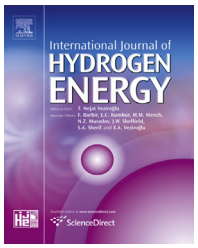
Available online at www.sciencedirect.com

ScienceDirect

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



Dry reforming of methane in a tip–tip arc discharge reactor at very high pressure

Samuel A. Iwarere [a,*], *Vandad-Julien Rohani* [b], *Deresh Ramjugernath* [a], *Laurent Fulcheri* [b]

[a] *Thermodynamics Research Unit, School of Engineering, University of KwaZulu-Natal, Howard College Campus, Durban 4041, South Africa*

[b] *MINES ParisTech, PERSEE Centre, CS 10207 Rue Claude Daunesse, 06904 Sophia-Antipolis, France*

ARTICLE INFO

Article history:
Received 6 August 2014
Received in revised form
23 December 2014
Accepted 1 January 2015
Available online 28 January 2015

Keywords:
Arc discharge
Dry reforming
Syngas
Very high pressure

ABSTRACT

Over the last two decades there has been growing research interest in the oxidative reforming of methane using carbon dioxide (CO_2), with the aim of producing syngas (mixture of H_2 and CO) which can be converted to synthetic fuels via the Fischer–Trospch process. Among the different options investigated, non-thermal plasma technology is considered to have a high potential for natural gas to syngas (and higher hydrocarbons) conversion at relatively lower energy consumption and cost. While many studies on plasma dry reforming of methane have been carried out over the years using different non-thermal plasma technologies, almost all these studies have been undertaken at near-atmospheric pressure. The aim of this paper is to study the influence of the pressure on the plasma dry reforming of methane. For this purpose, a tip–tip plasma batch-reactor connected to a high voltage direct current power supply has been used. This reactor has a maximum pressure limit of 20 MPa. All experiments were carried out with a CH_4/CO_2 reactant gas ratio of 1.8, a current of 350 mA, an interelectrode gap of 0.4 mm, and discharge duration of 60 s. The results presented in this paper show the variation of the concentration of the different obtained products: CO, H_2, C_2 and C_3 hydrocarbons versus the operating pressure. From these results, the selectivity, chemical yield, H_2/CO ratios and energy balances have been determined. The results from this study are compared to other plasma dry reforming studies in the literature. The high pressure reactor shows a high potential in terms of energy efficiency despite the low conversion due to the specific energy consumed by the reactant and the small discharge volume. The conversion could possibly be improved by increasing the interelectrode gap, and thus create a larger arc discharge reaction zone.

* *Corresponding author*. Tel.: +27 31 260 2858; fax: +27 31 260 1118.
E-mail address: Iwarere@ukzn.ac.za (S.A. Iwarere).

http://dx.doi.org/10.1016/j.ijhydene.2015.01.005

Introduction

In general, methane is the main component of natural gas, while methane and CO_2 are the major constituents of landfill gas. These two gases are very stable compounds, and thus difficult to convert to higher value-added products because of high reaction enthalpy [1,2]. The reforming of methane using carbon dioxide, a process otherwise called "dry reforming" have been investigated by several researchers starting from Fischer and Tropsch in 1928 [3]. This process has drawn lots of scientific and industrial interest because it uses two major greenhouse gases to produce industrially important syngas and also assist in reducing the net emissions of these gases provided the energy required for carrying out this reaction comes from a renewable energy source such as solar [4,5]. Another reason for the conversion of methane has been linked to the need to reduce the high cost associated with transporting it from "*remote regions to industrial complexes*" [6]. Thus, according to researchers such as Naeem et al. [6], there are several ongoing research aimed at investigating new technologies capable of converting methane into various value-added commercial products through its two common conversion routes [7]. However, dry methane reforming reaction requires high temperatures to achieve high conversion as well as high syngas values. Therefore, an alternative technological approach is the use of plasma reactors. It must be mentioned though, that researchers such as Oyama et al. [8] are investigating the use of membrane reactors for the dry reforming process.

