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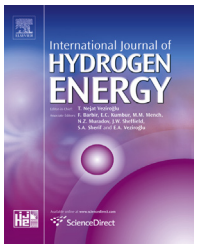

Hydrogen production via decomposition of methane over activated carbons as catalysts: Full factorial design

Amjed A. Al-Hassani [a,*], *Hazzim F. Abbas* [b], *W.M.A. Wan Daud* [a]

[a] *Department of Chemical Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia*
[b] *Department of Chemical Engineering, University of Nizwa, Al-Dakulaya, Oman*

ARTICLE INFO

Article history:
Received 28 November 2013
Received in revised form
30 January 2014
Accepted 13 February 2014
Available online 15 March 2014

Keywords:
Methane decomposition
Activated carbon
Empirical model
Factorial design

ABSTRACT

The thermo-catalytic decomposition of methane is proposed as an alternative for producing hydrogen without CO_2 emissions. The present study was divided into three parts. First, a screening study of the rate of methane decomposition (R_{CH_4}) was performed using two types of activated carbons as catalysts with progressive time of methane decomposition at four different temperatures. The catalysts differed in textural properties. A full factorial design consisting of 20 experimental points for each catalyst was applied in the second part. Quadratic R_{CH_4} models as functions of the relative time of catalyst deactivation and decomposition temperature were developed by regression analysis of variance. The results of the R_{CH_4} models showed that the relative time had twice as much influence as temperature. Finally, a general R_{CH_4} model was then developed representing both catalysts regardless of their textural properties. All the empirical models were consistent with experimental results and were adequate for designing the methane decomposition process.

1. Introduction

Hydrogen is a promising clean fuel because of its CO_x-free combustion [1]. Typical applications of hydrogen include its use in fuel cells and in manufacturing gases [2]. Free hydrogen is not naturally available in large quantities but can be produced by water electrolysis, thermo-chemical reformation, and steam reforming of hydrocarbons [3,4]. Bacteria and algae can also produce hydrogen via biomass transformation [5].

A process of thermo-catalytic decomposition (TCD) of methane is a viable technological approach for hydrogen production, $CH_4 \rightarrow 2H_2 + C_{(s)}$. This process is a promising alternative to other conventional methods, such as steam methane reforming wherein $CH_4 + 2H_2O \rightarrow 4H_2 + CO_2$ [6]. The main advantage of methane TCD is the production of CO_2-free hydrogen, which can be used directly as fuel [7]. In contrast, steam methane reforming emits large quantities of CO_2, i.e., one mole of CO_2 per mole of CH_4 decomposed. Additional units are then required to separate and capture the CO_2, which

* *Corresponding author*. Tel.: +60 017 229 2927; fax: +60 379 675 371.
E-mail addresses: amjed@siswa.um.edu.my, amjedoct@yahoo.com (A.A. Al-Hassani), hazzim_f@yahoo.com (H.F. Abbas), ashri@um.edu.my (W.M.A. Wan Daud).

http://dx.doi.org/10.1016/j.ijhydene.2014.02.075
0360-3199/

increases the cost of hydrogen production [8]. Furthermore, the energy consumed in methane TCD (37.8 kJ/mol of hydrogen) is slightly less than half the energy of steam methane reforming (68.3 kJ/mol of hydrogen) [9].

Methane decomposition occurs at >700 °C [3]. Thus, catalysts allow reductions in the decomposition temperature and increase the reaction kinetics. Various criteria should be considered in catalyst design, such as activity and high thermal stability [10]. Metal-based catalysts for methane TCD, e.g., Ni, Ni/Cu, Co, and Fe, exhibit significant activity [11–14]. Nevertheless, the produced carbon is deposited and blocks the active sites of the catalyst [6]. Thus, regeneration of the catalyst by burning deposited carbon also results in CO_2 emissions.

Alternatively, carbonaceous materials have been used in methane TCD, offering the following advantages [8]: lower cost, high-temperature resistance, and high tolerance to potentially harmful compounds. In addition, the carbon formed may be more easily marketable. Varieties of carbonaceous catalysts, such as coal char [15], activated carbon (AC) [16], carbon black [17], ordered mesoporous carbon [18], and graphite [19] have been investigated. Previous studies have shown that the activity of carbon catalysts relates to their structural (crystalline) and textural surface properties [20].

