

**Research Article****Effect of Space Velocity and Temperature of Gas in the Oxidative  
Coupling of Methane, OCM Reactor****Mahmoud bayanak<sup>1\*</sup>, Alireza Azimi<sup>1</sup>  
and Soroush Zarinabadi<sup>1</sup>**<sup>1</sup>Department of Chemical Engineering,  
Mahshahr Branch, Islamic Azad University, Mahshahr, Iran

\*Corresponding author: Email:m\_bayanak2003@yahoo.com, Tel: +98-9166138439

**ABSTRACT:**

The aim of this study was to investigate the effect of space velocity, and temperature of the gas flow, in coupling oxidation of methane in the OCM reactor, in this study it is shown that GHSV, and the ratio of methane to oxygen, effects on methane conversion and selectivity to ethane. In this regard, a new idea for OCM process is proposed, in which the flow became (split flow mode), and feed of the OCM-reaction including methane and air, heated to reaction temperature before entering the reactor, and in this plan the reactor should have a heat exchange with the environment by convection and radiation. OCM reactor is designed to have a good potential for heat transfer, and isothermally remain in the service. In the semi-industrial units' reactor, natural gas is converted to ethane and ethylene is in contact with air. The results showed that under certain conditions of GHSV and a certain proportion of methane to oxygen, increasing the methane conversion and reduced selectivity of C<sub>2</sub> coupled together are, therefore, condition assessment, should consider the conversion and selectivity, which have opposite effects on optimal efficiency. The results show that in a constant GHSV, there is optimal ratio of methane to oxygen ( $CH_4 / O_2 = 2$ ), which the highest yields of C<sub>2</sub> creates. It has been observed, that when the higher oxygen content (ratio of  $CH_4 / O_2$  lower) at the entrance of the reactor is used, the highest percentage will be converted to methane, which leads to increased production of oxidized carbon.

**Keywords:** catalytic reaction, a fixed bed reactor, the oxidative coupling of methane, GHSV**[I] NTRODUCTION**

Several different methods have been used to convert natural gas (methane) to the fuel or chemical compounds. The process of catalytic conversion of methane to chemicals, can be divided into direct and indirect methods (1). Direct catalytic conversion to hydrocarbons higher, which is followed by oxidative coupling of methane (OCM), is a reaction that attentioned by researchers (2). During the process of coupling oxidative catalytic of methane, in addition to the

products of hydrocarbon is desirable, such as ethylene and ethane (as products of C<sub>2</sub> also called), undesirable products and non-selective, such as CO and CO<sub>2</sub> (as products of CO<sub>x</sub> also called) also generally be achieved. Conversion of methane to CO<sub>x</sub> is an undesirable process that reduces the efficiency of the reaction (3). In the last ten years, much work has been done, for developing a process to maximize production of C<sub>2</sub> and minimize the production of CO<sub>x</sub> in system

(7-4). For the development of selective catalysts for OCM, and various factors such as the structure of the new catalyst, and calcination temperature, the activity and stability of catalysts, a survey was conducted (8 and 9). Some researchers have reported that these parameters have a great effect on the catalytic performance and the performance of different reactors, in OCM (10 and 11). They also lead to parametric studies, the effect of GHSV, and a combination of methane and oxygen in the feed examined (12). Another parametric studies on the effects of temperature, contact time and the inert gas in the feed were predictions based on models (13 and 14).

Oxidative coupling methane, OCM was first raised by chlorine and Bhasyn in 1982 [1]. They used a bunch of metal oxides as a catalyst in a process cycle, so that the methane and air separately is injected into the catalyst bed and then the flow is interrupted, and the nitrogen gas removed extra oxygen in the catalyst bed. In this method, methane reacts with the catalyst, so that all of the catalyst surface oxygen consumed, and the reaction is stopped. Much research has been done, for the direct conversion of methane to ethylene, methanol and formaldehyde [2-4]. Convert methane to ethylene, is studied in both gas phase reactions (non-catalyst and often at high pressure) and catalytic reactions on solid surfaces. Most of the research on the direct conversion of methane by oxidative coupling reaction involving the catalytic conversion of methane and oxygen to ethane and water, have been done that at a later stage should be converted to ethylene. In these reactions amounts of unwanted products such as CO and 2 CO are formed. OCM is a catalytic process and is carried out in the presence of various catalysts such as oxides, chlorides and oxychloride [5-9]. High stability of methane, and unfavorable thermodynamic conditions, methane creates problems in the pathway activation. Since the direct dehydrogenation methane to ethylene or ethane, thermodynamically is very difficult ( $\Delta G > 0$ ), the use of amplifier hydrogen, such as N<sub>2</sub>O and O<sub>2</sub>, thermodynamically can make these

transition more easily [2]. In fact, the presence of an oxidizer is required for the reaction [3]. In general, the direct conversion of methane to heavier hydrocarbons can be done in two ways: pyrolysis of methane into methane oxidation by using the catalyst [1]. Oxidative coupling of methane, the main component of natural gas, as a possible way to produce ethylene, has attracted the world's attention, and demonstrates the high potential for ethylene production in comparison with existing technologies. The reaction is necessarily carried out at atmospheric pressure, and temperature of 973-1373K, and feed ratio of methane to oxygen 10-2. Industrial operations, methane conversion per pass 30-20% in the selectivity of products C<sub>2</sub>, converted fraction of methane to ethane and ethylene 80-70% is considered acceptable. For OCM process different types of reactors have been proposed [10]. For highly exothermic reaction, often fluidized bed reactors are intended for industrial use. But the increasing scale of such reactors is not an easy task, especially if a new process has been designed such as OCM. therefore, for such processes fixed bed reactor design is more developed [11].