A review of open literature indicates that a significant amount of research has been carried out on CH_4–CO_2 reforming for syngas production and hydrocarbon synthesis at sub-atmospheric to atmospheric pressure conditions using several plasma reactors [9–43]. However, for higher pressures, there are very few articles that report experimental data at pressures up to 0.4 MPa [13,18,37]. Some of the conventional non-thermal discharges such as the low-pressure glow, corona and radio frequency discharges have been limited to operating at sub-atmospheric pressure and low gas temperatures which sometimes does not allow for good conversion of the reactant, which is important from an industrial point of view [30]. Thus, discharges of a non-equilibrium nature capable of delivering high power to drive chemical processes within the reactor, and still provide high chemical selectivity at atmospheric or higher pressures would be of great interest.

Steam reforming of methane, partial oxidation of methane, and carbon dioxide reforming of methane are three common routes for the production of synthesis gas from natural gas. Each syngas production route uses different oxidant, and gives varied ratio of hydrogen (H_2) to carbon monoxide (CO) as the main products. In terms of energetics, the steam reforming, and dry reforming are highly endothermic reaction and therefore requires high temperatures in order to attain high syngas conversion thermodynamically. According to a recent review by Pakhare and Spivey [3], every reforming process has its advantages and disadvantages. While steam reforming is the major industrial route for the production of hydrogen that is used in the synthesis of ammonia, methanol, and many refinery reactions [8,44–46], it produces CO_2 whose removal is a concern for the petroleum industry. On the other hand, the partial oxidation of methane is an exothermic reaction which gives a H_2/CO ratio of 2; a ratio desirable for Fischer–Tropsch process to liquid fuels. However, some researchers have pointed out safety issues associated with its operating at "*high space velocity*" [3,47]. Dry reforming has been reported to produce synthetic gas with high purity [48]. However, the inevitable deposition of carbon is identified as its major disadvantage since it results in deactivation issues in catalytic reforming process [49,50]. Nonetheless, it has been reported that dry reforming has an operating cost that is a fifth of the other reforming processes [51].

According to Bakkerud [52], syngas production may account for more than 40% of the capital investment in a gas-to-liquid complex while Wilhelm et al. [53] reported that the cost might exceed 50% of the capital investment. Other authors such as Rostrup-Nielsen [54] cite values as high as 60% of the investment in a Fischer–Tropsch (FT) plant. Dry [55,56] reported that syngas production from "*coal-based FT complex or methane-based operation typically accounts for 60 to70% of the capital and running costs of the total plant*". The authors are of the opinion that syngas production may account for 40–70% of the total process cost depending on the products on the production route employed. The syngas obtained is converted to higher hydrocarbons via the Fischer–Tropsch (F–T) process for the coal-to-liquid (CTL), as well as the gas-to-liquid (GTL) process routes. For the gas-to-liquid process like every other chemical process, an energy efficiency calculation is necessary for analysis of the energy performances, while the conversion, product selectivity as well as the product yields is essential for the reaction performances in order to compare with other experimental plasma devices used for dry reforming.

The conversion of methane (the main constituent in natural gas) is generally through two routes, namely, the direct and indirect routes. The indirect route, which involves the conversion of methane to syngas followed by the catalytic conversion of the syngas into other useful liquid hydrocarbons has gained global scientific attention from the last two decades, and therefore, will be at the heart of this brief review. However, a short paragraph will be dedicated to the direct route. The indirect route for natural gas conversion, which is through methane reforming with steam (H_2O) or carbon dioxide (CO_2) in the presence of a solid catalyst, has been reviewed by several researchers [57,58]. Another indirect route for the conversion of methane into valuable chemicals is by the use of oxygen in a limited stoichiometric ratio, which is referred to as the partial oxidation of methane. Lunsford [59] reviews the challenges associated with reforming, as well as partial oxidation processes for methane conversion into syngas, higher hydrocarbons and other valuable chemicals using solid catalysts. Edwards and Maitra [57] discuss various catalysts that have been employed in reforming of CH_4 with CO_2, where the formation of carbon deposits has been identified as the major drawback as it causes the deactivation of the catalyst. Thus, the drive currently in the field of catalytic reforming of natural gas is the search for commercial catalysts that are capable of operating without carbon formation [57,60]. With the various challenges already identified as pertinent to the development of a commercial carbon dioxide reforming