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Experimental investigation of hydrogen production by variable volume membrane batch reactors with modulated liquid fuel introduction

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ABSTRACT

A novel dynamically-controlled membrane batch reactor, which combines the variable volume operation of CHAMP (CO_2/H_2 Active Membrane Piston) with the direct injection of liquid fuel of DDIR (Direct Droplet Impingement Reactor) for enhanced power density, is demonstrated and experimentally characterized in this study. A laboratory-scale CHAMP-DDIR, consisting of a variable volume piston-cylinder reactor chamber and an actively-controlled micro injector for liquid fuel atomization, is used with a Pd–Ag foil membrane and $Cu/ZnO/Al_2O_3$ catalyst to steam reform methanol for hydrogen generation. Two modes of CHAMP-DDIR operation, pulse-modulated fuel injection and batch reaction with dynamically-adjusted reactor volume, were investigated, and their performance was quantified using metrics such as hydrogen yield and volumetric power density, and compared with those for a baseline operation (single fuel injection with fixed reactor volume). The experimental results showed that the residence time for the same hydrogen yield can be reduced by compressing the reactor volume during the conversion cycle. The residence time reduction was primarily as a result of higher hydrogen partial pressure in the reactor chamber and thus higher rates of hydrogen permeation. In addition, pulse-modulated fuel injection experiments revealed that a significant reduction in required reactor volume can be achieved with multi-shot split fuel introduction. Both the reduction in required cycle time and the reduction in required reactor volume increase the volumetric power density of CHAMP-DDIR. The demonstrated power density enhancement achieved through the dynamic compression of reactor volume was 17%, and the enhancement achieved through time-modulated fuel introduction was 38% (for 85% hydrogen yield efficiency and under the constraints of the same maximum operating pressure and total amount of fuel).

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Introduction

A compact, efficient, and high performance power source has become a critical component for most portable and mobile devices, as power consumption in small-scale devices has increased dramatically [1,2]. Similarly, for power sources which use hydrogen as a fuel (e.g., PEM fuel cells), a compact and efficient fuel reformer is needed to convert high energy density liquid fuel into hydrogen [3–6]. In particular, power density (on both per unit mass- and volume basis) is one of the most important metrics for portable fuel processors. Miniature or micro methanol steam reformers (MSR) operating in a continuous-flow, steady-state mode have attracted great interest as a route to high power density portable fuel reforming [7–9]. They present advantages such as high surface-to-volume ratio for heterogeneous catalytic reaction and enhanced heat and mass transfer characteristics, although at the expense of increased heat losses [10–12]. However, the efforts on developing microchannel reactors, using the design methodology of straight-forward scale down of industrial unit operation reactors, were at best partially successful, in part because plant scale reforming processes are optimized for cost effective production and high-fuel-conversion efficiency [13]. Particularly acute problems faced by such microchannel MSR reactors include pressure oscillations and flow rate variations while vaporizing the liquid feed in the microchannels, and flow maldistributions within intake manifolds [13–16].

CHAMP-DDIR (CO_2/H_2 Active Membrane Piston [17–19] - Direct Droplet Impingement Reactor [20–22]) exploits multi-functional components and batch operation to achieve improved power density while avoiding the problems faced by microchannel MSRs. In CHAMP-DDIR (Figs. 1 and 2), a liquid fuel mixture is pulse-injected onto the heated catalyst surface for rapid flash volatilization and on-the-spot reaction, and a hydrogen selective membrane is collocated with the catalyst to reduce the diffusion distance for hydrogen transport from the reaction zone to the separation site [23]. In addition, CHAMP-DDIR exploits dynamic variation of the reactor volume to control the residence time and reactor conditions, thus improving both the reaction and separation processes, as well as enabling on-demand dynamic variation in hydrogen throughput without sacrificing fuel conversion. The hydrogen throughput variation is a clear benefit for CHAMP-DDIR over continuous-flow type reactors which generally operate optimally at a single flow rate and slowly respond to changes in operating conditions [18].

In a previous study for CHAMP-DDIR, the coupled reaction-transport-permeation reactor models were developed using state-of-the-art, reduced-order analytical framework of increasing complexity and were used to investigate the optimal design and operation of CHAMP-DDIR [23]. The idealized theoretical analysis of the model revealed that significant improvement in the volumetric power density under a constraint of maximum operating pressure can be achieved by combining time-modulated fuel injections with volume modulation during a batch cycle.

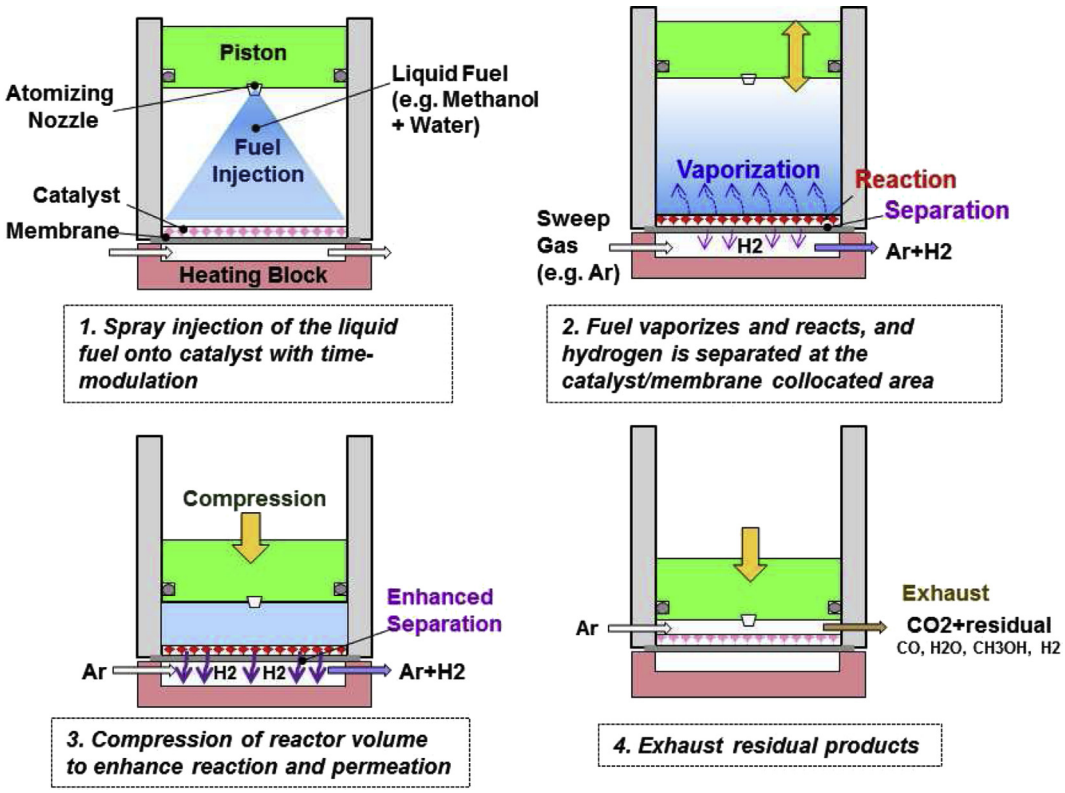

Fig. 1 – Four sequential steps in a CHAMP-DDIR cyclic operation to produce hydrogen via methanol steam reforming. The key underlying physical processes are fuel evaporation, catalytic reactions, membrane selective separation, and species transport during active variation of reactor thermodynamic conditions.