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The Potential of Using Autothermal Reformation With Copper-based Catalysts in Vehicle Applications

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Abstract

In the development of fuel cell vehicles, onboard steam reformation of hydrogen has been an option for providing hydrogen fuel. However, steam reformation generally has a slow response time to the transient requirements, and thus, autothermal reformation has been proposed as an alternative. This paper discusses the theoretical aspects of autothermal reformation with copper-based catalysts using high flow rates of methanol, and presents areas in which future research is needed. The parameters targeted in this study are fuel conversion, hydrogen selectivity, catalyst degradation, response time, and reformer volume.

Keywords: methanol, steam reformation, autothermal reformation, hydrogen

1 Introduction

Steam Reformation (SR) of methanol can be used for converting hydrocarbons into hydrogen, and has been used onboard fuel cell vehicles to produce hydrogen [1]. However, steam reformation is an endothermic reaction, requiring heat addition from external sources. This can yield a slow response time to transients, as well as a slow start-up time [2]. To ensure complete fuel conversion within the processor during periods of high demand, the reformer typically has been sized much larger than is minimally necessary [3]. As smaller sized units are required for mobile onboard applications, this over design is undesirable for vehicles. One possible option for improving steam reformer performance is to operate in an Autothermal Reformation (ATR) mode by adding oxygen to the fuel stream during startup and transients [4, 5]. The exothermic reaction caused by adding oxygen provides the heat necessary for the steam reformer to produce hydrogen, reducing or eliminating the need for external heating. This type of hybrid operation of using a steam reforming catalyst in an ATR mode, may provide a fast response by taking advantage of the exothermic properties of the ATR reaction, and allow high conversion of the reactant stream for high flow rates, while simultaneously minimizing the volume required for the reformer within the vehicle and ensuring steam-reformer-like product concentrations [6]. This paper discusses the possibilities of such advancements.

2 Fuel Conversion and Hydrogen Selectivity at High Space Velocity

Figure 1 shows that using traditional steam reformation, near 100% fuel conversion can be achieved for flow rates up to 3.0 Liquid Hourly

Space Velocity of Methanol (LHSV-M) [7]. During steady state operation, as would be experienced by properly designed vehicles at constant power draw, this is likely to provide an adequate supply of hydrogen for a fuel cell vehicle. Above 3.0 LHSV-M, however, fuel conversion drops for steam reformation. This could become problematic during times when high power is required, such as during acceleration or hill climbing. Figure 1 also shows that ATR with a copper-based catalyst has near 100% fuel conversion up to 6.0 LHSV-M. Based on the results from the preliminary study, it is likely that high fuel conversion can be achieved for even higher values of LHSV-M using different configurations of the reformer system. Using a higher flow system with proper vaporization, it is possible to achieve flow rates higher than 6.0 LHSV-M with ATR. Hydrogen selectivity and product gas concentrations of CO, CH_4, and CO_2 can be collected for both the ATR and SR modes. Using the hybrid method of ATR with a copper-based catalyst allows for similar output gas concentrations with nitrogen dilution [8]. Clean-up units such as palladium membrane separators or pressure swing absorbers will be necessary downstream of the reformer to remove nitrogen from the product stream before it reaches the anode of a fuel cell. However, the use of copper catalysts in the reformer may allow a decrease in the amount of air required to produce heat for the reaction, which will reduce the need for clean-up.

