A Review of Methanol Production from Methane Oxidation via Non-Thermal Plasma Reactor

M. Khoshtinat, N. A. S. Amin, and I. Noshadi

Abstract—Direct conversion of methane to methanol by partial oxidation in a thermal reactor has a poor yield of about 2% which is less than the expected economical yield of about 10%. Conventional thermal catalytic reactors have been proposed to be superseded by plasma reactors as a promising approach, due to strength of the electrical energy which can break C-H bonds of methane. Among the plasma techniques, non-thermal dielectric barrier discharge (DBD) plasma chemical process is one of the most future promising technologies in synthesizing methanol. The purpose of this paper is presenting a brief review of CH_4 oxidation with O_2 in DBD plasma reactors based on the recent investigations. For this reason, the effect of various parameters of reactor configuration, feed ratio, applied voltage, residence time (gas flow rate), type of applied catalyst, pressure and reactor wall temperature on methane conversion and methanol selectivity are discussed.

Keywords—Dielectric barrier discharge, methane, methanol, partial oxidation, Plasma.

I. INTRODUCTION

METHANOL is a key and major raw material in production of various chemicals in the petrochemical industry such as MTBE, formaldehyde, acetic acid and Biodiesel via trans-esterification. It can be used as an extended potential fuel especially as a feedstock for supplying the electrical energy in a PEM fuel cell for on-board applications. Development of automobiles and power plants which consume pure methanol would be highly environmental-friendly. Releases to the water and ground are not significant since it can be degradable by photo-oxidation or bio-degradation processes.

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Methanol is presently produced mainly from natural gas by a costly two-step process including syngas conversion to methanol after production of syngas by steam reforming of methane. Steam reforming of methane is not only air-polluted as it emits a substantial amount of green-house gases, but is also considerably energy-intensive due to the stability of methane molecule so that needs a nickel base catalyst and a high temperature in the range of 800-1000°C to be converted to syngas [1-3]. Subsequently, the second process including methanol production from syngas needs high pressure of 50 bar and temperature of 250 °C. Utilizing a direct method such as using CH_4 along with CO_2 and/or O_2 as reactants in order to produce methanol can mitigate global warming issues and diminish both capital and operating cost. But the drawback of methane partial oxidation in a thermal reactor is that the conditions which will induce methane oxidation will certainly induce methanol oxidation leading to carbon oxides production and lowering methanol selectivity. The methanol yield in reported investigations is below 2%, which is less than the expected economical yield of about 10% in order to scale up for industrial production [2, 6]. This is the reason that highly selective single-step methanol production has not been possible so far. Conventional thermal catalytic reactor for methanol production have been proposed to be superseded by several new technologies consisting of catalyst and plasma reactors as a promising approach, due to strength of the electrical energy which can break C-H bonds of methane [4, 5]. Among other plasma techniques, non-thermal dielectric barrier discharge (DBD) plasma chemical process is one of the most future promising technologies in synthesizing methanol [6-8]. A DBD reactor consists of high voltage and grounded electrodes that are separated by a dielectric substance like quartz. Discharges are produced by inducing a high voltage to the electrodes. Excited, ionized, metastable compounds and radicals can be generated by collision of energetic electrons and reactant particles. These energetic electrons have higher temperature than the background gas result in non-equilibrium plasma which decreases the reaction temperature even up to room temperature, more promising than what a catalyst does in a thermal reactor.

A brief review based on the recent investigations of CH_4 oxidation with O_2 in DBD plasma reactors is presented and the effect of various parameters of reactor configuration, feed ratio, applied voltage, residence time (gas flow rate), type of

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applied catalyst, pressure and reactor wall temperature on methane conversion and methanol selectivity are discussed.

II. EFFECTIVE PARAMETERS ON METHANOL PRODUCTION

A. Reactor Configuration

Most of designed dielectric barrier discharge (DBD) plasma reactors consisted of a typical quartz tube that was partly covered by a metallic cylinder from outside which played the role of a grounded electrode [9-13]. A metal rod was located in the symmetric axis of the quartz tube which acted as a high voltage electrode. Decreasing the gap distance (D) between grounded and high voltage electrode enhances the electrical field in the plasma media. Since the electron energy is proportional to electrical field (E), higher electrical field means higher electron energy and more O_2 dissociation energy that is responsible for creating higher MeOH selectivity [9]. According to eq. 1 increasing the gap distance (D) lowers the reduced electrical field (E/P) and consequently a decrease in average electron energy for the plasma region occurs which influence on the energy deposition of different types of collision processes. P and V in (1) are pressure and voltage, respectively. Therefore, the product distribution and composition can be affected by the amount of energy deposition [8, 9]. It is apparent from previous investigation, that smaller gap distance is favourable for obtaining higher methanol selectivity especially at higher pressure (2 atm) [7, 8]. According to Larkin's et. al [8] work, organic oxygenates selectivity lowered from 46% to 24% when gap distance of the reactor was increased from 1.9 to 4 mm at pressure of 2 atm and ambient temperature[8].

