Fuel Processing Technology 179 (2018) 32–41

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Research article

Single step conversion of methane to methanol assisted by nonthermal plasma

Piu Chawdhury, Debjyoti Ray, Ch. Subrahmanyam*

Department of Chemistry, Indian Institute of Technology Hyderabad, Telangana 502 285, India

ARTICLE INFO

Keywords:
Methane
Partial oxidation
Dielectric barrier discharge
Packed beds
Methanol

ABSTRACT

Present study reports the application of non-thermal plasma approach for the partial oxidation of methane to methanol. The target was achieved by employing oxygen under ambient condition in a dielectric barrier discharge (DBD) reactor, which was later operated as a packed bed DBD. A variety of packing materials of different nature (Al_2O_3, TiO_2, CeO_2 and glass beads) are tested and corresponding reaction pathways also have been shown. In addition, the influence of the feed gas composition, total flow rate and specific input energy has been investigated. Formation of CH_3OH, H_2, CO, CO_2, C_2H_6, and HCHO has been identified. Typical results indicated that the plasma reactor operating under a packed bed configuration showed better performance than the reactor without packing. Among the packing materials used, glass beads packing provided the best selectivity of ~35% to methanol, whereas, it was around 25% with DBD reactor without packing. In a similar manner, the yield of methanol increased to 5.4% with glass beads packing against 1.7% with DBD reactor with no packing. The good performance with glass beads packing is due to the uniform distribution of the microdischarges and improved filed strength.

1. Introduction

The global energy requirement has been increasing time to time. Even though the dependency on the natural gas is expected to continue, its availability in remote locations limits the applications [1]. One alternative to solve this problem is to convert the natural gas into oxygenates/liquid fuels, such as methanol, which reduces the transportation cost. Methanol is a major feed stock in the petrochemical industry and is used for the production of various chemicals such as formaldehyde, acetic acid, MTBE, biodiesel, etc. It is also used as a solvent and gasoline additive [2, 3]. Most importantly, for the replacement of gasoline and diesel fuels, methanol is an alternate energy source [4, 5]. Development of automobiles and other power vehicles which consumes pure methanol are highly beneficial as per energy consideration and environment. Thus the wide application of methanol inspires its large scale production. Methane, the major component of natural gas is a potential greenhouse gas and also an energy resource [6–8]. The current industrial methanol synthesis is by the initial conversion of methane to syngas via steam methane reforming, followed by conversion of syngas into methanol was over the Copper-Zinc-Alumina catalyst at operating pressure 50–100 atm and at 220–300 °C [1, 9, 10].

$$CO + 2H_2 \leftrightarrow CH_3OH \quad \Delta H_{298K} = -90.7 kJ/mol$$

When compared to the widely tested process, partial oxidation of methane to methanol is very attractive. However, thermal methods for methane partial oxidation to methanol (MPOM) requires a high temperature (400–1000 °C) and pressure (> 10 atm) [11–14]. Although various attempts are made, the methanol yield achieved was very low [15–17]. As methane is a highly stable molecule, activation of methane demands high input energy [18, 19]. One of the possible alternatives is the decomposition of methane by using non thermal plasma (NTP) approach [20, 21]. In NTP activation of methane, the electrical energy is primarily used for the production of high energy electrons that are capable of breaking C—H bonds, whereas, the global gas temperature remains under ambient conditions [22–25]. Various discharge configurations like dielectric barrier discharge (DBD), corona discharge, gliding arc discharge, microwave plasma discharge are tested for the activation of various organic molecules, including methane [18, 26, 27]. DBD is characterised by the formation of filamentary microdischarges throughout the discharge volume and the reactive species produced in the discharge plasma initiate the chemical reactions under ambient reaction condition.

Various attempts have been previously made for using O_2, air, N_2O as co-reactant in MPOM. Shepelev et al. showed that the methanol selectivity about 20% in a DBD reactor with CH_4 and O_2 as reactant [28]. A pulsed corona/DBD discharge experiment also produced 2.4% yield

* Corresponding author.
E-mail address: csubbu@iith.ac.in (C. Subrahmanyam).

https://doi.org/10.1016/j.fuproc.2018.06.009
Received 29 March 2018; Received in revised form 17 May 2018; Accepted 10 June 2018

of methanol with 33% selectivity [29], whereas, Okumoto et al. reported the maximum liquid selectivity (CH_3OH and HCHO) of 64 mol% with O_2 as the oxidant [30]. Mahammadunnisa et al. showed ~35% methanol selectivity with 5 wt% Cu-Ni/CeO_2 catalyst with N_2O as the oxidant [31], whereas, Chen et al. observed 10% selectivity with Fe_2O_3/CP based catalyst while using air [32].

In this context, DBD plasma may offer advantages like filamentary discharge and presence of high energy electrons. In addition, it allows the operation under packed bed configuration, where the catalyst or packing materials can be directly integrated in the plasma zone. It is known that synergy between a catalytic action and plasma activation is dependent on both the nature of the packing material and the discharge characteristics [33]. Packing integration on plasma may have the positive or negative effect depending on the change in discharge property, electric field, sorption effects etc. However, there is very few well established explanation on how various packed materials of different nature influence the performance for a chosen reaction. With this background, the present study has been aimed at understanding the promise of DBD plasma for the partial oxidation of methane. The effect of the packing materials in DBD reactor is to cause the surface activation (dielectric/porous solids) or catalytic action (metal oxides/support). We have made an attempt to address this issue by choosing the materials like Al_2O_3, TiO_2, CeO_2 and glass beads to understand the influence of the surface area, photocatalytic activity, the oxygen storage capacity and purely dielectric heating, respectively. Various parameters were optimised with the objective of achieving the best liquid selectivity.