3 Under Hood Volume Requirements of Autothermal Reformation vs Steam Reformation

Steam reformers typically are sized much larger than minimally necessary when used onboard vehicles to ensure proper handling of transients. Only a small portion of catalyst is used to facilitate the reaction, and further portions of catalyst become used only when higher flow rates are required. For a reformer sized too small, operation during transients can lead to propagation of the cold region through the reactor as the endothermic reaction draws energy, yielding poor response and poor quality of hydrogen [7]. For high changes in flow rate, the cold region extends past the reactor until as the reaction draws more heat from the catalyst to proceed. When this happens, any additional heat bands begin to supply extra heat to compensate, and until the temperature is stabilized the overall function of the reactor is reduced. A small reactor may be able to be used with ATR and achieve acceptable results even during the transient periods if the heat generated during oxidation is sufficient to activate the catalyst. Also, due to the potentially exothermic property of the ATR reaction, the need for insulation on the reformer is potentially reduced or eliminated, freeing valuable space under the hood of a vehicle for other components. To contain more heat within the reactor, radiation shielding such as bluff bodies or a non-reactive substance placed before the catalyst layer on the inlet can be used. The reduced amounts of nitrogen present in the product stream can potentially reduce the size of downstream clean-up units, as well. Any reduction in reformer or clean-up component size may pave the way for easier adoption of liquid hydrocarbon fueling for fuel cell vehicles. Values of required volumes are calculated based on the empirical values of the maximum attainable space velocity using ATR and SR methods. Furthermore, an energy balance is performed to determine if operating in a hybrid reforming mode yields an acceptable drop in efficiency over a typical drive cycle.

4 Catalyst Degradation

Hybrid mode operation of the copper-based catalyst can lead to increased temperature at the catalyst which may in turn lead to faster degradation [9]. As low catalyst lifetime may be a detriment when using copper-based catalysts in a hybrid mode, it is necessary to examine the degradation rate. Preliminary results have shown that the process of reducing a catalyst using an initial stream of methanol and air can cause sintering due to the temperature spikes in excess of 600 ^oC that are experienced [4]. As shown in Figure 2, the catalyst provides near 100% fuel conversion much longer than an unreduced catalyst. It would then be undesirable to operate with an unreduced catalyst. However, the lifetime of a reduced catalyst is still necessary to investigate.

5 Transient Response

Preliminary data on transient operation has shown that sudden changes in flow rate affect fuel conversion differently for ATR and steam reformation. Figure 3 shows that hydrogen output can be greater for steam reformation than autothermal reformation during transient operation. This result could be different if the oxidation rate is increased in ATR along with the flow rate [7]. Figure 4 shows that conversion percentage for steam reformation is generally much lower than for autothermal reformation, and that generally steam reformer performance degrades with time. During transients, the steam reformer briefly shows higher conversion than the autothermal reformer, which is likely due to excess heat in the reformer being used to briefly process the higher amount of fuel flow. Once this heat is consumed, SR conversion is lower than that of the ATR method. At this point, ATR is more able to handle transients than the steam reformer, although its performance is noticeably reduced from its steady state capability. Depending on the length of the transient, ATR may be significantly better in converting fuel to hydrogen. Lean mixtures (those with higher O_2/CH_3OH ratios) during transients give rise to larger temperature spikes, which potentially reduce the life of the catalyst [10]. For future research, it would be beneficial to investigate reformer performance during transients.

6 Summary

Previous research shows that autothermal reformation methods may be used with copper catalysts to reduce reformer size and potentially the underhood volume requirements of a vehicle. Additionally, the ATR method using a copper-based catalyst potentially allows better response to transients. High conversion at space velocities above 3.0 LHSV-M have been attained using this technique, and higher values may still be achieved with variations in processor configuration. It may be possible to reduce radiation on the inlet of the reactor with the addition of bluff bodies or a layer of inert material placed before the catalyst layer, which would help contain heat within the reactor to facilitate the chemical reactions to produce hydrogen more effectively. Comparisons of conversion with both SR and ATR in transients has suggested that while steam reformer performance degrades rapidly, autothermal reformer performance remains relatively even. In ATR with copper based catalysts degradation may be elevated due to the presence of oxygen in the reformer. Further testing of autothermal reformation using copper-based catalysts will be valuable to determine the effectiveness of this technique.

2 Figures, Tables and Equations

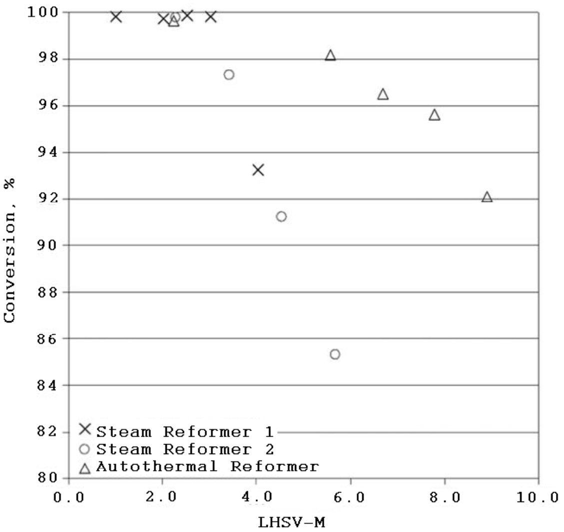

Figure1: Conversion vs. LHSV-M for SR and ATR using a copper-based catalyst [7]