$$\frac{E}{P} = \frac{V}{P.D} \qquad (1)$$

Chen et. al [8], showed that methanol yield decreases from 2.2 to 1.9 % ,while gap distance increases from 0.5 to 2.5 mm at atmospheric pressure and ambient temperature.

B. Gas Feed Ratio

According to some researches [3, 9], the feed ratio of CH_4/O_2 has a crucial role in MeOH selectivity and methane conversion. Generally, more O_2 concentration in the reactant feed produces higher CH_4 conversion [7, 9, 16]. It was reported that when changing from pure methane feed to a 3:1 methane to oxygen feed, with constant applied voltage of 16 kV and the same residence time, the methane reaction rate was increased by a factor of three[9]. It can be deduced that the active species produced from molecules of O_2 are able to activate methane molecules.

It was shown that for at CH_4/O_2 ratio lower than 3:1 produced methanol tends to convert to CO_x and thus, methanol selectivity is decreased due to this over-oxidation [9]. At very high CH_4/O_2 ratio the methanol production decreases as the sufficient atomic oxygen is not available to react with methane and formed species [7, 9]. Chen et. al [7], using a mixture of methane/air as a feed, flow rate of 300 cm^3/min and input power of 140 W reported nearly the same quantity (CH_4/O_2=3.3) in which methanol selectivity starts to decrease.
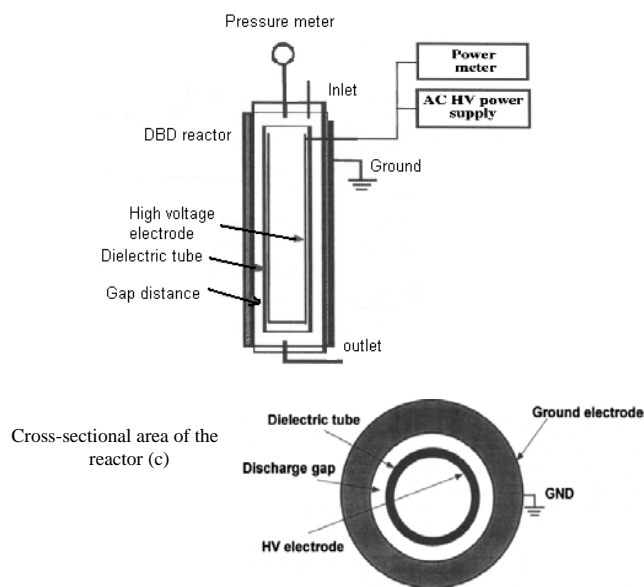
In the other research [16], when a voltage of 9 kV and flow rate of 500 cc/min applied, methanol selectivity began to decrease at CH_4/O_2 ratio less than 6.
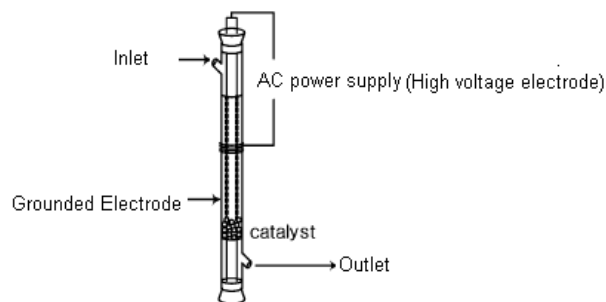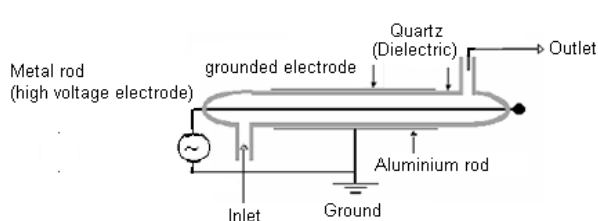