2. Experimental section

A schematic diagram of the reactor set up is shown in Fig. 1. Briefly, the DBD reactor consists of a cylindrical quartz tube with an inner diameter of 20 mm and outer diameter of 23 mm. A stainless steel rod of diameter 11 mm placed at the centre of the quartz tube acts as the inner electrode, whereas, a stainless steel mesh wrapped on the outer surface of the quartz tube serves as the outer electrode. The inner electrode is connected to an AC high voltage source, whereas, the outer electrode is grounded through a capacitor (0.4 μF). The total discharge volume was about 24 mL and the discharge length was 11 cm. The discharge was ignited by varying the AC high voltage in the range 16 to 22 kV at a fix frequency of 50 Hz. The gas flow rate was controlled with mass flow controllers (GFC-17, Aalborg, USA). An Agilent 34136A HV probe was used to measure the applied voltage and the charge-voltage (Q-V) signals wave forms were recorded with a digital oscilloscope (Tektronix TDS2014B). The energy dissipated in the discharge was calculated from the Q-V Lissajous figure [20, 34, 35].

The product analysis was done with a SHIMADZU GC-2014 equipped with a packed column (Hayasep A, 80/100 mesh, 3 m) and a TCD detector. An infrared CO_x analyser (Fe, Japan) was used to monitor the CO, CO_2 produced in the reaction. The emission spectrum of the discharge was measured by an emission spectrometer (Princeton Instrument Action SpectraPro® SP-2300), equipped with an optical fibre to collect the spectrum. The emission experiment was conducted with 600 g mm^{-1} gratings with 500 nm Blaze. Infrared characterization was also performed in a FTIR spectrometer (BRUKER ALPHA E). The packed materials used in this present experiment are- TiO_2 (~3 mm, Alfa Aesar), Al_2O_3 (~3 mm, Alfa Aesar), CeO_2 (~2 mm, Sigma-Aldrich), Glass beads (3.5–4.5 mm, SD-fine chem limited). The conversion of the reactant, selectivity and yield of products, specific input energy (SIE), energy efficiency were calculated as follows:

$$CH_4 \text{ conversion } (\%) = \frac{CH_4 \text{ converted (mmol/min)}}{CH_4 \text{ input (mmol/min)}} \times 100 \quad (1)$$

$$\text{Selectivity of } H_2 \ (\%) = \frac{H_2 \text{ produced (mmol/min)}}{2 \times CH_4 \text{ converted (mmol/min)}} \times 100 \quad (2)$$

$$\text{Selectivity of } C_xH_y \ (\%) = \frac{x \times C_xH_y \text{ produced (mmol/min)}}{CH_4 \text{ converted (mmol/min)}} \times 100 \quad (3)$$

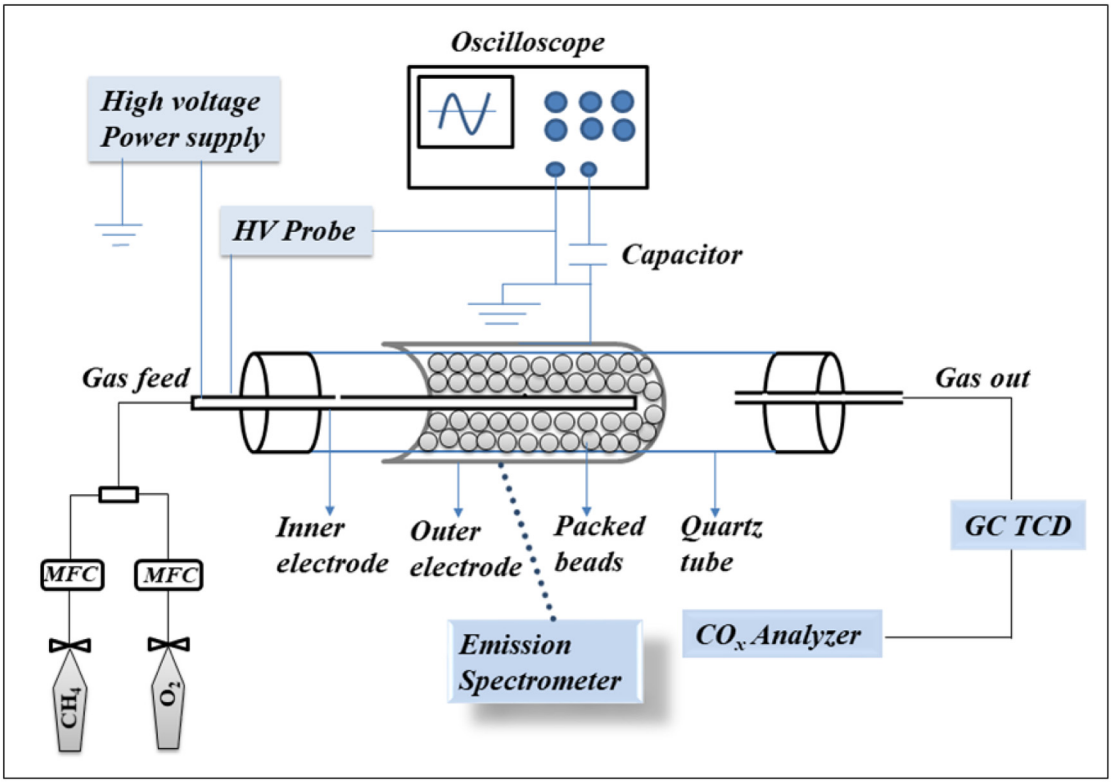

Fig. 1. Schematic diagram of experimental set up.