Previous research results OCM [15-12] have shown that the scaling process is one of the critical parameters of the temperature control. OCM reaction at high temperatures is done, and also is an exothermic reaction, and in this situation there is the possibility of adverse reactions, which reduce yields desirable; Therefore, by temperature control, and reduce the residence time of in the reactor feed, can reduce the risk of adverse reactions, including the formation of soot. The results of performed tests in previous studies, about increasing scale to Bench Scale, showed that at temperatures higher than 800 ° c, the decomposition reaction and pyrolysis is done. Also in reactor Bench Scale, the heating and heat transfer from the reactor, both done in one system, accurate temperature control possibility in quantities of 30 grams and higher catalyst was very difficult [17-16].

Allocated intense effort to study the coupling oxidation of methane in a wide range of catalysts and in recent years has shown that accurate path of reaction and its kinetic depends on the type of catalyst used and its composition (16). Therefore, in this study, because of the importance of the type of catalyst, Perovskite- titanate, was chosen for parametric studies of OCM reactions. However, a small number of researchers have catalytic performance Sn / BaTiO<sub>3</sub> and studies have shown improvement in OCM process. In contrast, the previous empirical studies in a fixed bed reactor differential, are carried out with Perovskite-titanate catalysts. In this study, optimal GHSV and optimal ratio of methane to oxygen is investigated to maximize the production of the catalyst C<sub>2</sub>. In addition, a significant effect of GHSV in a wide range (1 to 5.7) is investigated. Main messages of this study are as follows:

- \* Evaluation gas hourly space velocity (GHSV) and the effects on the catalytic performance
- \* Introduction of optimum operating conditions to achieve the highest efficiency of C<sub>2</sub> in performance isotherm reactor

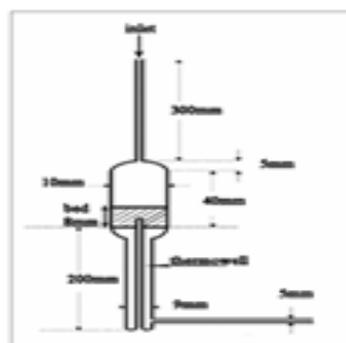
### Catalyst

The studies are carried out with the catalyst Sn / BaTiO<sub>3</sub>. The fact that it has been determined that this catalyst in the studies, in differential fixed bed reactor, is a selective catalyst (17). Catalyst used in this study were prepared in our laboratory, by Sol-gel method. Perovskite- catalyst has a chemical formula ABO<sub>3</sub>. Cations manufacturer's capacity are as A<sub>n</sub> + and + B<sub>m</sub> (m = 4, 5 and n = 1, 2, 3). Production method is as follows: (1) Production of a liquid slurry comprising an alkaline earth metal salt, a metal salt powder and a transition metal oxide powder. This slurry was produced by spreading powdered alkaline earth metal salt in the water. Alkaline earth metal salt from the group consisting of barium salt and Asneronsium with 0.67 molar ratio was selected. (2) Addition of transition metal oxide powder to water, metal oxide is titanium oxide. (3) adding an adhesive polymer to slurry to form a dough (4)

drying the dough to produce powder (5) heating the powder with the increase of temperature as predetermined cutting, proportionate to the adhesive polymer and (6) calcination the heated powder at 973-1073 K for 8 to 10 hours to produce a Perovskite- catalyst. Then the catalyst powder is pressed to becomes cylindrical tablets. mesh size 30-35 of the powder was used in laboratory experiments.

### Reactor

To better control the temperature, and therefore a higher reaction efficiency, the use of differential fixed bed reactor is recommended. In the integral reactors, temperature controlling is more difficult, and long contact time under high temperature of reaction, can considerably reduce the efficiency of the reaction (18). Differential tube fixed bed catalyst reactor, is designed for oxidative coupling of methane (OCM). As a result, the differential fixed bed reactor, with a diameter of 10 mm and a length of the catalyst bed 8 mm, are used in all experiments. The small particle size, the catalyst bed was diluted with quartz with the same diameter. Figure 1 shows the schematic details of the reactor and set of thermocouple used in the study. Temperature is measured by a thermocouple type K, located at a suitable Thermowell. Internal thermowell quartz, is concentrated along the length of the catalyst bed. Catalytic reactor is placed in an electric oven, equipped with a programmable temperature controller, to track reaction temperature, in the hottest area.



**Figure 1.** Schematic of differential fixed bed reactor, a thermocouple and furnace that used in this study

### Pre-heating method

Delivering reactant gas temperature, to reaction temperature is not easy, because the reaction temperature is high. In industry, virtually burner is used to heat the gas stream that passes through pipes, or the exhaust gases of incinerators (for more energy efficiency over) is used; Such as that used in the production of synthesis gas takes place. In smaller scale, there is no possibility of using the burner, and laboratory electric furnaces, is the most appropriate way to create high heat. In cases where there is heat transfer in gases, compact exchangers are considered. Limits of pressure drop, and low conductivity of gases (rather than water), reduces the heat transfer rate, per unit area, and therefore large surface area, is characteristics of gas heat exchangers sample. Required area of gas exchangers, might be ten times the evaporator condenser surface or liquid-to-liquid exchangers. Heat transfer surfaces for gas applications, where have high surface density, are called compact surfaces heat transfer, the main characteristic of the heat flux surface compared to high pressure drop, called high surface performance. It should be noted, that the compression surface leads to high efficiency, because compact surfaces have small channels, and heat transfer coefficient  $h$ , always changed as negative exponent of hydraulic diameter of the channel, so surface compact due to their nature have high heat transfer coefficient. In addition to the impact of hydraulic diameter, modified surface geometry problem, thereby increasing the heat transfer coefficient can also be effective in increasing heat transfer [20-18].

Use surfaces the matrix surfaces, are among the most common ways to increase the heat transfer area, the flow of gas heat transfer by passing through such surfaces. The most common matrix surfaces, it can be pointed to the matrix bullet, or other geometric shapes, that used as packed-bed.