(a) DBD plasma reactor with 2 thin wire as HV electrode by Indarto et. al [12]
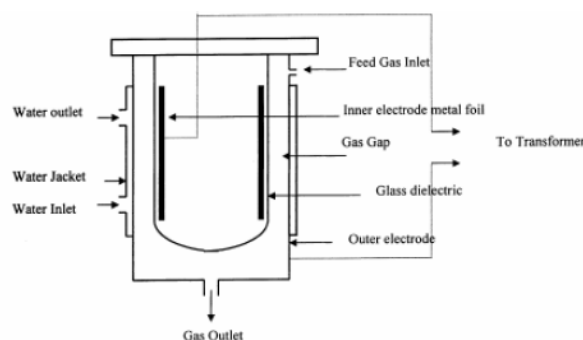
(b) Double cylindrical tube reactor with passing reactants between the outer grounded electrode and inner quartz tube by Larkin et. al [8]

(c) Dielectric barrier discharge configuration with passing reactants between the outer grounded electrode and inner quartz tube by Zhou et. al [6]

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(d) DBD plasma reactor with passing the gas feed between HV electrode and quartz tube by Aghamir et.al [1]

Fig. 1 Different schematic diagram of some types of reactor used for methanol production [13]

As a result, the CH_4/O_2 ratio in which the methanol selectivity starts to go down in various investigations is different which approves the synergistic effect of different parameters such as applied voltage, residence time and the wave form of the supplied power can make contradict results. Thus, it is possible to get the optimum CH_4/O_2 ratio for methanol production by adjusting the involved and effective parameters in the process performance.

C. Applied Voltage

In non-equilibrium plasma reactors, input power which is directly proportional to the applied voltage has presented as the most effective agent in changes of the number of generated electrons and subsequent excited or ionized species. More input energy or exerted power results in higher conversion of reactants. It can be expressed such when increasing the external voltage, the internal electrical field across the region between the anode and cathode enhances, then, the number of the energetic electrons goes up. This phenomenon makes the electron density get larger; therefore, more collisions between methane molecules and those energetic electrons take place and the degree of the methane dissociation and conversion increases [10]. This fact has been established that increasing the applied voltage enhances the quantity of the electricity passing between two electrodes and thus current. There are many imperfections on the surface of the electrode that is the agent of starting discharges of electrons and keep on the potential difference between the electrodes. Thus, increasing the applied voltage would not affect the potential difference, but only it increases the discharge sites on the surface of the electrodes leading to increase the initiation rate of the electron driven reactions [16].

Although many researches was performed for understanding the effects of the input power on product distribution in partial oxidation of methane, its exact and general effect is disputable in the reason of synergistic effects of waveforms of the supplied power and gap distance between the electrodes [16, 17]. Contrary to some investigations [10, 16] that present nearly linear increase in methanol selectivity with enhancing the applied voltage, Indarto et. al [12] reported a decreasing trend in which methanol selectivity lowered from 14% to about 3% for power in the range of 50-150 W. He explained his results that fragmentation reactions are more

preferable at higher applied power rather than recombination reactions to generate higher molecules [12, 18]. Generally, some reports signified that there is an optimum supplied power to the reactor for methanol production [15]. In addition, 18 v/cm/torr of reduced electrical field should be supplied to produce methanol and it is the quantity of energy for dissociation of oxygen molecules to oxygen atoms for associating in methanol production [8].

D. Residence Time

At the other constant parameters of temperature, pressure and methane/oxygen feed ratio and applied voltage increasing the gas flow rate enhances MeOH production [9, 14, 15]. Larkin et. al [9] presented that at residence time < 2.5 S, MeOH selectivity had the highest value, then started to decrease sharply and after that gradually lowered. In fact, a fraction of produced MeOH oxidizes with O_2 to generate formic acid and formaldehyde as both tend to enhance sharply before a residence time <10 s. CO_x concentration was more at higher residence time as over-oxidation of methane and also produced oxygenates occur [7, 14, 15]. In fact, Higher residence time or lower feed flow rate leads to a high SIE (specific input energy) that in turn causes extensive decomposition of newly formed oxygenates to produce CO_x [7, 14]. However, the appropriate residence time to reach an optimum amount of methanol yield needs a medium residence time, since at residence tome longer than 2.6 s (flow rate of 300 cm^3/min) methanol yield decreases [7]. A maximum methanol yield of 2.19 % was reported at residence time of 1.79 s (flow rate of 300 cm^3/min) [7].

E. Type of Applied Catalyst

In heterogeneous catalytic reactions, the catalyst is often exploited to enhance the formation of species. The DBD plasma reactor combined with a selective catalyst may modify the chemical reactivity. In order for feed gas located in a discharge gap to activate, maximum contact between the energetic electrons and the natural feed gas species is necessary. Rather than other modification of electronic properties, the selective catalyst located in the discharge gap can increase the contact probability. Istadi[3] was given a review of research on the methane conversion with CO2 in the hybrid plasma-catalyst systems . The catalyst could influence the reaction products as a result of surface reaction [19].Although the combination of catalyst and plasma can modify the reactant conversions and higher selectivity but the exact role of the catalyst in the DBD plasma reactor is still not clear from chemistry point of view. Moreover, conductive surface in the case of metallic catalyst located in the plasma zone can affect the plasma properties.