In earlier contributions, researchers were interested in the effects of variables and textural properties of catalysts for methane TCD. A factorial design (FD) technique is a useful tool to determine these effects, as well as develop an empirical model to design chemical processes [21]. Abbas and Baker [22] studied the influence of catalyst weight, decomposition temperature, and methane partial pressure for the initial R_{CH_4} on AC by applying full FD. The authors also reported that the initial R_{CH_4} was correlated as a function of temperature and partial pressure. To the best of our knowledge, FD for methane TCD has not been fully investigated in the previous literature.

This study focused on hydrogen production by methane TCD using a fixed-bed reactor. The R_{CH_4} values were investigated using two AC catalysts that differed in their textural properties. The timing of methane decomposition at temperatures of 820, 860, 900, or 940 °C was investigated. Full FD was then performed to correlate two quadratic R_{CH_4} models for each catalyst as a function of decomposition temperature and relative time. A general R_{CH_4} model for both catalysts was also developed. An analysis of variance (ANOVA) was used to validate all models with the experimental results and the effects of variables by regression analysis and statistical parameters.

2. Materials and methods

2.1. Materials

Methane and nitrogen gases with 99.99 vol% purities were purchased from Mox-Linde Gases Sdn. Bhd, Malaysia and used without further purification. Two commercial ACs were selected as reference catalysts, namely, palm shell AC (ACPS) and Norit-RB3 AC (named NORIT) supplied by Bravo Green Sdn. Bhd, Malaysia and Norit Nederland B.V, Netherlands, respectively. The main properties of the ACs are summarized in Table 1. The ACs were crushed and sieved to sizes of 500–590 μm (35–30 US mesh). The ACs were washed with deionized water (>18 MΩ cm) several times to remove dust and then dried at 105 °C overnight in oven.

Table 1 – Properties of the virgin ACs.

AC[a]	Biomass source	Ash wt%	Elemental analysis, wt%			
			C	H	N	O[b]
ACPS	Palm shell	3.54	90.37	0.41	0.28	08.94
NORIT	Hardwood	5.20	86.27	0.42	0.34	12.97

[a] Steam activation process by activating agent.
[b] Calculated by the residual value.

2.2. Experimental setup

We designed and assembled a bench-scale methane TCD unit (Fig. 1). A quartz tube for methane TCD (3.556 cm ID, 4 cm OD, and 120 cm in length) was supplied by Technical Glass Products (Painesville, USA). The quartz tube was placed inside a stainless steel tube (SS310S; 4.28 cm ID and 120 cm in length). The space between the tubes was sealed with high temperature-resistant silicone. The stainless steel tube protected the quartz tube from external stresses and connected the inlet and outlet pipelines. A quartz frit (3.5 cm diameter, 0.3 cm thick, and 150–200 μm porosity) standing on a 55 cm long quartz rod supported the catalyst.

The heat required for methane TCD was supplied by an electric annular furnace (Model TVS 12/600, Carbolite, UK). Two thermocouples (K-type Inconel, 1/16 in diameter, Omega, USA) were used to measure temperatures. One thermocouple was placed in the external wall of the stainless steel tube,

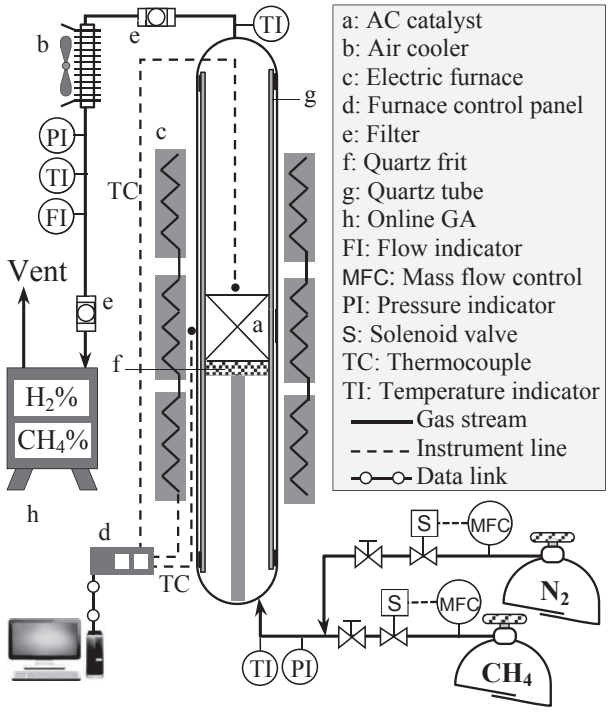

Fig. 1 – Schematic diagram of the experimental apparatus.