### Packed-bed

In such models, the gas stream passed through the bed of solid particles, and by creating chaos and

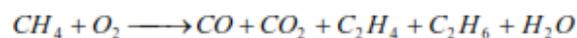
increase the surface of heat transfer is done well. In a packed-bed, a large heat transfer area is gathered in a small volume, and erratic flow that passes among empty space between the particles, increases the heat transfer due to turbulence in the mix. Study of heat transfer in such beds, because of the wide use of packed bed reactors, especially catalytic beds, is very important, because large amounts of heat in these reactors, absorbed or excreted. In general, heat transfer in exchangers that heat transferred with flow of gas inside the solid substrate, can be divided into five different methods [18].

- 1- Conduction in flow of gas, because of the temperature gradient
- 2- Conduction within solid particles, and from particle to another particle, by film separator
- 3- heat transfer between solids and main fluids
- 4- enthalpy change, due to flow of fluid
- 5- In the case of the reaction heat generated by the reaction

Our proposed method in this study is the use of compressed or packed bed to preheat the feed to the reactor OCM, which is shown schematically in Figure 2.

### Thermodynamic Study of OCM reactions

Basically, the thermodynamic reviews, offers two types of information on the design, the heat released in the reaction, and a maximum of advancement in reaction. In general, in the process of OCM, the following reactions takes place [21].



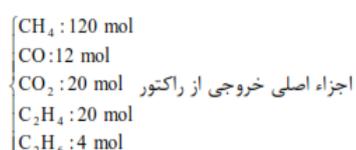
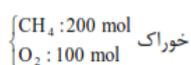
These components have been fully identified in previous studies [23, 22] by GC. Reaction (1) consists of several reactions. The most important of these reactions and enthalpy change is provided below:

As can be seen in reactions (2) and (3) oxidation of methane occurs and these reactions are typically exothermic. Reactions (4) and (5) are type of hydrogen-making reaction, which these reactions are generally endothermic. So the four minor reaction occurs, that two reactions are

exothermic and other two reactions are endothermic. With regard to the change in enthalpy of the reaction, it is observed that the amount of heat released in the exothermic reaction is far more than the amount of heat absorbed by the endothermic reactions. Now, by using the change in enthalpy of reaction (2) to (5) should specify the enthalpy of final interaction, the reaction (1), and according to the reactor test [16, 24, 25] and the balance of components of the input-output coefficients of the stoichiometry is determined. Mass the balance of is dependent on the amount of methane conversion, therefore, to create a more comprehensive, in three conversions 40, 45 and 50 percent, the balance of reaction (1) is done. Practically in most tests, the conversion was in the range of 40-50% [16, 17, 22 and 23]. For the full balance of the reaction (1), in addition to amount of methane conversion, the need for selectivity of the product components CO, CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>, respectively, 15, 50, 25 and 10 percent are considered.

For three different methane conversion rate, the balance of the reaction (1) is done as follows. In the calculations, 200 moles methane, as available basis, and accordingly, the moles of other components is calculated and determined.

First case: the conversion of methane is equivalent to 40 percent:

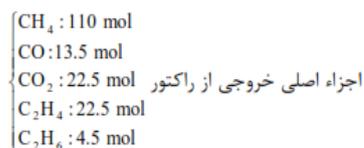


Mass balance of the reaction (1) by assuming 40% conversion of methane is as follows:

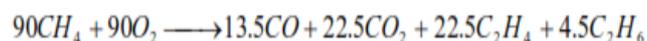


So per mole of methane entering the reactor, the reactor produces heat equivalent to 34.2 Kcal.

Second case: the conversion of methane is equivalent to 45 percent:

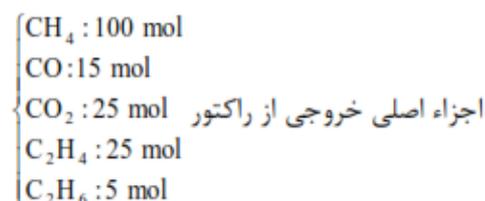
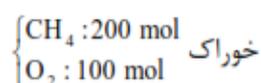


Mass balance of the reaction (1) by assuming 45% conversion of methane is as follows:



So when the methane conversion rate is 45%, per mol of methane entering the reactor, the equivalent of 38/5 kcal thermal energy is produced.

The third case: the conversion of methane is equivalent to 50 percent:



In the case of methane conversion rate is 50%, per mole of methane entering the reactor, the equivalent of 42/8 kcal thermal energy is produced.

Methane Conversion Rate			
50%	45%	40%	Released heat
-42/8	-38/5	-34/2	Released heat per mole of methane input (Kcal / mole)
-2000	-1800	-1600	Released heat in the reactor (J / s)
-17330	-15600	-13865	Heat flux from the reactor (J / m <sup>2</sup> .s)

### Select the type of catalytic reactor

According to Table 1 see that when the conversion rate will increase 5 percent from 40 percent, the heat of reaction increased about 13 percent. When the conversion rate increased from 40 percent to 50 percent, the amount of increases heat about 25 percent. So in OCM reactor design, should be anticipated released heat, in the range of 34-43 kcal, per mole of methane in the feed. This heating rate is calculated by assuming constant

temperature during the reaction. OCM catalytic reactor design is based on a constant temperature. With respect to process optimization [22, 23, 12 and 13] The optimum temperature for OCM process with perovskite catalysts, is temperatures of 775 ° C. So in OCM reactor design, constant is temperature and in all parts of beds should be 775 ° C. Therefore, heat of reaction must somehow be separated from the catalyst bed, to substrate temperature not increased. With this issue, it is necessary that the reactor is in service as Isothermal, so amount of heat is calculated based on the feed methane. Naturally, however molar ratio be more in food, the amount of heat generated will also increase in the same proportion. But now needs to be investigated, that catalytic reactor design isotherm, with a temperature of 775 ° C is. In the chemical industry, various and different designs for catalytic reactors. Depending on the nature of the reactions and the amount of heat transfer, design requirements, became compulsory and more limited, but always in the selection and design of catalytic reactors, a fixed-bed catalytic reactor is selected. Because the simplest catalytic reactors in terms of design and operation are fixed-bed catalytic reactors. This type of reactors, especially when the catalyst has little mechanical resistance, are more important. Other designs such as fluidized bed catalyst in the absence of the use of fixed bed reactors faced with restrictions on heat and mass transfer, are selected.

