values of the functional parameters of the reactor such as reactor length, space time, space velocity, selectivity and yield were also obtained. These optimum operating conditions and parameters were used to design the hypothetical reactor.

## NOMENCLATURE

| Symbol | Meaning | Unit |
|---|---|---|
| $B_i^0$ | First Virial Coefficient of Component i | Dimensionless |
| $B_i^1$ | Second Virial Coefficient of Component i | Dimensionless |
| $C_{io}$ | Initial Concentration of Component i | mole/m$^3$ |
| $C_i$ | Final Concentration of Component i | mole/m$^3$ |
| $Cp_i$ | Specific Heat Capacity of Specie i | J/mole K |
| $D_r$ | Reactor Diameter | m |
| $F_{io}$ | Initial Molar Flow Rate of Component i | mole/sec |
| $F_i$ | Final Molar Flow Rate of Component i | mole/sec |
| i | Species (A, B,C,D,E,F) | Dimensionless |
| $K_1$ | Rate Constant of Partial Methane Oxidation | mole$^{-1.5}$m$^{4.5}$sec$^{-1}$ |
| $K_2$ | Rate Constant of Total Methane Oxidation | sec$^{-1}$ |
| k | Optimum Effective Rate Constant | – |
| Lr | Reactor Length | m |
| $P_i$ | Partial Pressure of Component i | bar |
| $P_T$ | Total Pressure | bar |
| $Pr_i$ | Reduced Pressure of Component i | Dimensionless |
| $Pc_i$ | Critical Pressure of Component i | bar |
| R | Universal Gas Constant | Jmol$^{-1}$K$^{-1}$ |
| $r_{A1}$ | Rate of Partial Methane Oxidation Reaction | mole·m$^{-3}$sec$^{-1}$ |
| $r_{A2}$ | Rate of Total Methane Oxidation Reaction | mole·m$^{-3}$sec$^{-1}$ |
| $r_A$ | Overall Rate of Reaction | mole·m$^{-3}$sec$^{-1}$ |
| $S_T$ | Space Time | hr |
| Sv | Space Velocity | hr$^{-1}$ |
| Sco | Selectivity of Partial Methane Oxidation Reaction | Dimensionless |
| T | Outlet or Final Temperature | Kelvin (K) |
| $T_r$ | Reference Temperature | Kelvin (K) |
| $Tr_i$ | Reduced Temperature of Component i | Dimensionless |
| $Tc_i$ | Critical Temperature of Component i | Kelvin (K) |
| $V_o$ | Feed Gas Volumetric Flow Rate | m$^3$/sec |
| $V_{io}$ | Volumetric Flow Rate of Component i | m$^3$/sec |
| Vr | Reactor Volume | m$^3$ |
| $X_A$ | Methane Fractional Conversion | Dimensionless |
| Y | Yield | Dimensionless |
| $Y_s$ | Yield of Synthesis Gas | Dimensionless |
| $Y_{CO2}$ | Yield of Carbon Monoxide | Dimensionless |
| $Z_i$ | Compressibility Factor of Component i | Dimensionless |
| $\varepsilon$ | Viodage | Dimensionless |
| $\Delta H^o_{A1}$ | Standard Heat of Partial Methane Oxidation Reaction | J/mole |
| $\Delta H^o_{A2}$ | Standard Heat of Total Methane Oxidation Reaction | J/mole |
| $\Delta H_{RxA1}(T)$ | Heat of Partial Methane Oxidation Reaction at Temperature T | J/mole |
| $\Delta H_{RxA2}(T)$ | Heat of Total Methane Oxidation Reaction at Temperature T | J/mole |

**Greek Letters**

| Symbol | Meaning | Unit |
|---|---|---|
| $\tau$ | Ratio of Temperature(T) and Reference Temperature ($T_r$) | Dimensionless |
| $\omega_A$ | Acentric Factor of Methane | Dimensionless |
| $\omega_B$ | Acentric Factor of Oxygen | Dimensionless |

## REFERENCES

Al-Sayari, S. A., (2013), Recent Developments in the partial oxidation of methane to syngas, The open catalysis Journal, 6, 17-28.

Biesheuvel, P. M. and Kramer, G. J., (2003), Two-section reactor model for autothermal reforming of methane to synthesis gas, AICHE J., 49. 1827-1837

Collodi, G. and Wheeler, F., (2010), Hydrogen production via steam reforming with $CO_2$ capture. Chem. Eng. Trans., 19, 37-42.

Coulson, J. M. & Richardson, J. F., (1991), Chemical Engineering, Volume 3, Third Edition, Elsevier Pte. Ltd., India. PP 39 - 41, 57.

De Groote, A. M. and Froment, G.F., (1996), Simulaation of the catalytic partial oxidation of methane to

synthesi gas, Applied Catalysis A. General, 138, 245-264

De Smet, C. R. H., (2000), "Partial Oxidation of Methane to Synthesis Gas: Reaction Kinetics and Reactor Modeling", Ph. D. Thesis, Eindhoven University of Technology, Terneuzen, Netherlands.

