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Syngas production from heptane in a non-catalytic counter-flow reactor

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ABSTRACT

Hydrogen-based power systems, such as fuel cells, are promising clean energy technologies. A significant obstacle, however, is the production and distribution of hydrogen. Production at the site of use is widely believed to be a viable near-term solution. Hydrocarbon fuels that are readily transported can be reformed into synthesis gas, or syngas, which is a gaseous mixture of hydrogen, carbon monoxide and other species. Fuel reforming therefore permits high density energy storage that can effectively replace or supplement batteries for remote applications. Current industrial methods of syngas production do not scale down efficiently, but an alternative method, non-catalytic partial oxidation, is a viable option for small scale production. An advantage of this method is the lack of catalyst, which is expensive and prone to damage. In this paper we present the experimental results of syngas production from heptane using a non-catalytic reactor based on the concept of counter-flow heat exchange. The reactor operates on the principle of heat recirculation in order to achieve temperatures that are superadiabatic, or higher than those predicted by equilibrium, thereby permitting increased oxidation rates of reactant mixtures. A key advantage of this type of reactor is that the reaction zones are stationary, allowing continuous operation. Previous studies have examined the reforming of methane and propane using the counter-flow reactor, and those results are compared with the results of the current study. Heptane is notably the first liquid fuel to be reformed using the counter-flow reactor. This is important for establishing the fuel flexibility of the reactor and, in conjunction with previously acquired data, guiding future design and operation.

1. Introduction

In recent years interest has increased in hydrogen-based technologies, such as fuel cells, to replace petroleum-dependent power generation. One of the largest impediments to the implementation of such technologies, however, is the lack of infrastructure for the production and distribution of hydrogen. An abundance of hydrogen is bound in organic fuels such as natural gas, petroleum-based fuels, and biofuels, and the molecular hydrogen needed for fuel cells can be generated from such sources. The process of converting these fuels into a hydrogen-rich gas, known as syngas, is called reforming. Syngas is a gaseous mixture consisting of hydrogen, carbon monoxide and other species and has many uses as a fuel or as a feedstock for further refinement. It can be used directly in internal combustion engines and solid-oxide fuel cells (SOFC), or processed to separate hydrogen for other applications such as proton exchange membrane (PEM) fuel cells [1].

Distribution of hydrogen and other gaseous fuels is a significant challenge. There is currently a limited hydrogen pipeline network, and hydrogen is expensive to store and transport in either gaseous or liquid form. Hydrogen gas has low volumetric energy density at standard conditions, and a significant amount of energy must be expended to compress it to a density suitable for transportation. Liquid hydrogen requires cryogenic systems, and a large amount of energy is required for liquefaction and storage. These challenges are overcome if hydrogen is produced at the site of use from fuels that are more readily transported. These include natural gas and liquid hydrocarbon fuels, the latter of which have high volumetric energy density [2,3]. The ability to reform liquid fuels on a small scale and at the site of use therefore has the potential to replace or supplement batteries for energy storage. Known methods of syngas production include steam reforming and partial oxidation, of which steam reforming currently accounts for the majority of hydrogen generation in the US. One major limitation of steam reforming is the use of a catalyst, which is both expensive and prone to degradation and poisoning, thereby limiting the process to relatively narrow operating conditions, moderate temperatures, and high quality reactants [4]. Another major limitation of steam reforming is that it is less economical at small scales, meaning hydrogen produced at the site of use is more expensive than fuel that can be delivered through conventional means such as gasoline [5].

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Non-catalytic partial oxidation, or combustion of fuel-rich mixtures, is a reforming technique that does not have the same restrictions as steam reforming due to a lack of catalytic surface that is prone to damage. Instead of using a catalyst to accelerate chemical reactions at low or intermediate temperatures, partial oxidation utilizes elevated temperatures to increase reaction rates. A category of reactors used for partial oxidation reforming achieves elevated temperatures through internal heat recirculation. Heat is transferred by conduction and radiation from hot combustion products to incoming reactants resulting in preheated reactants. The result is that peak temperatures within the combustion zone can significantly exceed the adiabatic equilibrium temperature, or the temperature predicted by chemical equilibrium. This is known as excess enthalpy combustion at superadiabatic temperatures [6].

Various reactors have employed the concept of heat recirculation through a solid matrix, with some designs having a means of stabilizing the reaction front. A two section porous media reactor can support a stationary combustion zone and this design has been used to reform rich mixtures of methanol, methane, octane and automotive-grade petrol [7]. Alternatively, a diverging section of porous media permits stabilized reaction zones for fuel reforming in porous media and has been used successfully in several studies [8–10]. In some heat recirculating reactors, the reaction front is not stabilized and propagates through the solid matrix. When the front propagates downstream, it passes over preheated solid and the gas gains additional energy, resulting in superadiabatic temperatures. These higher temperatures increase reaction rates and potentially result in high conversion efficiencies [11,12]. A disadvantage of this design is that the wave ultimately reaches the end of the reactor requiring periodic restarting or reversal of the flow [13].

