INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2017) 1–11

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# Hydrogen formation from methane rich combustion under high pressure and high temperature conditions

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ARTICLE INFO

*Article history:*
Received 22 December 2016
Received in revised form
1 April 2017
Accepted 3 April 2017
Available online xxx

*Keywords:*
Hydrogen
Methane
Rapid compression machine
Species sampling
Soot

ABSTRACT

Experimental and computational studies on the hydrogen conversion from methane combustion were carried out in methane rich conditions. The experiments were conducted in a rapid compression machine (RCM) over conditions with varied pressures (18–24 bar), temperatures (962–1060 K) and equivalence ratios (2.0–2.6). Both major combustion products ($H_2$ and CO) and intermediate species ($H_2$, $CH_4$, $C_2H_2$, $C_2H_4$, $C_2H_6$, $C_3H_6$, CO, and $CO_2$) were sampled and analyzed by a fast sampling system equipped with gas chromatography (GC). Computational methods including chemical equilibrium and chemical kinetic modeling were used for comparison. The results showed that kinetic model was inadequate to predict hydrogen production at fuel rich conditions due to soot formation. The competition between chemical equilibrium and soot formation resulted in an optimal equivalence ratio at $\varphi = 2.4$, where hydrogen production is the highest. Besides, higher pressure and temperature within the test range also attributed to hydrogen formation.



## Introduction

Increasing concerns on global warming have pushed countries worldwide to enact more stringent vehicle fuel economy standards. In some countries, air pollution has become a severe problem. To meet the increasingly stringent pollutant criteria and green house gas emission regulations, a practical approach is to utilize high H/C ratio fuels, such as natural gas. Natural gas is a promising alternative fuel due to its high octane number, clean combustion characteristics, and abundant supply. Natural gas engines are able to meet the U.S. EPA regulation by adopting stoichiometric combustion with a three-way catalyst (TWC) [1]. The natural gas engines can significantly reduce $CO_2$ emissions while providing power comparable to gasoline engines [2]. Lower pumping loss and heat loss can be achieved by introducing exhaust gas recirculation (EGR), resulting in low fuel consumption. Meanwhile, a higher compression ratio can be applied to natural gas engines due to the superior anti-knock characteristics of natural gas, which attributes to higher thermal efficiency.

However, adding EGR deteriorates the combustion stability and engine power, especially for natural gas spark ignition engines [3]. The low burning velocity and poor auto-ignition characteristics of methane are reported as the primary reasons [4]. In contrast to natural gas, hydrogen has much faster

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http://dx.doi.org/10.1016/j.ijhydene.2017.04.022

laminar flame speed, better resistance to quenching, and better combustion stability than hydrocarbons [5]. Therefore, hydrogen addition is a promising method to improve the performance of spark ignition (SI) natural gas engines [6]. With hydrogen addition to methane, the burning velocity dramatically increases under spark ignition (SI) engine conditions [7]. Furthermore, the engine power, thermal efficiency, and emissions are improved as well [8]. The mechanism that hydrogen promotes combustion has been revealed as introducing more reactive radicals such as H•, O•, and •OH with the addition of hydrogen [9–11]. As a consequence, both upper and lower flammability limits are widened [12]. In practical applications, the lean operation limit of natural gas engine with EGR were extended to more diluted conditions without the penalty of increased cycle-by-cycle variation [13–18].

Despite of the benefits of hydrogen addition, on-board hydrogen storage is still a challenge in practice. Therefore, some studies on on-board hydrogen production have been carried out. Exhaust gas fuel reforming was firstly proposed by Tsolakis et al. [19] and hydrogen formation was classified into four categories: steam reforming, partial oxidation, auto thermal reforming, and thermal decomposition. Up to 16% hydrogen in the exhaust gas was achieved using a diesel engine. Afterwards, the hydrogen production was further promoted to 29% through water addition and partially premixed charge compression ignition (PPCI) [20,21]. The studies using catalytic reforming was reported to generate over 20% hydrogen [22,23]. However, the catalytic reforming required a dedicated reactor which would increase system cost and vehicle weight. A catalyst-free system was proposed by post injection in lean-burn diesel engine [24,25]. By changing the post injection timing, a maximum volume fraction of 0.76% was observed, which might not be adequate to significantly improve combustion in diesel engines.