In all scale up tests, fixed-bed catalytic model was considered for reactor [17-12]. Therefore, due to the simplicity of these reactors, and are usually fixed-bed catalytic reactors have also been the basis of much of the OCM research, at this stage, fixed-bed catalytic reactor for pilot plant is proposed. Note that, for the use of the fluidized bed reactor catalyst model, the mechanical strength of OCM catalyst, is a necessary condition that usually some catalysts, such as perovskite have no mechanical resistance against abrasion. In the chemical industry, when it is scheduled to use isotherm catalytic reactors with fixed bed,

usually design the reactor as shell and tube exchanger, so that the catalyst is distributed in the tubes, and a fluid like water without minerals enters in the shell. Because of exothermic reaction, the heat transferred to the tubes filled with catalyst, to the fluid inside the shell (water), and because of this heat transfer water evaporated, and steam is produced. Because the vapor and liquid water in equilibrium with each other in the shell, then shell and tube of catalyst temperature, is always constant, and equal to boiling point of water in the shell. It is clear that whatever increases the vapor-liquid equilibrium pressure, water boils at a higher temperature, and the reactor can be kept in service at higher temperatures, as Isothermal.

Maximum temperature that water and steam can be in equilibrium with each other, and the liquid phase and vapor exist separately, is the temperature 374 ° C and 218 bar pressure. At temperatures higher than 374 ° C, essentially there is no phase equilibrium, and water and steam are as supercritical fluid, it is natural that in these circumstances possibility of using latent heat of vaporization to absorb the heat of the exothermic reaction is not possible. So in the process of OCM at isotherm temperature 775 ° C, to control the temperature of the reactor, basically cannot use the shell and tube reactors which are very common in the chemical industry. These reactors are applicable in isotherm processes that temperature is 300 ° C and less than it. For example, Fischer-Tropsch process, and sell company's technology, and in the process of preparing ethylene oxide catalysts with silver, because the process temperature is less than 300 ° C, the reactor shell and tube are used. With the above explanation, it was found that there aren't possible to use of shell and tube reactors and use of water in the shell. The use of other fluid that due to their latent heat of vaporization, provided isotherm conditions in the reactor, is rejected. In a fixed-bed catalytic reactor, how much the bed diameter is greater it's harder to heat transfer from inside of the bed to the reactor and subsequently its absorption by a

cooling material in around of the reactor body is more difficult.

So what is important in terms of design, is the diameter of the catalyst bed. Practically when reactions are highly exothermic, should be used catalytic beds with a small diameter, to minimize the temperature gradient in the radial direction in the bed.

### Reactor design and determination of the catalyst bed

Catalytic reactor in pilot plant, is proposed as a catalyst tube. Catalyst tube diameter selected 1-1.5 inches, this diameter should not be too high, to be created temperature gradient in the radial direction on the bed. Considering the conditions of integral reactors, length of catalyst bed is also considered to be about one meter. Of course, how much tube length is longer, proportionally volume rate (GHSV) of feed increased? As a result, the catalytic reactor OCM, will be formed of a tube with a nominal diameter of 1 inch and a length of 120 cm. Of course from 120 cm length of the reactor, about 110 cm length of it will be filled by catalyst. In this reactor about one kilogram of catalyst can be tested. Calculating the volume of catalyst bed by assuming the use of titanium perovskite catalyst is done [16]. According to calculations related to determine the volume of the catalyst bed and with regard to the issue of space velocity appropriate, in scale up experiments [16 and 17] GHSV = 5000(h-1) were obtained approximately. Heat generated calculations is done on the basis of Table 1 assumptions, and are presented in Table 2. To remain reactor temperature stable must be absorbed thermal energy described in Table 1 from the reactor. Heat transfer surface is also a very important factor in estimating the rate of heat transfer. If the reactor with a nominal diameter of 1 inch is used, calculations of reactor's surface heat transfer performed in three different modes, and heat flux is obtained from the body of the reactor. In reactor output current must be placed a temperature controller, as soon as the temperature increases in output current, send blocking command to the

control valve located on the flow of natural gas, and thus stop the flow of natural gas into the reactor. In this case, with the airflow through the reactor and the absence of combustion reactions, the reactor temperature gradually decreases.

Pressure	1 atm
Temperature	750 K
Catalyst density	1/65 g mol <sup>-1</sup>
GHSV	5000 h <sup>-1</sup>
CH <sub>4</sub> / O <sub>2</sub>	2
ID	1 in
Bed height	110cm
Total input gas flow	50/8 lit min <sup>-1</sup>
The total external surface of reactor	1154 cm <sup>2</sup>

Because the reactions are exothermic OCM as fast as heat is generated in the bed with the same speed, the heat must be transferred out of bed (reactor). However, to prevent an increase in temperature in the reactor outlet stream from the reactor, the reactor and catalyst protection system should be implemented, so that if the outlet temperature is increased to 790 ° C, an electrical signal send close command to the outlet valve in the flow of natural gas, and this valve is completely cut off the flow of natural gas, so reaction is stopped, and the reactor temperature quickly decrease. In brief two following cases summarized and recommended:

- (1) to absorb thermal flux is calculated, should reactor heat transfer with the environment, by convection and radiation, and the heat generated by the reaction removed from the reactor, so reactor body without insulation is predicted.
- (2) seems to be the best option for pre-heating the feed gases, is the use of filled beds, because simply increase the heat transfer significantly.