The advantage of superadiabatic temperatures has been realized in other reactor designs as well. A Swiss roll reactor [14–16] has been used for both reforming and thermal oxidation [17]. In this reactor, heat from the exhaust is transferred through the walls to the incoming reactants. This basic principle is applied in the current study of a counter-flow reactor consisting of straight channels which simplify the geometry and permit a wide range of stable operating conditions. Figure 1 is a schematic of the reactor. The flow direction alternates in adjacent channels so that energy from hot combustion products is transferred to cold incoming reactants. The preheated reactants may reach temperatures in the combustion zone that are superadiabatic. The counter-flow reactor design has been proposed analytically [18–20] and validated in two experimental studies on the reforming of methane [21] and propane [22].

One of the compelling characteristics of non-catalytic reactors is their ability to operate on various fuels. There have been numerous studies on the production of syngas from gaseous fuels [7,9,23–25], but fewer have done so from liquid fuels. In this study we present experimental results for reforming the first liquid fuel, heptane, in the counter-flow reactor. The current results augment those obtained on an identical reactor using methane [21] and propane [22]. Heptane is a particularly interesting liquid fuel as a surrogate for commercial fuels. Dixon et al. [26] presented experimental and numerical analyses of syngas production from heptane in a porous media reactor. Equivalence ratio (ϕ) and inlet velocity (u) were varied, and exhaust gas hydrogen concentrations were found to increase with both of these parameters. These trends are similar to those found in previous filtration combustion studies [7,24]. Pastore and Mastorakos [27] reformed heptane to syngas in a two-section porous burner and obtained comparable results to Dixon et al. [26] at some operating conditions but with a more limited stable burner range.

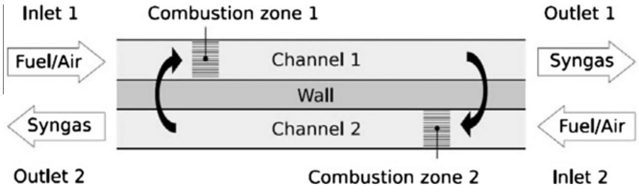

Fig. 1. Counter-flow reactor utilizes heat transfer from hot combustion products through channel walls to preheat incoming reactants.

The earlier study of the porous media reactor operating on heptane provided guidance for the current work. In that study [26], the reactor operated near the conventional flammability limit of heptane without prohibitive soot formation causing any observed degradation in performance. At more extreme conditions, soot buildup did pose a challenge, and Dixon et al. [26] developed a regeneration procedure that is utilized in this study as well. The non-catalytic surfaces of the counter-flow reactor imply that small amounts of deposits should not degrade the performance as long as the channel dimensions and wall properties are not significantly changed due to buildup, thus opening the possibility of using fuels that may produce more soot.

In this work, we focus on conversion of heptane to syngas in the counter-flow reactor. The operating limits and conversion efficiencies are determined, and these quantities are compared to those for the same reactor operating on methane and propane.

2. Experimental and numerical approach

2.1. Experimental apparatus

Figure 2 shows the counter-flow reactor, which is the same design used in previous studies on reforming of methane and propane [21,22]. It consists of four 4 mm high parallel channels constructed of 1 mm thick silicon carbide (SiC) walls. The reactor is 17.3 cm long, with a 91.5 mm long main section and two 40.8 mm long reactor heads where inlets and outlets are located. Also located in the reactor heads are end plugs, which prevent the mixing of combustion products and unreacted fuel/air mixture, and two 6.4 mm wide sections of SiC porous foam (17.7 pores/cm, 9% density) which act as flow straighteners and flame arresters. Two alumina walls spaced 33.6 mm apart enclose the SiC channels. Fine wire B-type thermocouples are inserted into the channels through the alumina insulation 10 mm apart. They sit flush with the channel wall in order to prevent flame holding. The whole reactor is shrouded in alumina insulation to minimize heat losses. Further details about the reactor construction can be found in Schoegl and Ellzey [21].

n-Heptane (Fisher Scientific, HPLC grade) is pumped to an atomizing nozzle mounted inside a mixing chamber. Air is fed to the mixing chamber using a Hastings mass flow controller. Downstream of the controller the total air is split between the atomizing nozzle and heater air by a control valve. The heated air is introduced into the annular space surrounding the nozzle in order to vaporize the atomized heptane and prevent condensation of heptane on the mixing chamber walls. The vaporized fuel/air mixture is fed into a manifold that splits the flow among the four channels. The delivery system, from the mixing chamber to the inlet ports, is wrapped in heat tape and monitored using K-type thermocouples to maintain the system above 150 °C.

Exhaust gas composition is analyzed using a Varian CP 4900 gas chromatograph (GC) with three columns: a molecular sieve (Molsieve) measures diatomic hydrogen (H_2), nitrogen (N_2), oxygen (O_2), carbon monoxide (CO) and methane (CH_4); a porous polymer unit (PPU) gives concentrations of carbon dioxide (CO_2), ethylene (C_2H_4), ethane (C_2H_6), acetylene (C_2H_2) and propane (C_3H_8); and