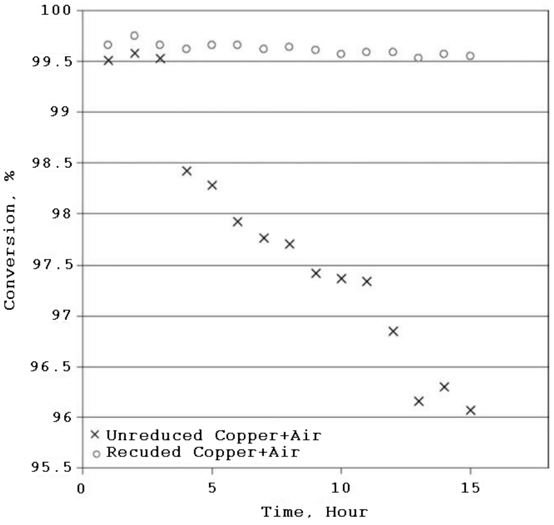

Figure 2: Conversion vs. time for a reduced and unreduced copper catalyst [7]

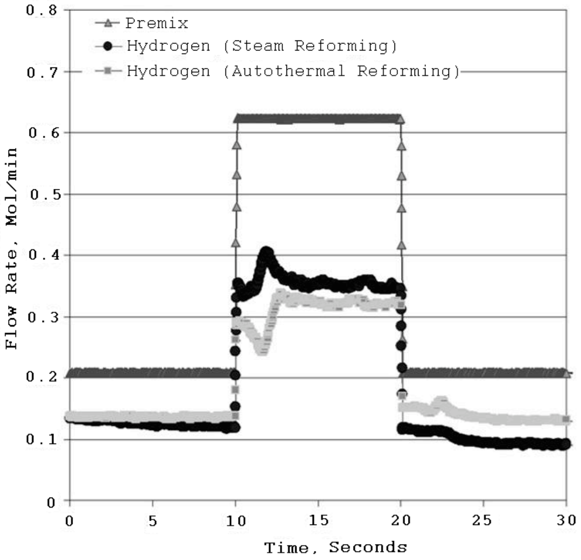

Figure 3: Hydrogen output for methanol SR and ATR with copper-based catalyst [7]

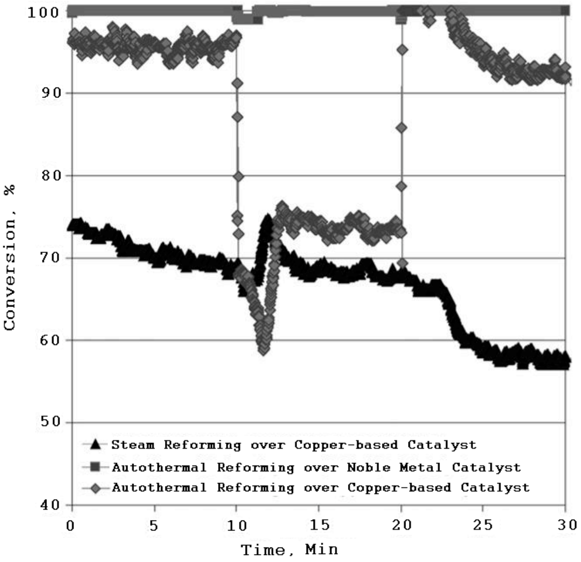

Figure 4: Conversion change for methanol SR and ATR with copper-based catalyst [7]

2.1 Tables

Table1: Power levels for charging (230V)

	Current (A)	Power (kW)
Standard	16	3,5
Semi-fast	32	7,0

Tables shall have their own sequential numbering independent from the figures numbering, and captions shall placed above the table. Tables spreading over 2 columns should be placed at the top or the bottom of the page.

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