### Reaction conditions

All tests are in a constant temperature (T = 1048 K). Contact time in terms of GHSV is set, and between (8000-12000-17000 h<sup>-1</sup>) is changed, and the mass of catalyst 0.7-1.5 g is used, and also feed gas will be considered as (1, 2, 3, 4, 7.5). All laboratory tests are done at a pressure of 0.98 atm

for different GHSV and different ratio of methane to oxygen.

## RESULTS AND DISCUSSION

Operating conditions in the range of conditions, will change with empirical limitations, to study these effects on C2 production efficiency. Under a given set of flow conditions, also Perovskite-titanate catalyst performance after reaching steady state at a given temperature, is analyzed.

**Table 1.** The physical properties of the catalyst

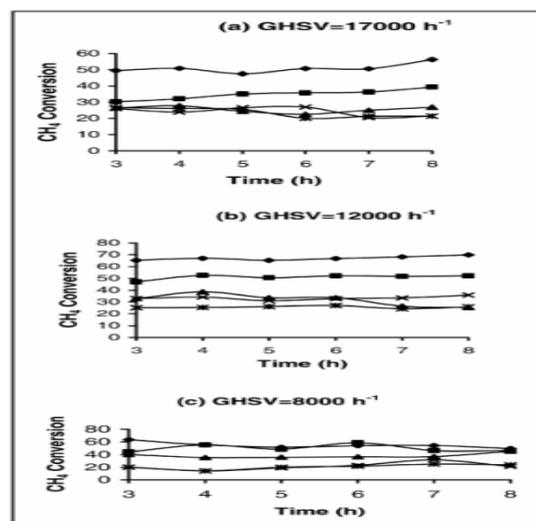
Density [kg m <sup>-3</sup> ]
Heat capacity [J kg <sup>-1</sup> K <sup>-1</sup> ]
Specific surface area [m <sup>2</sup> kg <sup>-1</sup> ]*
*measured by BET

### Effect of GHSV

It has been reported that contact time is important in catalytic oxidative coupling of methane, for secondary oxidation products of hydrocarbons. In this study, the effect of residence time investigated by changing the flow rate of feed in terms of GHSV. By comparing the curves of each section a, b, c, d and e in Figures 3 to 5 can be observed that high levels of GHSV, optimized the speed of formation of C2 (selectivity), which is similar to values reported previously, (19).

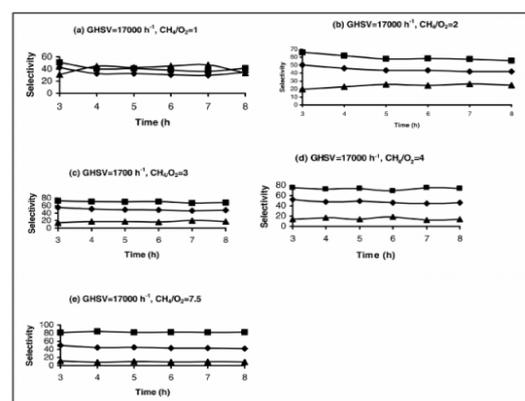
For this reason, despite the reduced residence time, increase in production rate C2 (selectivity C2) can be seen. In all curves in Figure 2, with GHSV decreased (increased residence time), methane consumption rate (conversion) increased. Reduced consumption of methane (methane conversion) is because of reduce of contact time, which in turn hydrocarbon production became desirable (14).

There is a contradiction between the increase of selectivity and decrease of conversion, because efficiency is obtained from multiplying of selectivity and conversion, therefore, efficiency must be considered as a controller parameter.

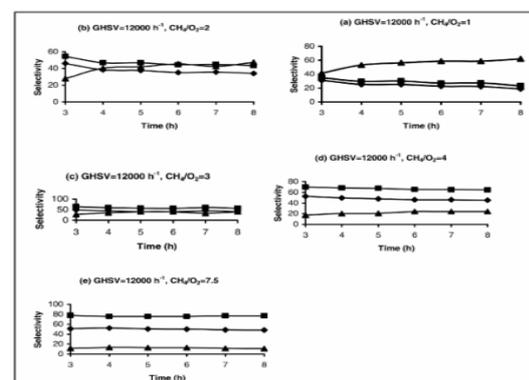


**Figure 2.** The methane conversion against time on different GHSV and different ratio of methane to oxygen

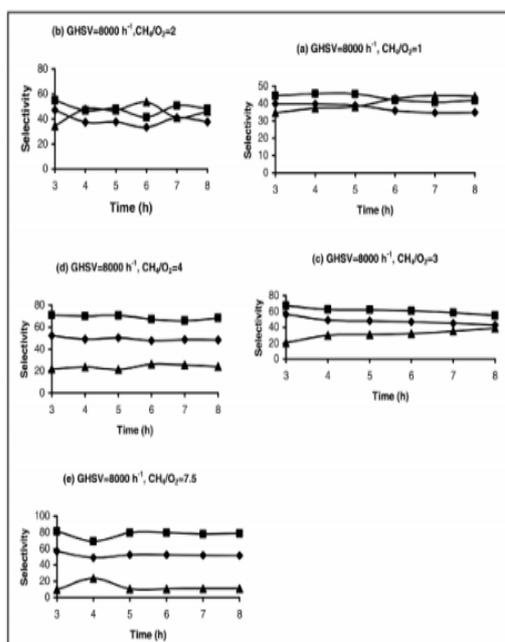
(♦, CH<sub>4</sub>/O<sub>2</sub>=1; ■, CH<sub>4</sub>/O<sub>2</sub>=2; ▲, CH<sub>4</sub>/O<sub>2</sub>=3; ×, CH<sub>4</sub>/O<sub>2</sub>=4; \*, CH<sub>4</sub>/O<sub>2</sub>=7.5)