Hybrid catalytic plasma reactors as a promising analog to a conventional thermal catalytic reactor have been and are being paid to attention in recent decade [7, 12, 13]. Indarto et. al tested $Cu-Zn-Al_2O_3$ (the well-known catalyst of methanol synthesis) at ambient temperature in the presence of plasma for direct partial oxidation of methane to methanol. It

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displayed a higher activity and methanol selectivity than non-catalytic plasma process [12]. They found that adding a small quantity of Fe, Y or Pt can improve the methanol selectivity by 20%. Y presented the most promising selectivity among these additives and raised methanol selectivity from 24% for a DBD plasma reactor loaded with Cu-Zn-Al$_2$O$_3$ to 30%. In another research [7], Fe$_2$O$_3$/CP (impregnated ceramic pellet with Fe$_2$O$_3$) showed a better performance, longer stability and resistance against carbon deposition in compare with Pt/CP and CeO$_2$/CP during the process. CP (ceramic pellets) with having low specific surface area can avoid a long time adsorption of reactants, favoring partial oxidation rather than total oxidation. Furthermore, at ambient temperature, all three catalysts were inactive for methanol production and methane conversion. At temperature of 250 °C, methanol selectivity and methane conversion increased up to 10% and 26.5% for Fe$_2$O$_3$/CP, respectively [7]. However, Methanol selectivity and methane conversion were 8.2% and 24.5% at ambient temperature.

F. Pressure

In all considered studies which were performed previously, methane conversion was decreased with increasing the pressure [6, 8, 15]. Larkin et. al [8] explained that while the system's pressure increases the feed concentration increases and, hence, resulting in a decrease in the energy consumption per molecule of methane converted and subsequently, a decrease in methane conversion.

According to some researches [8, 15], using pressures higher than atmospheric presented contradict results for methanol selectivity. Larkin et.al [8] reported that organic oxygenate liquids selectivity and yield were lowered with increasing pressure from 1 to 2 atm for 1.9 and 4 mm gas gaps, since the lower energy deposition at higher pressure (see eq. 1) is not sufficient for oxygen dissociation as a responsible agent in organic oxygenate production. Therefore, those reactions which can be occurred by a small quantity of energy deposition such as methane coupling toward C$_2$ production improve leading to a decrease in methanol selectivity. However, Zhou et. al [6], reported a converse results so that with increasing pressure from 1 to 2, methanol yield went up. Furthermore, Zhou et. al [6] compared the discharge stability between mixtures of methane with air and in those with pure O$_2$ and reported that by increasing pressure the discharge stability was more stable in mixture of methane with air.

G. Reactor Wall Temperature

Temperature as important process parameter plays a key role on increasing methanol selectivity when it decreases from 75 °C to ambient temperature [9]. The reason can be explained by decreasing the saturation pressure of methanol in the gas phase and condensing to liquid phase. Therefore, the quantity of methanol in the gas phase decreases and the probability of over-oxidation to form CO$_x$ are minimized [9]. Furthermore, the nearly constant methane conversion, increasing CO$_x$ production and decreasing methanol selectivity with increasing the temperature means methanol can be over-oxidized to CO$_x$. Unlike results were obtained when some selective catalyst towards methanol were used in a DBD plasma reactor in which raising temperature caused higher methanol selectivity [7].

III. CONCLUSION

As the methanol yield in reported investigations is below 2%, many researches has been attributed to direct methanol production by partial oxidation of methane via plasma technology in order to realize the effects of different parameters on the performance of the plasma reactor. It is apparent from previous investigation that smaller gap distance and relatively higher flow rate of reactants (lower residence time) are in favor of MeOH production. The CH$_4$/O$_2$ ratio in which the methanol selectivity starts to go down in various investigations is different which approves the synergistic effect of different parameters such as applied voltage, residence time and the wave form of the supplied power with feed ratio can make contradict results. Meanwhile, the exact effects of the input power on product distribution effect are disputable in the reason of synergistic effects of waveforms of the supplied power and gap distance between the electrodes. Using pressures higher than atmospheric presented contradict results for methanol selectivity. Moreover, transient and noble oxide metallic catalyst including Fe, Cu, Y and Pt are suggested to be efficient for increasing the MeOH yield at even ambient temperature.

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