1. ABSTRACT

Experimental investigation for dry reforming of methane with carbon dioxide was carried out. This study was aimed to explore the effect of changing the ratio of methane to carbon dioxide in the feed gas. The experiments were carried out using seven different ratios of methane to carbon dioxide that range from 0.25 – 4.0, three different temperature 773, 823, 848 K as well as three different total feed flow rate 10, 15, 20 ml/ min. at atmospheric pressure .The runs were carried out in AMI – 2000 Zeton-Altimira microreactor. The results indicate that increasing the ratio of methane to carbon dioxide decreases methane conversion, increases in carbon dioxide conversion and decreases hydrogen yield at each temperature used. Changing total feed flow rate has no effect on either conversion or hydrogen yield.


2. LITERATURE REVIEW

Steam reforming of CH4 using nickel catalyst has been industrialized for a long time [1]. In recent years, the carbon dioxide reforming of methane known as dry reforming has gained increasing importance and rapidly growing interest in the catalytic conversion of CH4 and CO2 to synthesis gas (syngas) because this reaction has many potential incentives with economical and environmental benefits [2-9]. Reforming equations of methane are given below:

- Dry reforming reaction:
  \[ \text{CH}_4 + \text{CO}_2 \leftrightarrow 2\text{CO} + 2\text{H}_2 \]  \[ \Delta H_{298}^\circ = 247 \text{ kJ/mol} \]

- Steam reforming reaction:
  \[ \text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2 \]  \[ \Delta H_{298}^\circ = 206 \text{ kJ/mol} \]
Nevertheless, the dry reforming reaction is now being recommended for the chemical energy transmission system (CETS) to replace steam reforming [3-5].

Fakeeha et.al [6-7] and Al-Fatish [8] performed comprehensive studies for dry reforming of methane using nickel based supported catalyst . Their studies concentrated on the effect of using different supports (alumina, silica, TiO₂, ZrO₂), different promoters (Co, Ce, Mo, Ca, Sb, Sn), calcination temperatures. The prepared catalysts were tested at different conditions of pressure, temperatures and flow rates. The results indicate that catalyst prepared with high surface area alumina using Ce as promoter is the best among the tested catalysts; it has the highest activity and is stable for at least 98 hours.

Gadalla and Sommer [10] studied and characterized an industrial Ni catalyst supported on CaO – TiO – Al₂O₃. The catalyst was used for methane reforming with carbon dioxide, and compared with catalyst containing Ni on other supports. Conversion close to 100% were achieved during 51 hours on stream for a CO₂: CH₄ ratio of 2.64:1 using a weight hourly space velocity of 7.38 h⁻¹ despite the solid state reaction and sintering which decrease the surface area.

Stagg et al. [11] studied the reforming of CH₄ with CO₂ at 800 °C over SiO₂ and ZrO₂ supported Pt-Sn catalyst. Several preparation methods were investigated. It was found that the Pt/ZrO₂ catalyst had much higher activity and stability than the Pt/SiO₂ catalyst due to ability of the ZrO₂ to promote CO₂ dissociation on this catalyst. The decomposition of CH₄ and the dissociation of CO₂ occur via two independent pathways. The long-term activity of the catalyst is dependent upon the balance between the rate of CH₄ decomposition and the rate of cleaning of carbonaceous deposits. The Co-impregnation of Sn and Pt on the ZrO₂ results in lower activity and stability than the monometallic catalysts. Depending on the reaction conditions, disruption of the Pt-Sn alloys may occur causing deposition of tin oxide that inhibits the role of the ZrO₂. Special preparation methods can result in the controlled placement of Sn on the Pt particle minimizing the promoter-support interaction. The catalysts exhibit higher activity and stability than the monometallic catalyst under severely deactivating conditions, 800 °C and 3:1 ratio of CH₄: CO₂. It is possible to deposit Sn onto Pt/ZrO₂ catalyst in manner, which reduces carbon deposition without inhibiting the beneficial role of the support.
Liu and Au [12] reported that investigation for dry reforming has been renewed due to environmental and commercial reasons. Synthesis gas with a low $H_2$: CO ratio is preferred for the production of liquid hydrocarbons and oxygenated derivatives. One advantage of CO$_2$/CH$_4$ reforming is the low $H_2$: CO ratio in syn gas formation; the process opens the possibility of combining steam reforming, partial oxidation, and dry reforming for the generation of a syn gas with a desired $H_2$: CO ratio. For environmental protection and to fight against global warming, it makes sense to study the utilization of CO$_2$ and CH$_4$. Both compounds are considered as greenhouse gases. In addition, since there is CO$_2$ ($\geq$ 25 vol. %) in field gases, it is beneficial to utilize CO$_2$ directly in methane, reforming rather than separating it from methane.