**Figure 3** products selectivity against time on GHSV = 18000 h<sup>-1</sup> and different ratio of methane to oxygen



**Figure 4.** Product selectivity against time on GHSV = 12000 h<sup>-1</sup> and different ratio of methane to oxygen



**Figure 5.** Product selectivity against time on GHSV = 8000 h<sup>-1</sup> and different ratio of methane to oxygen

### The effect of feed gas composition

Initial concentration of methane is one of the most influential factors in the process of OCM. In overall stoichiometric oxidation, the  $\text{CH}_4 / \text{O}_2 = 1/2$  in all experiments, the concentration of oxygen in the feed is considered below this ratio. As indicated in the table for GHSV = 8000 h<sup>-1</sup>, the acceptable range for the ratio of methane to oxygen is 1 to 3 and for GHSV = 12000, 17000 h<sup>-1</sup> the best results to the efficiency of C<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> in the  $\text{CH}_4 / \text{O}_2 = 2$  is obtained. As a result, we maximize ethane production in the methane to oxygen ratio will be equal to 2. This phenomenon occurs because: when the amount of oxygen is reduced from the optimum amount oxygen, the production of methane through oxidative reaction increased. In a micro reactor with full amount of catalyst, 0.7 to 1.5 g and 30-35 mesh size, taking into account the optimization of methane to oxygen ratio, is recommended.

### Methane conversion

Methane conversion vs. reaction time is shown in Figure 2. Each section of this figure shows the

results in a constant GHSV, and different ratio of methane to oxygen. Figure 2 shows that the maximum methane conversion takes place in methane to oxygen ratio equal to 1. In other words, when the feed is rich of oxygen, methane conversion increases. Methane conversion curves a, b and c in Fig. 2 respectively 50%, 65-70% and 50-65%. That is why this phenomenon occurs: when the amount of oxygen in the feed increases, general oxidation reactions are more unfavorable and therefore reduced production rate C<sub>2</sub>. As a result, methane to oxygen ratio equal to 1 is not recommended. Three curves mentioned above, show the lower oxygen concentration in the feed,  $\text{CH}_4 / \text{O}_2 = 4, 7.5$ , and at a minimum conversion of methane (about 30% -20) is obtained. On the other hand, the extra amount of feed that passes without changing throughout the bed, this situation is not desirable from the standpoint of processing. In the curves a, b and c in Figure 2. It can be seen that the best situation for methane conversion is 30%, and thus the efficiency of C<sub>2</sub>, with the use of methane to oxygen ratio of 2, was obtained.

### Selection of desirable and undesirable products

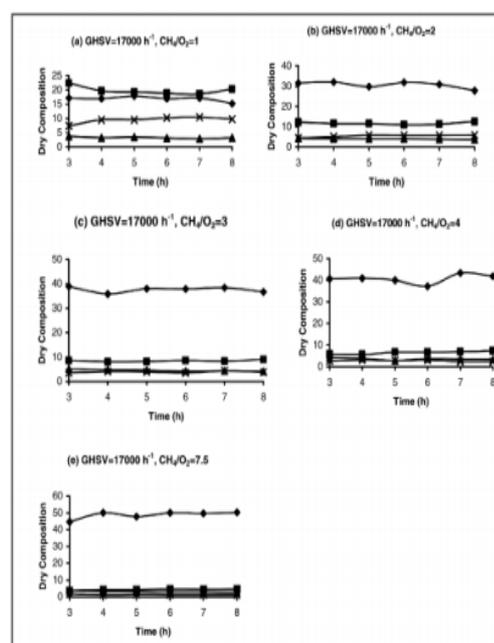
The oxygen concentration is one of the main variables that controls the speed of reaction. In this study, different ratios of methane to oxygen in the reactor performance is evaluated as shown in Figures 3 to 5. These figures show that the catalytic performance for various mole fraction of methane (methane to oxygen different ratios) in the feed. In these figures compare rate of formation of the products also between different levels of methane to oxygen ratios under different GHSV is shown. It can be found in Figure 3, that when  $\text{CH}_4 / \text{O}_2$  (methane partial pressure) increases, the production rate CO<sub>x</sub> (choice of CO<sub>x</sub>) decreases slightly. The highest (47%) and the lowest (10%) selectivity of CO<sub>2</sub>, can be respectively  $\text{CH}_4 / \text{O}_2 = 1, 7.5$  is achieved. As previously mentioned, when the balance of feed increases, general oxidation rates became more adverse. Methane to oxygen ratio has a significant effect on the rate of methane consumption. When

the concentration of oxygen in the feed stock and CO<sub>x</sub> production rate increase, methane is consumed more quickly. In all the curves a, b, c, d and e in Figures 3 to 5, because of reduce of the amount of oxygen in the feed gas, CO<sub>x</sub> production rate is always lower than the production rate C<sub>2</sub>. Increasing the ratio of methane to oxygen, leads to increasing C<sub>2</sub> and ethylene selectivity, and consequently, the highest selectivity of C<sub>2</sub> is obtained in CH<sub>4</sub> / O<sub>2</sub> = 7.5, 82%. As a result, it seems that the ratio of methane to oxygen, is appropriate to reduce CO<sub>2</sub> production, and the best results is obtained in CH<sub>4</sub> / O<sub>2</sub> = 7.5. On the other hand, methane conversion should also be considered. As previously mentioned, Figure 2 shows the conversion of methane in 5 different amount of compound feed, where the highest methane conversion occurs in CH<sub>4</sub> / O<sub>2</sub> = 1, and from this point of view, CH<sub>4</sub> / O<sub>2</sub> = 7.5 is undesirable. By considering the effects of conversion and selectivity, both at maximizing the efficiency of ethylene products, methane to oxygen ratio equal 2 is recommended. It is well known that oxygen as an initiator, to create the activation energy for methane decomposition reaction helps. Oxygen also helps to produce methyl radicals, and thus forming hydrocarbons C<sub>2</sub>. As a result, to increase the selectivity of C<sub>2</sub>, a higher ratio of CH<sub>4</sub> / O<sub>2</sub> must be considered in reaction OCM, but if we consider much higher ratio of CH<sub>4</sub> / O<sub>2</sub>, the activation energy for the decomposition of methane was not available and methane conversion decreases. Therefore, yield is reduced. Therefore, the optimum amount of CH<sub>4</sub> / O<sub>2</sub> = 2 is presented in all our experiments. If the concentration of methane in the inventory feed increased both efficiency and production rate of C<sub>2</sub> will decrease. Based on the next reaction by increasing the amount of oxygen in the feed gas, non-selective products, such as CO and CO<sub>2</sub> increased, and the desired product C<sub>2</sub> selectivity decreased. These results show that the maximum efficiency was obtained when the ratio of methane to oxygen in the feed gas is 1 to 3. Highest efficiency of C<sub>2</sub> is in methane to oxygen ratio

