

Effects of catalytic bed position on hydrogen production by methane decomposition

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ABSTRACT

CO_x free hydrogen can be produced by thermal decomposition of methane. Such process is carried out in a fixed bed catalytic reactor. Where heterogeneous catalytic reaction occur when methane come in contact with catalyst bed at a temperature range of 650-900°C. In this work effect of different catalyst bed positions are investigated on the overall methane conversion to hydrogen. Experimental studies are carried out to in a Fixed Bed Reactor at 700°C, by placing a catalyst bed of same porosity $\mu=0.2$ at 25%, 50%, 75% column height, and at top of reactor. It is found that same catalyst has shown different results when placed at different heights in reactor column. Highest methane conversion of 85% is found when catalyst bed is placed at 25% column height from bottom. It is found that for endothermic reactions like methane decomposition catalyst bed position has its significance due to its effects on process thermal conditions and on bed expansion by carbon deposition.

Keywords: Hydrogen, Methane Decomposition, Fixed Bed Reactor, Catalyst Bed.

INTRODUCTION

Recent increasing demand of CO_x free hydrogen for fuel cell and other applications has motivated researchers to look for alternate resources of hydrogen production [1-5]. Lot of articles has been published recently on this topic [6-10]. Among various hydrogen production techniques direct thermo-catalytic decomposition of methane to produce pure hydrogen gas has shown most promising results [11-13]. In this process methane is decomposed directly to pure hydrogen and carbon, later being in the form of carbon nanofibers or nanotubes on the surface of catalyst [14]. As the process continues, amount of deposited carbon increases, filling the voids between catalyst particles to the point where it completely plugs the reactor [15]. Expansion of catalyst bed inside reactor is greatly affected by its position inside the reactor [16]. Catalyst bed position also has its effects on catalyst temperature, since temperature inside the reactor column is not consistent throughout the reactor length. Also reactant gases travels different distances before coming into contact with catalyst bed and are at different temperatures [17]. This ΔT between reactant gas and catalyst bed affects the overall performance. In this aspect position of catalyst bed in fixed bed reactor greatly matters [18, 19]. While discussing catalyst sintering in a fixed bed reactor Blasco et al. have observed a change in coke

deposition pattern at different positions of catalyst bed [20]. In another study, it is discussed in detail that thermal and kinetic behaviors are not consistent throughout the reactor length especially in the case of endothermic reactions [21]. Since, catalytic methane decomposition is an endothermic process [22], and all these factors are dependant over catalyst bed position, it is imperative to investigate the effects of catalyst bed position inside a reactor.

In this work conventional nickel supported over alumina catalyst is tested at different positions inside the reactor and its effects on % conversion of methane are discussed.

METHODS AND MATERIALS

Synthesis of catalyst

Ni supported over alumina catalyst was synthesized by simple wet impregnation method [23]. Nickel nitrate ($\text{NiNO}_3 \cdot 6\text{H}_2\text{O}$) salt was impregnated over high surface area alumina (SA-6175), and was then dried for 14h at 110°C . The material was then calcined at 800°C for 3h.

Methane decomposition tests

Experiments of hydrogen production by methane decomposition were carried out in a stainless steel reactor. Total height of column reactor is 2 ft 6 in (0.76 m). Reactor column was enveloped in a high temperature furnace. K-type thermocouple is attached at the outer periphery of reactor column. Another movable K-type column is inserted inside the reactor in a thimble. Height of this thermocouple can be adjusted to measure inside reactor temperature at different positions. During each experiment 5g of catalyst is used and rest of column is filled with non-reactive silica clay for proper heating of reactant gases. An online HY-OPTIMA® 700B H_2 gas analyzer is attached at the end to analyze the H_2 % in effluent gases.

Each experiment is carried out at a fixed temperature of 700°C , and at weight hour space velocity of $8.5 \text{ l}_{\text{CH}_4} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$. Before introducing methane, catalyst was in-situ activated by 99.999% pure hydrogen at 700°C for 3h. Column was then flushed with nitrogen gas. Methane decomposition reaction was carried out by passing 20% methane-balanced nitrogen ($20\% \text{CH}_4/80\% \text{N}_2$) gas through the column. Reactant gas is injected at room temperature and at atmospheric pressure. Hydrogen produced is analyzed by the online HY-OPTIMA® gas analyzer.