Wargadalm et al. [13] studied methane reforming with CO$_2$ in hot temperature in a thermal diffusion column reactor. The temperature effect on tungsten, molybdenum and chromel wires showed molybdenum to be the best wire. As the ratio of CO$_2$: CH$_4$ changes from 1.97 to 0.55, the CO: $H_2$ ratio changed from 1.56 to 0.74. Accordingly, it may be possible to change the composition of the synthesis gas to suit the utilization to which it is intended.

Huang et al [14] performed CO$_2$ reforming of CH$_4$ at atmospheric pressure by alternating current discharge plasma in Y type reactor. The investigators studied the effects of reaction parameters such as input voltage, total flow rate, mole fraction of methane to carbon dioxide, selective excitation of either reactant, and micro-arc formation, on product distribution and energy efficiency. Their result showed the dependence of CH$_4$ and CO$_2$ conversions and selectivity on the CH$_4$/ CO$_2$ ratio. With an increasing of CH$_4$/ CO$_2$ ratio from 1/9 to 9/1, the conversion of CH$_4$ (97.3-84.2) and selectivity to hydrogen (74.5-28.6) and to CO (98.9-21.5) decreased while the conversion of CO$_2$ (22.0-77.5) and to hydrocarbons increased.

The specific objectives of this research is to investigate the effect of changing the percentage of methane to carbon dioxide in the feed for the production of synthesis gas using nickel based catalyst at different temperatures and flow rates.

3. EXPERIMENTAL

In this work Ni - base supported catalysts were used. The support used is $\gamma$-alumina (SA-6175) with surface area of (230 – 290 m$^2$/gm) Impregnation of the support was carried out
with aqueous solutions of nickel-nitrate. Cerium (Ce) is used as promoter in preparation of the supported Ni-based catalysts. The resulting catalyst dried in the oven at 110°C for 13 hours then calcined at 600°C in air atmosphere for 5 hour. The reproducibility of the results was checked during this work period by repeating the experiments under the same conditions several times.

**Experimental Set-up**

The heart of the experimental setup used in this study is a micro-reactor made by ZETON-ALTAMIRA (model AMI 2000). The whole experimental setup is shown schematically in Fig. 1. The system is composed of the following sections:

I. Feed Section: The feed section contains three gas cylinders for CO₂, CH₄ and N₂. Gases coming from the regulators pass through in-line filters then introduced to the Mass Flow Controllers (MFC), obtained from Brooks. The gases are mixed and passed to the reaction section. On line samples from the feed gas mixture are directed to gas chromatograph for analysis.

II. Reaction Section: The micro-reactor overall length is 0.43 m, with inside diameter of 6.35x10⁻³ m made of stainless steel and surrounded by three zones heater. Each zone temperature can be controlled separately. The temperature in the reactor is measured by a thermocouple located in the catalyst bed. The outlet from the reactor (bottom end) is passed through a backpressure regulator (BPR) to control the pressure in the reactor and the product gases from the BPR were sent to analysis section.

III. Analysis Section: The analysis was carried out by using Varian gas chromatograph (model 3400 CX) with TDC detector; the TDC detector is equipped with Hysis column.

**Catalysts Characterization:**

The BET surface area for selected catalysts are measured by using equipment model (ASAP2010), samples of catalysts were analyzed by using Scanning electron microscope (SEM) model "JEOL, JSM – 6360A" to get pictures for the surface of the catalysts.
Activation procedure

The activation procedure is as follow:

A. Introduce hydrogen to the reactor at 20 ml/min for 2.5 hr.
B. Then hydrogen is stopped while N₂ is introduced at 40 ml/min for one hour

This pretreatment process was found to be essential for the reaction to take place [6-8].

Figure 1: Schematic diagram of experimental setup:

HV1, HV2 and HV3: Filters, MFC’s Mass Flow Controller, PG Pressure Gauge CV1, CV2 and CV3 Shut off Valves, SV1: Sampling Valve, F: Furnace, R: Reactor, T1, T2 and T3: Temperature Measurement location (by Thermocouple), GC: Gas Chromatograph, PCV: Pressure Control Valve.
4. RESULTS AND DISCUSSION:

The experimental runs were carried out in order to achieve the objectives of this investigation by finding the effect of changing the ratio of methane to carbon dioxide in the feed gas. The effect of changing total feed flow rate were also investigated. To insure reproducibility of the results, the experiments were repeated under similar conditions several times during the course of this work.