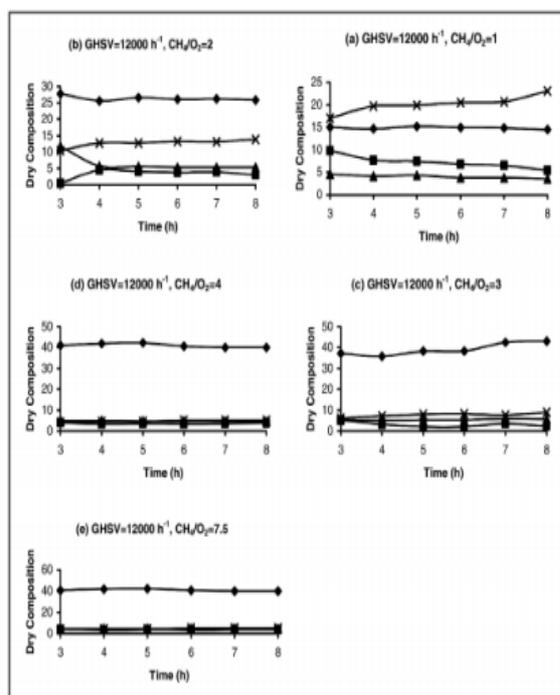
equal to 2, 17/28% (selectivity 55% and 50% methane conversion).

### Output component

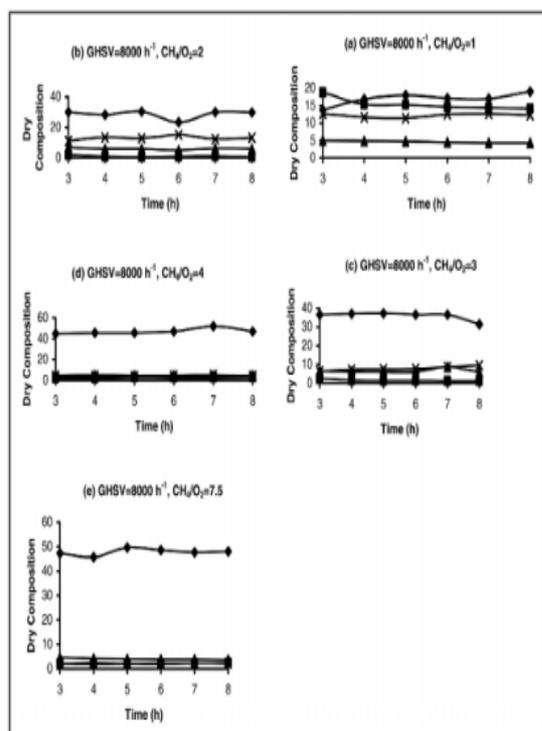
Figures 6 to 8 show output component of the micro reactor, in three GHSV with different ratios of methane to oxygen. Comparing the five curves, in any figures, it is observed that with Increasing the ratio of methane to oxygen, the oxygen concentration is reduced from 20% to 5%. In other words, reduce amount of oxygen in the feed gas, leading to its consumption through the reaction and reduce its concentration in the output. Also oxygen is the main factor and the initiator of oxidative reactions, therefore, its small amount reduced oxidation reaction, and the high amount of it increased the combustion reaction. On the other hand, when the ratio of methane to oxygen is increased, the concentration of methane in output will increase from 17% to 50%. This phenomenon that occurs due to increase in this ratio lead to reduce of methane conversion, and thus reduce the production of hydrocarbons is favorable. Therefore, output component evaluation has same results of selectivity and conversion.



**Figure 6.** dry composition of products, versus time, in GHSV = 17000 h<sup>-1</sup>, and with different ratios of methane to oxygen



**Figure 7.** dry composition of products, versus time, in GHSV = 12000 h<sup>-1</sup>, and with different ratios of methane to oxygen



**Figure 8.** dry composition of products, versus time, in GHSV = 8000 h<sup>-1</sup>, and with different ratios of methane to oxygen

## CONCLUSION

OCM method for industrialization suffered from low efficiency and selectivity of C<sub>2</sub>. However, except the catalyst type, the condition and the shape of reactor and mode of operation plays a fundamental role in the production of ethylene with high efficiency and high selectivity. Most studies have already been conducted to assess the activity of the catalyst in a fixed bed reactor, and less discussed about the effect of various process parameters on the system performance. Since the OCM reaction, in both homogeneous and heterogeneous considered in studies, therefore, process parameters and the type of reactor used in it, have a key role. Due to this, in the studies were evaluated reactors such as: fixed bed reactor, Membrane Reactor, the cooled plasma reactor (Corona Reactor), Reverse Flow Reactor, Counter Current Moving bed reactor and a fluidized bed reactor, to evaluate the overall performance of reactors for the OCM reaction. The present study describes experimental control improvement in OCM reactor in which the ratio of methane to oxygen as the control variable is intended to maximize the production of C<sub>2</sub>. In all experiments, the main products were hydrocarbons C<sub>2</sub> and CO<sub>x</sub> products.