Experiments were carried out by placing catalyst of same porosity of $\mu=0.2$ (calculated on the basis of bed density and particle density), at five different positions, at top of column, at 75% column height- position A, at 50% column height- position B, at 25% column height-position C, and at bottom of column. Details and notations of these positions are shown in Figure 1. Each experiment was carried out with fresh catalyst sample and methane decomposition process was carried out continuously for 5h. In order to analyze significance of difference between methane % conversions at different bed positions a statistical ONE-WAY ANOVA analysis is carried out.

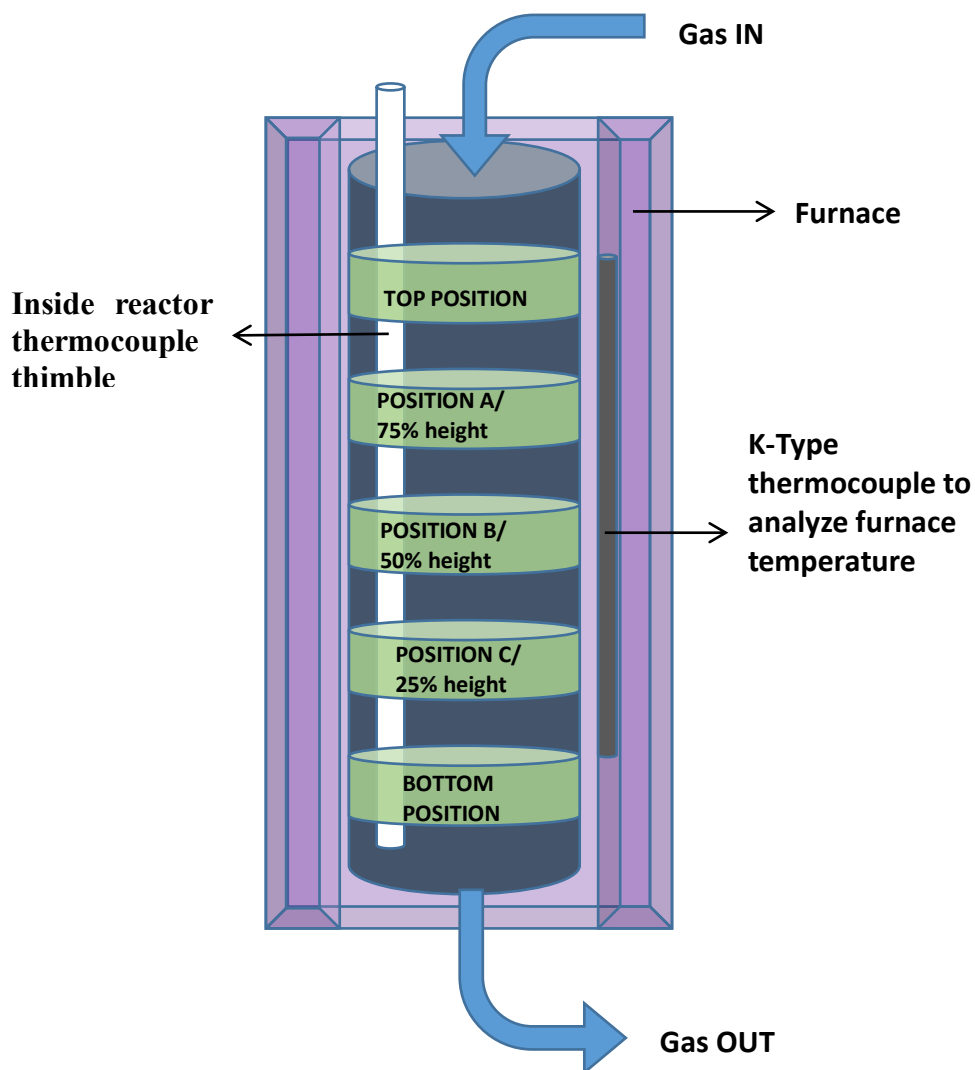


Figure 1: Schematic diagram of a fixed bed reactor

RESULTS AND DISCUSSION

Figure 2 shows the % conversion by volume of methane at 700°C over the same catalyst when placed at different positions. Different amount of conversion is observed at different positions of catalyst bed. Increasing amount of methane conversion is in following order, top < bottom < 75% height < 50% height < 25% height. Amount of heat transfer along the reactor length is non uniform due to the difference in reactant temperature and flow profiles, as explained by Nijemeisland et. al [24]. Catalyst bed is normally operating at a low temperature compared to initial temperature before gas is introduced [25, 26].

Comparison between catalyst bed temperature at different position prior to reactant gas flow and during gas flow is shown in Figure 3.