Inspired by syngas production, a super-adiabatic combustion method using ultra-rich methane-air mixtures was proposed to generate reformed gas [26]. At rich equivalence ratio (up to 8) conditions, significant conversion of methane to hydrogen and carbon monoxide was observed. Further, dedicated EGR (D-EGR) system was introduced by Southwest Research Institute (SwRI) for on-board hydrogen generation [27]. It combined the EGR with rich combustion reforming and used a dedicated cylinder served as a hydrogen generator for the other cylinders. Numerical analysis on a four-cylinder SI engine has demonstrated that D-EGR can improve the thermal efficiency and reduce NOx emissions [28]. A maximum hydrogen fraction of up to 17% in the exhaust gas from the reformed cylinder was achieved at $\varphi = 2.2$ and a maximum thermal efficiency of 43% for the normal cylinders was achieved. Similar computations of fuel rich combustion of natural gas/air mixture were investigated at $p = 10\sim25$ atm, $T = 600\sim900$ K, and $\varphi = 3\sim5$ using a perfectly-stirred reactor (PSR) [29]. The results showed that the peak methane to hydrogen conversion was observed to be 1.5 at equivalence ratio about 3.0. Besides, simulation of homogeneous charge compression ignition (HCCI) condition was carried out with a piston motion model. The hydrogen production peaked near $\varphi = 2.5$ at various engine speeds [30].

Moreover, few natural gas rich combustion were studied under engine relevant conditions. A practical D-EGR SI engine was investigated by Zhu et al. [31]. However, the deteriorated combustion stability resulted in a less than 4% hydrogen production. The optimal condition was realized at $\varphi = 1.2$ in terms of emissions, combustion stability, and thermal efficiency. It was worth mentioning that the first systematic experimental study of rich methane partial oxidation was carried out in a flow reactor coupled with molecular beam mass spectrometry (MBMS) [32]. The experiments were conducted at atmospheric pressure, $\varphi = 2.5$, temperature range from 1100 K to 1800 K. Significant discrepancies were observed between modeling and experimental results due to the lack of soot chemistry in the reaction mechanism.

Up to now, the optimal equivalence ratio and the maximum hydrogen production condition in D-EGR engines are still difficult to determine. In this study, both experimental and computational studies were conducted to investigate the methane rich combustion under engine relevant conditions using a rapid compression machine (RCM). The purpose was to better understand the optimal operation conditions that achieved the maximum methane to hydrogen conversion ratio.

## Experimental methods

### *Rapid compression machine*

All experiments were performed in the RCM at Tsinghua University (TU). A detailed description of the TU-RCM can be found in Di et al. [33]. The mixture in the test section was compressed to a high pressure and high temperature within 25–30 ms. A creviced piston design was applied to minimize gas motion after compression. A piezoelectric pressure transducer (Kistler 6125C) was mounted on the test section combined with a charge amplifier (Kistler 5018A) for pressure measurement.

A typical pressure profile is shown in Fig. 1 and the same method was used for data processing as in paper [33]. The start point ($t_0 = 0$ ms) indicates the end of compression (EOC). The effective pressure ($p_{eff}$) and effective temperature ($T_{eff}$)

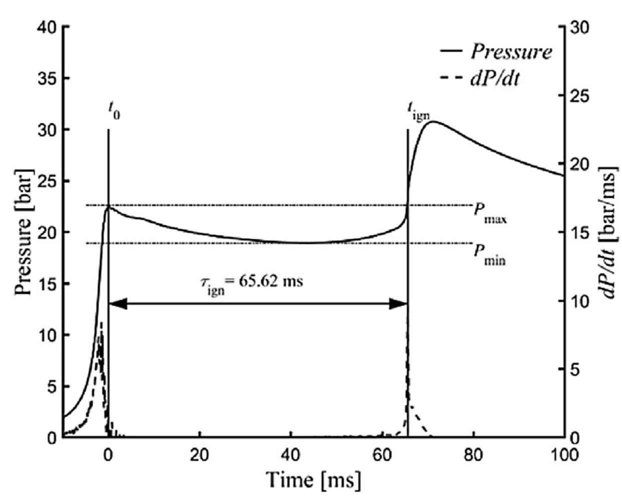


**Fig. 1 – Pressure trace in the combustion chamber at $p_{eff} = 20$ bar, $T_{eff} = 980$ K, $\varphi = 2.5$, $Ar/O_2 = 8.2$.**

Please cite this article in press as: Wang Y, et al., Hydrogen formation from methane rich combustion under high pressure and high temperature conditions, International Journal of Hydrogen Energy (2017), http://dx.doi.org/10.1016/j.ijhydene.2017.04.022