The results showed that under certain conditions of GHSV and a certain ratio of methane to oxygen, increasing the methane conversion and reducing the selectivity C<sub>2</sub> coupled together, so the evaluation of optimum conditions should consider both the conversion and selectivity, which have opposite effects on optimal efficiency. The results show that in a constant GHSV, optimum ratio of oxygen to methane (CH<sub>4</sub> / O<sub>2</sub> = 2) that creates the highest efficiency of C<sub>2</sub>. It has been observed that when the higher oxygen content (ratio of CH<sub>4</sub> / O<sub>2</sub> lower) at the entrance of the reactor is used, the highest percentage of methane will be converted, which leads to increased production of oxidized carbon. One of the major problems for industrialization of OCM process, is that OCM reaction highly exothermic. Therefore, the reaction should be done in the

reactors, which allows you to harness the large amount of heat, to maintain process safety, and guarantee the selectivity of high hydrocarbon products. Among conventional reactors for reactions that have a significant thermic, fluidized bed reactors are a suitable option, which has been studied by researchers [33-31]. However, many active and selective OCM catalysts such as Li / MgO, NaOH / CaO, Na<sub>2</sub>SO<sub>4</sub> / CaO, cannot be fluid, or do not show sufficient mechanical strength such as Sm<sub>2</sub>O<sub>3</sub>. Moreover, since OCM, involves a network of mixed reactions, selectivity and efficiency of C<sub>2</sub> + does not depend only on the catalyst, but also depends on the type of reactor and the reaction operating conditions, and affected by hydrodynamics of fluidized bed reactor.

The optimal reaction conditions, is a specific desired intent, as C<sub>2</sub> + efficiency and selectivity, not only depends on the temperature and the partial pressure of reactants, but also is often influenced by the back mixing gas, porosity of the bed and mass transfer between bubbles and emulsion phase. To follow the above objectives After selecting a catalyst, usually a minimum flow rate of the catalyst with nitrogen at temperatures near OCM reaction temperature is measured. For example, for catalyst Zr / La / Sr minimum fluidity speed at temperature ° C600 equal to 0.018m/s. The short and shallow fluidized bed, is selected to achieve a stable fluidity, (1.3-4.2cm) [33]. After fluidity and mechanical stability experiments, and controversy surrounding the gas canalizing in fluidized bed, pay to study various factors affecting the performance of a fluidized bed reactor in the process of coupling oxidative conversion of methane. These factors include the temperature, gas feed composition (ratio of methane to oxygen or the presence of inert gas as diluent), the effects of gas velocity, bed height and size of catalyst particles. But another category of factors that in terms of priority are in next respectively, which include the presence of ethane gas in the feed, the presence of solid inert with the catalyst, the temperature of the top of the catalyst

bed, distribution of oxygen feed and secondary oxygen distributor design. The above parameters were studied practically or in the form simulation and modeling in the process of coupling oxidative conversion of methane in a fluidized bed reactor.

The effect of temperature and composition of the feed gas. Contrary to fixed bed reactor, in order to manage heat that released by the OCM reaction, feed diluting is not necessary. Improving C<sub>2</sub> + selectivity and its efficiency, by diluting feed in the fluidized bed, often for catalyst PbO /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> have been reported [33]. This effect can be explained by the selective and non-selective nonlinear dependence of early stages of the reaction, to the partial pressure of methane and oxygen. However, increasing the efficiency and selectivity of C<sub>2</sub> + when feed is diluted generally is not valid. For example, for La<sub>2</sub>O<sub>3</sub> / CaO was observed no effect the dilution feed on C<sub>2</sub> + selectivity of when the reaction was done in a fluidized bed, [34]. C<sub>2</sub> + selectivity increasing with temperature, can be explained by higher activation energy of the selective reaction stage, compared to non-selective stages. The maximum temperature depends on the selectivity of catalysts and reaction conditions. The temperature is generally changes between 740 to 840 ° C for PbO /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> [ 32 ] from 880°C to 840°C for La<sub>2</sub>O<sub>3</sub> / CaO [ 36 ] and 830°C to 850°C for catalyst CSRIO [ 33 ]. For various catalysts include Na as NaOH / CaO, C<sub>2</sub> + selectivity between 710° C and 820° C or over a wide temperature range, relatively is constant and does not change [32-31]. Depending on the path of reaction it is plausible that the catalyst for the series reaction (conversion reactions of ethane and ethylene to carbon oxides) is less active. This is an important quality of the catalyst, which when using distributed feed, oxygen for Improving C<sub>2</sub> + selectivity is considered [33]. The effect of temperature and composition of feed gas, similar to those on a fixed bed reactor has been determined, that for both types of reactor in the range of high temperature 880° C, increases methane conversion, selectivity of C<sub>2</sub> + and efficiency,

with temperature, and when the feed diluted (Figure 3-1 and 3-2). However, when applying the same partial pressure of reactant and compare the performance of both types of reactors at temperatures were determined similar, i.e. hot spots in a fixed bed reactor, and the temperature of the bed in a fluidized bed reactor, measured selectivity of C<sub>2</sub> + and less efficient in the reactor fluidized bed [33]. Loss of selectivity of C<sub>2</sub> + and efficiency, as compared to the fixed bed, is due to the limitations of mass transfer between dilute phase (bubbles) and the condensed phase (emulsion), which, even when using a higher bed, compared with the height of the bubble formation area, is not negligible (Figure 3-2).

In addition, the C<sub>2</sub> + selectivity and efficiency, is affected by the large quantities of gas back mixing. Both effects, and blend the mass transfer gas back mixing for high selectivity, for an intermediate product, are harmful.

This is confirmed by the high selectivity of hydrogen, and the ratio of carbon monoxide to carbon dioxide in the fluidized bed. However, strengthened gas phase reactions effect, which are non-selective, cannot be excluded by a higher porosity in comparison with fixed bed.

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