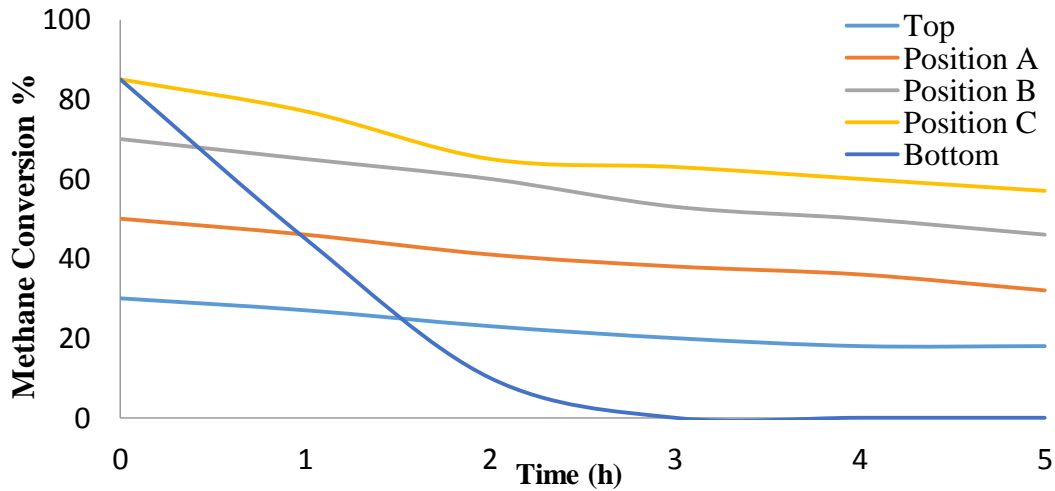


Fig 2: Methane conversion % at different positions for 5h

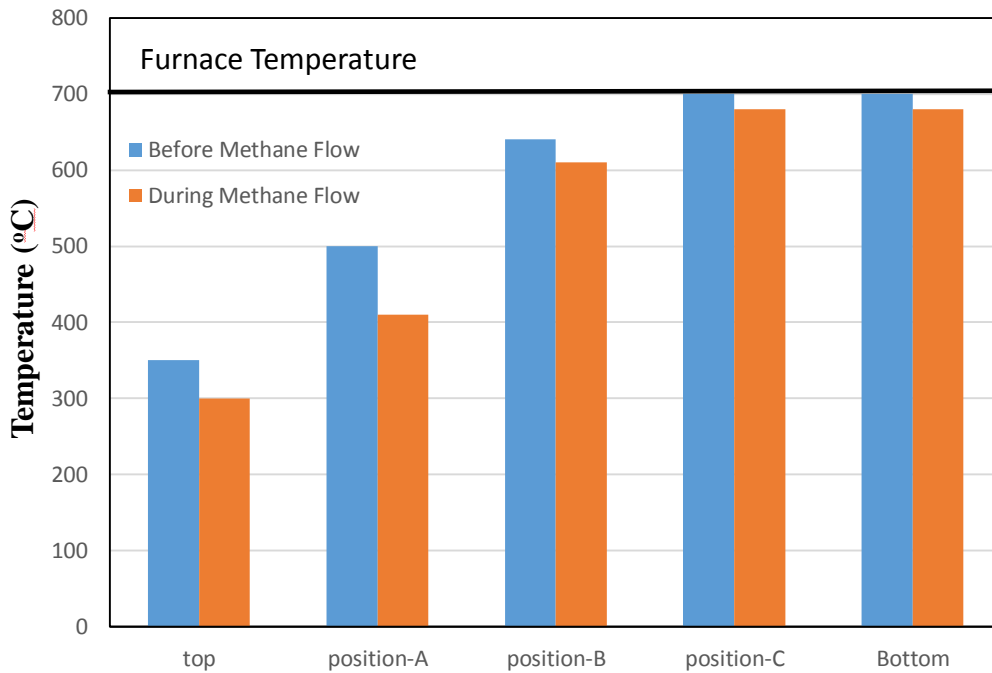


Figure 3. Catalyst bed temperature before and during flow of methane.

Since reactant gases are fed to the reactor at room temperature, they are at a relatively low temperature at the top of column height and its temperature increases as they pass through the column packing [27]. Very low conversion is observed when catalyst bed

is placed at top of the reactor due to insufficient thermal energy. However, case is entirely different when catalyst bed is placed at bottom. Temperature observed at bottom of reactor is maximum when in operation (i.e. reactant gas is flowing through the column). Initially conversion for bottom and position-C is same as they are at same temperature but as the time passes % conversion at bottom decreases rapidly to a full halt after two hours operation. This phenomenon is due to the unavailability of empty voids between catalyst particles at the bottom [28]. As the process continues the amount of deposited carbon on catalyst surface increase and fill the voids between catalyst particles, to the point where no voids for gas passage is available and catalyst bed is completely choked or clogged. Due to the catalyst bed position at bottom of reactor, expansion of bed is not possible, which is essential for the continuity of heterogeneous catalytic reaction in a fixed bed reactor [29]. As the process continues bulk density of bed increases and porosity decreases to zero, where no gas passage is available for methane [30].

At positions A, B, and C, catalyst bed has shown good results with little variations in the overall conversion of methane. Among three positions, least amount of methane conversion is observed at position A. Again this phenomenon can be attributed to the high temperature difference between furnace temperature and bed temperature. Also it implies that sufficient amount of free space must be provided to reactant gases to approach