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Experimental and numerical analysis of a methane thermal decomposition reactor

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ABSTRACT

An indirectly heated tubular reactor is fabricated and used to study methane thermal decomposition conversion and determine kinetic parameters. A combined perfectly mixed reactor with bypass (CPMR) is proposed as an alternative to the traditional perfectly mixed and plug flow reactors. The CPMR model is used in order to account for buoyancy flow in the reactor. Results comparing the numerical predictions from all three models to experimental data show that buoyancy effects are significant in the reactor under study and also in most reactors in the literature. Including this effect might significantly improve the accuracy of the model predictions. The CPMR reactor model with a reaction rate constant of 5.43×10^{15} 1/s and an activation energy of 420.7 kJ/mol is capable of reproducing the obtained experimental data in this study and in the literature.

Introduction

Hydrogen production is expected to rise to approximately 9–32 Mt by 2030 and to 104–309 Mt by 2050 [1]. Steam methane reforming is the conventional technology used to produce nearly all HH_2 [2]. However, steam methane reforming is CO_2 intensive, producing about 11.9 kg of CO_2 per kg of H_2 [2,3]. Therefore, other methods of H_2 production that minimize greenhouse gas emissions need to be developed.

Thermal decomposition of methane provides an alternative to steam methane reforming. Since this process results only in hydrogen and solid carbon, it does not produce any CO_2 as long as the thermal source does not produce emissions, and therefore any greenhouse gas emissions are eliminated as long as all methane is consumed during the reaction. The produced solid carbon can then be collected and stored and, in some instances, used for commercial applications such as to produce rubber and catalyst supports. Table 1 contains a review of experimental and numerical work performed to date to investigate CH_4 decomposition, also known as cracking. Non-catalytic cracking is the focus of this article, even though most researchers have studied reactors with catalyst such as carbon black, activated carbon and metals. The cracking process produces carbon as a byproduct, which may be autocatalyzing. Steinberg [4] found that fine sub-micron carbon particles formed by CH_4 cracking can autocatalyze the reaction. However, Muradov et al. [5] found that the carbon produced by CH_4 cracking is insufficient to autocatalyze the

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Table 1 – Experimental and kinetic studies found in literature.

Author	Year	Study type	Operating conditions	Catalyst	λ	k_0 (1/s)	E_a (kJ/mol)
Eisenberg and Bliss [9]	1967	Both	1373–1473 K 101 kPa	None	Not first	–	–
• 7 mm fused quartz tube. Heated by electric resistance coils • Dimensionless PMR assumed. • Five reaction mechanism • Temperature profile measured using thermocouple. Isothermal effective temperature assumed using an integration of the Arrhenius equation over the reactor length. • Study suggests that the overall reaction was not first order within the operating temperature.							
Khan and Crynes [33]	1970	Both	Various	none	n/a	1.30×10^{14}	151–422
• Range of kinetic parameters given in review. • Few overall pre-exponential factors given because review is of proposed reaction mechanisms. • Most papers reviewed assumed first order kinetics.							
Billaud et al. [10]	1992	Both	1263 K 101 kPa	none	n/a	–	–
• 12 mm ID alumina tube. Heated by an electric furnace. • Dimensionless PMR assumed. • Temperature profiling likely an effect because tube extended out of furnace at both ends. Isothermal temperature was assumed. • 119 reaction mechanism.							
Olsvik et al. [11]	1995	Both	1473–1773 K 101 kPa	none	1	1.00×10^{13}	366
• 4 or 9 mm ID alumina tube. • 1D PFR comprised of 30 micromixed reactors assumed. • Temperature profile measured using thermocouple. Isothermal effective temperature assumed using an integration of the Arrhenius equation over the reactor length. • 36 reaction mechanism used, however overall kinetic parameters were calculated.							
Steinberg [4]	1998	Both	973–1173 K 2837–5674 kPa	none	1	5.4×10^3	131
• 2.54 cm ID Inconel 617 tube. Total heated tube length is 2.44 m, with 0.91 m cooling zone. Heated by clamshell electric heaters. • Isothermal temperature assumed. • PMR assumed.							
Dahl et al. [23]	2002	Model	1533–2144 K 101 kPa	carbon	4.4	6×10^{11}	208
• Reactor based off of 7.6 mm ID porous graphite tube fluid wall reactor designed by Ref. [40]. • Gas and carbon temperatures assumed to vary axially. Wall temperature is assumed to be isothermal. • 1D PFR model assumed. • Heterogeneous reaction mechanisms were ignored.							
Hirsch and Steinfeld [12]	2004	Exp	900–1550 K 101 kPa	Carbon	–	–	–
• Vertically orientated 10 cm ID steel-alloy vortex flow reactor. Heated by direct concentrated solar energy. • Difficulties in keeping the quartz window clean were noted due to buoyancy effects.							
Trommer et al. [13]	2004	Both	900–1060 K 101 kPa	carbon	1	1.07×10^6 PFR 7.54×10^6 PMR	147 PFR 162 PMR
• Vertically orientated vortex flow reactor. Heated by direct concentrated solar energy. • Kinetics found assuming a single isothermal temperature • Kinetics found assuming a single isothermal temperature • 1D PFR and dimensionless PMR models assumed. • Volume expansion factor used in analysis.							
Abanades and Flamant [14]	2006	Both	1563–1813 K 101 kPa	none	1	2×10^8	147
• Vertically orientated 17 mm OD by 61 mm long graphite tube. Heated with a beam-down solar furnace, thus higher temperatures are at the top portion of the tube. • E_a set to 147 kJ/mol as per Trommer et al. [13] findings. • Kinetics assumed from Trommer et al. [13]. • 1D PFR model of reaction gas-filled reactor was created. Temperature and CH_4 conversion equations were included. Heterogeneous reactions ignored, but kinetics assumed were for particle seeded reactor. A mean wall temperature was assumed using experimental pyrometry measurements. • 2D model of an inert gas-filled reactor was created assuming laminar parabolic velocity profile with conduction and radiation. A mean wall temperature was assumed using experimental pyrometry measurements. • 3D model including CFD, mass and energy transport, and chemical reactions was created. A constant solar heat flux was assumed, allowing varying wall temperatures. Governing equations were not defined.							
Abanades and Flamant [15]	2007	Both	1500–2000	none	1	$2.5 - 4.5 \times 10^7$ $5 - 8 \times 10^{10}$ $4.5 - 5.5 \times 10^{13}$	147 250 350

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