Effect of Changing Methane to Carbon Dioxide Ratio in the Feed:

Seven methane to carbon dioxide ratios were selected during this project: 2/8 (0.25), 3/7 (0.43), 4/6 (0.67), 5/5 (1), 6/4 (1.5), 7/3 (2.33), and 8/2 (4). The runs for each set of experiment were carried out at constant flow rate of 10 ml/min and total pressure of 14.7 psi and specific temperature. The results for methane conversion, carbon dioxide conversion and hydrogen yield are shown in figures 2-4, respectively. Three different sets were performed at three different temperature 773, 823, 848 Kº. For methane conversion, Figure (2) indicates that as the ratio of methane to carbon dioxide increases at 773 Kº, the methane conversion decreases sharply up to a ratio of 5/5. Then the conversion decrease reduces slowly up to a ratio of 7/3 then it become constant after that within our experimental range. The methane conversion decreased from 30% at a ratio of 2/8 to almost 10% at a ratio of 8/2. The same trend for the effect of changing methane to carbon dioxide ratio was obtained at 823 Kº, but with more sharper decrease at the start. The methane conversion decreased from a value of 58% at a ratio of 2/8 to 24% at a ratio of 8/2. Similar behavior was obtained at 848 Kº with methane conversion decreased from 70% at a ratio of 2/8 to 30% at a ratio of 8/2 methane to carbon dioxide.

The reasons for the decrease in methane conversion can be explained using the La chatelier principle.

\[ CH_4 + CO_2 \leftrightarrow 2 CO + 2H_2 \]

At low CH_4 / CO_2 ratio since CO_2 is in excess, it forces CH_4 to be converted to CO and H_2 (according to La chatelier principle). As CH_4 / CO_2 ratio increased, the CO_2 amount decreased causing lower CH_4 conversion. When the ratio increased above 1, CH_4 starts to decomposed to carbon and hydrogen according to the following equation:

\[ CH_4 \leftrightarrow 2H_2 + C \]
This accounts for not continuing the decrease trend in methane conversion. As evidenced by the increased ratio of H₂: CO.

Figure (3) presented the conversion of carbon dioxide as function of methane to carbon dioxide ratios at a total flow rate of 10 ml/min, total pressure of 14.7 psi and three different temperature 773, 823 and 848 K°.

The trend here is opposite to what obtained for methane conversion, the carbon dioxide conversion increased as the ratios of methane to carbon dioxide increased. The carbon dioxide conversion is 15% at 773 K° for methane to carbon dioxide ratio of 2/8 and increased to almost 40% at a ratio of 8/2. The carbon dioxide conversion at higher temperatures 823, 848 K° are 25% and 31% at a ratio of 2/8 and increased to 55% , 65% at a ratio of 8/2 respectively. The increase in CO₂ conversion is due to increase in the amount of CH₄, which causes more conversion of CO₂ according to Le chatelier principle.
The hydrogen yield is shown in Figure (4). From the previously discussed cases, the effect of changing the ratios of methane to carbon dioxide is similar to that of methane conversion. Three set of results were plotted with total flow rate of 10ml/min and a total pressure of 14.7 psi and at temperatures of 773, 823, 848 K°.
Effect OF Flow Rate:
Three different flow rate were chosen 10 ml/ min, 15 ml/min and 20 ml/min . The total pressure used was 14.7 psi and methane to carbon dioxide was fixed at 0.25. Three different set of experiments were performed at these flow rates. Each set was performed at a specific temperature. The temperatures used for these sets are 773, 823, 848 Kº. The results are shown in Figure 5. and. There is almost no change in hydrogen yield at each set when flow rate changes within our experimental range. At 773 Kº, 30% hydrogen yield was obtained. As temperature increased the hydrogen yield increased. At 823 and 848 Kº, the hydrogen yield are approximately 51% and 64% respectively. The constancy in hydrogen yield with the change in flow rate indicates that the reaction reaches equilibrium condition.

The BET- surface area of the alumina support , fresh catalyst and used catalyst are 222.5 , 208.5 and 194 m² / gm. Picture for fresh and used catalyst are shown at figures 6&7.
Figure 6. Scanning microscopy of fresh catalyst at 500 magnification

Figure 7. Scanning microscopy of used catalyst at 900 magnification
5. CONCLUSION

Experimental investigation for the effect of changing the ratio of methane to carbon dioxide in the feed to dry reforming reaction were carried out in AMI- 2000 Zeton – Altimira micro-reactor. Seven ratios of methane to carbon dioxide that range from 0.25 –4.0 were selected in this study. Three different temperatures were used 773, 823 and 848 Kº. Similarly three different total feed flow rate were also used 10, 15, 20 ml/min. The following conclusions could be drawn from the results obtained in this investigation:

- Increasing CH₄ / CO₂ ratio led to decrease in methane conversion at each temperature used.
- Increasing CH₄ / CO₂ ratio led to an increase in carbon dioxide conversion at each temperature used.
- Increasing CH₄ / CO₂ ratio led to decrease in Hydrogen yield at each temperature used.
- As temperature increased the conversion of both gases as well as hydrogen yield increased.
- No effect on conversion or hydrogen yield was observed by changing total feed flow rate.

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7. REFERENCE