a required temperature when come in contact with catalyst bed [31, 32]. This also emphasize on the need of pre-heating treatment of reactant gases [33-35]. When a highly endothermic methane decomposition reaction occurs at position A there is a sudden decrease in bed temperature. There is no exothermic reaction to compensate as in the case of Fischer-Tropch reactions [36]. Position-B is in the center of reactor and has shown relatively high and constant conversion of methane throughout the five hours operation. At this point catalyst bed temperature is in concurrence with furnace temperature when not under a reaction. However during reaction, catalyst bed temperature slightly decreases due to the endothermic nature of methane decomposition reaction. Statistical ONE-WAY ANOVA ($F(2, 15) = 14.14, p = 0.0003$) analysis is results are, $F(2, 15) = 14.14, p = 0.0003$. Since p-value is less than 0.05, it is concluded that there is a statistically significant difference in % conversion at different bed positions. Best results are obtained when catalyst bed is placed at 25% column height. At position C which is the 25% height of column has shown the highest methane conversion to hydrogen. Temperature at this point is approximately same as of furnace temperature and a slight decrease is noted during the methane gas flow.

CONCLUSIONS

Hydrogen gas is successfully produced by catalytic decomposition of methane. It is found that appropriate catalyst bed position plays a vital role in catalyst bed expansion and effective heat transfer to the reactant gases. Catalyst bed when placed at different positions inside the reactor has shown statistically significant difference in results. Least amount of hydrogen is produced when catalyst bed is placed at the top of reactor. When placed at the bottom reactor is plugged after 2 h. No plugging is found at Position-A, B and C. Highest methane conversion is recorded when catalyst bed is placed at position C (25% column height).

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