Enger, B. C., Lødeng, R. and Holmen, A., (2008), A review of catalytic partial oxidation of methane to synthesis gas with emphasis on reaction mechanisms over transition metal catalysts. Appl. Catal. A: Gen., 346, 1-27.

Fogler, H. S., (1999), Elements of Chemical Reaction Engineering, Third Edition, Prentice – Hall Inc., India. PP 283 – 291, 426 – 503.

Han, S., Park, J., Song, S. and Chun, K. M., (2010), Experimental and Numerical study of detailed reaction mechanism optimization of syngas ($H_2$+CO) production by non-catalytic partial oxidation of methane in a flow reactor, International Journal of Hydrogen Energy, 35,16, 8762-8771.

Kolios, G., Frauhammer, J. and Eigenberger, G., (2000), Autothermal fixed-bed reactor concepts. Chem. Eng. Sci., 55, 5945-5967.

Konnov, A. A., Zhu, J. N., Bromly, J. H. H. and Zhang, D. K., (2004), Non-catalytic partial oxidation of methane into syngas over a wide temperature range. Combustion science and technology, 176(7), 1093-1116.

Lyubovsky, M., Roychoudhury, S. and LaPerre, R., (2005), Catalytic oxidation of methane to syngas at elevated pressures, Catalysis Letters, 99, 3-4, 113-117.

Mitri, A., Neumann, D., Liu, T. and Veser, G., (2004), Reverse-flow reactor operation and catalyst deactivation during high-temperature catalytic partial oxidation . Chem. Eng. Sci., 9, 5527-5534.

Naeem, M. A., Al-Fatesh, A. S. and Fakeeha, A. H., (2013), Syngas production from dry reforming of methane over nano Ni Polypl catalysts, International Jounal of Chemical Engineering and Apllications, 4, 5, 315 – 320, DOI: 10.7763/IJCEA.2013V4.317

Neumann, D. and Veser, G., (2005), Catalytic partial oxidation of methane in a reverse-flow reactor. AICHE J., 51, 210-223

Pena, M., Gomez, J. and Fierro, J. L. G., (1996), New catalytic routes for syngas and hydrogen production. Appl. Catal. A: Gen., 144, 7-57.

Perry, R. H., Green, D. W., Maloney, J. O., (1999), Perry's Chemical Engineering Handbook, Seventh Edition, McGraw-Hill Companies, New York.

Rostrup-Nielsen, J. R., Sehested, J. and Norskov, J. K. (2002), Hydrogen and synthesis gas by steam- and CO2 reforming. Adv. Catal., 47, 65-138.

Smith, J. M., Van Ness, H. C., Abbott, M. M., (2001), Introduction to Chemical Engineering Thermodynamics, Sixth Edition, Tata McGraw-Hill Publishing Company, New York, PP 116 – 140.

Tsang, W. and Hampson, R. F., (1986), Chemical Kinetic Data Base for Methane Chemistry, Chemical Physics Reference Data, Volume 15.

Wender, I., (1999), "Natural Gas to Fisher-Tropsch Products", Fuel Processing Technology Journal, 48, PP 247 – 249.

York, A.P.E., Xiao, T., Malcolm, L. H. G., (2003), Partial Oxidation of Methane to Synthesis Gas, Journal of catalysis, 22, PP 345 – 358.

Zhou, X., Chun, C. and Wary (2010), Multi-dimensional modeling of non-catalytic partial oxidation of natural gas in a high pressure reformer, International Journal of Hydrogen Energy, 35,4, 1620-1629

Zhu, J. N., (2001), A Feasibility study of Methane reforming by partial oxidation, Ph.D Thesis, Curtin University of Technology, Perth, Austrailia.

Zhu, J. N., Zhang, D., Bromly, I., Barnes, F., King, D. K., (2001), An Experimental Study of Partial Oxidation Reforming of Methane at 1000 – 1600K, Proceedings of the 6th World Congress of Chemical Engineering, Melbourne, Australia.

The IISTE is a pioneer in the Open-Access hosting service and academic event management.  The aim of the firm is Accelerating Global Knowledge Sharing.

More information about the firm can be found on the homepage:
http://www.iiste.org

## CALL FOR JOURNAL PAPERS

There are more than 30 peer-reviewed academic journals hosted under the hosting platform.

**Prospective authors of journals can find the submission instruction on the following page:** http://www.iiste.org/journals/   All the journals articles are available online to the readers all over the world without financial, legal, or technical barriers other than those inseparable from gaining access to the internet itself.  Paper version of the journals is also available upon request of readers and authors.

## MORE RESOURCES

Book publication information: http://www.iiste.org/book/

**IISTE Knowledge Sharing Partners**

EBSCO, Index Copernicus, Ulrich's Periodicals Directory, JournalTOCS, PKP Open Archives Harvester, Bielefeld Academic Search Engine, Elektronische Zeitschriftenbibliothek EZB, Open J-Gate, OCLC WorldCat, Universe Digtial Library , NewJour, Google Scholar