Emission-free fuel reformers for mobile and portable fuel cell applications

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Abstract

Conventional fuel reformers are complex, multi-component devices which produce large amounts of CO_2 emissions. The main objective of this work is to develop an efficient, compact and emission-free fuel reformer for mobile and portable fuel cell (FC) applications. The concept is based on single-stage catalytic pyrolysis of hydrocarbon fuels into hydrogen-rich gas and carbon products. This approach allows to eliminate the production of carbon oxides (CO and CO_2) and, consequently, the need for the water–gas shift (WGS) and gas separation stages which significantly simplifies the process. The paper presents the experimental results of CO_2-free production of hydrogen-rich gas via catalytic pyrolysis of hydrocarbon fuels (propane, methane and gasoline). The perspectives of CO_2-free fuel reformers for mobile and portable fuel cell applications are discussed in this paper.
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1. Introduction

Fossil fuel-based power sources are major producers of greenhouse gas (mostly, CO_2) emissions. Fuel cells (FCs) seem to be an answer to this environmental problem, however, the main question remains: what fuel and fuel processing technology should be used to produce hydrogen to be used in fuel cells. Conventional fuel reformers are based on complex, multi-stage processes, such as steam–methane reforming (SMR), partial oxidation (POx) or autothermal reforming (ATR). Initially, hydrogen-containing compounds (e.g. hydrocarbons, alcohols, etc.) react with oxidants (water and/or oxygen) resulting in the production of the mixture of hydrogen and carbon monoxide (synthesis gas). This is followed by gas conditioning (e.g. low- and high-temperature water–gas shift (WGS) reactions, preferential oxidation) and gas separation and purification stages. As a result, the conventional fuel reformers produce large amounts of CO_2 emissions which significantly diminishes an environmental appeal of fuel cell-based power systems. The pros and cons of different fuel reforming technologies and pertinent devices for the production of hydrogen to be used in FC are discussed elsewhere [1,2].

One alternative to conventional fuel reforming technologies is pyrolysis (or cracking, decomposition) of hydrocarbons into hydrogen and carbon in air/water-free environment:

$$C_nH_m \rightarrow nC + \tfrac{1}{2}mH_2$$
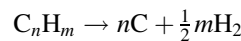
No carbon oxides are formed during the process, due to the absence of oxidants in the reactor; instead, the process produces a valuable byproduct—clean carbon. Another advantage of this approach is that it produces hydrogen in a single step, without WGS and CO_2 removal stages which significantly simplifies the system. The process is applicable to a variety of gaseous and liquid hydrocarbon fuels, and it can potentially produce a stream of hydrogen with the purity up to 95 vol.% (the balance-methane). Thus, the major advantages of fuel reformers based on hydrocarbon pyrolysis (namely, pyrolytic fuel reformers, PFR) are as follows: (i) fuel flexibility, (ii) relative simplicity and compactness, (iii) production of clean carbon byproduct, and (iv) significant reduction (potentially, elimination) in CO_2 emissions.

Thermal decomposition of hydrocarbons occurs at high temperatures (in case of methane, 1400 °C and higher). The use of transition metal catalysts (e.g. Ni, Fe, Co) significantly reduces the maximum temperature of the process, however, there is a catalyst deactivation problem associated with the carbon build-up on the catalyst surface. Fuel reformers operating in a cyclic pyrolysis-regeneration mode have been developed where carbon produced during hydrocarbon decomposition stage was combusted, providing heat for the endothermic reaction [3]. Burning the carbon

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produces more heat than is required to drive the endothermic hydrocarbon decomposition reaction; this results in the reduction in the overall energy efficiency and production of significant amounts of CO_2 byproduct. Earlier we reported that the use of carbon-based catalysts could potentially solve catalyst regeneration and CO_2 emission problems [4]. The objective of this work is the development of efficient CO_2-free fuel reformers based on catalytic pyrolysis of hydrocarbon fuels for mobile and portable fuel cell applications.

2. Fuel options for the pyrolytic reformer

The three major factors that dictate the choice of a fuel for the pyrolytic fuel reformer are: (i) hydrogen gravimetric density (HGD) of the fuel, (ii) ease of hydrogen extraction from the fuel, and (iii) its cost and availability. It is evident that the fuels with high HGD could potentially result in more compact and efficient reformer. Fig. 1 depicts the comparative assessment of different fuel storage options based on their installed (i.e. including storage tank) HGD (for the sake of comparison, liquid hydrogen is also included in the graph).

It can be seen that propane exhibits the highest value of installed HGD due to relatively high molar H/C ratio (2.67) and the possibility of storing it in a liquid form at room temperature and relatively low pressure. It is followed by liquid hydrogen and gasoline. Although methane has the highest possible molar H/C ratio (4), the conventional compressed NG storage systems exhibit relatively low HGD. However, recent breakthroughs in the development of superstrong carbon fiber-reinforced gas storage tanks can significantly increase HGD of the compressed NG systems. The major disadvantage of liquid NG as a fuel for mobile/portable applications relates to the difficulties of handling cryogenic systems.

The amount of energy required to extract 1 mole of hydrogen from methane, propane and gasoline via thermal
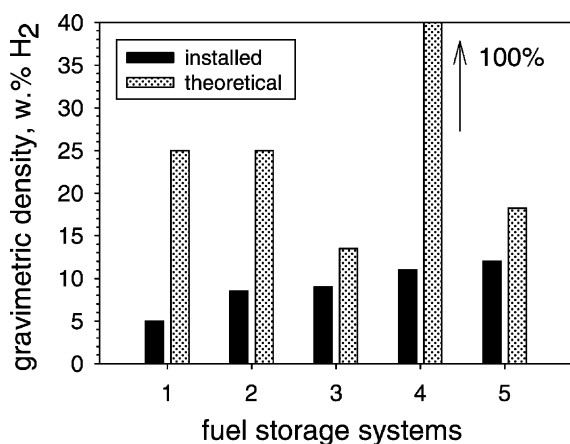

Fig. 1. Comparison of different fuel storage options based on their hydrogen gravimetric densities. (1) Compressed NG (conventional tank), (2) liquid NG, (3) gasoline, (4) liquid H_2, (5) propane.

decomposition reactions is equal to 37.8, 26.0 and $\sim$24 kJ/mole H_2, respectively (for the comparison, 63.3 kJ/mole H_2 is required for SMR). Due to a relatively weak C–H bond in propane molecule (402.2 kJ/mole) it is somewhat easier to thermally split propane than methane molecule (methane C–H bond energy is 440 kJ/mole). Additional advantages of using propane as a fuel for PFR are: (i) the possibility of its delivery into the catalytic reactor with no need for a fuel pump (thus, no moving parts), and (ii) its low cost and widespread availability. Thus, based on the comparative assessment of various fuels, propane would be a preferred fuel for PFR, although, compressed NG and gasoline could also be viable fuel options for the pyrolytic production of hydrogen to be used in mobile and portable power systems.

3. Experimental

3.1. Reagents

Methane (99.99 vol.%, Air Products and Chemicals Inc.) and propane (99.0 vol.%, Praxair) were used without further purification. Samples of gasoline were dried over Drierite for three days before the experiments. The samples of activated carbons (AC) were obtained from Barneby Sutcliffe Corp. (e.g. CL-20, KE, GI), NORIT Americas (Darco KB-B, Darco 20-40, G-60) and Kanzai Coke and Chemicals (MSP-15 and MSP-20). Cabot Corp. supplied different samples of carbon black (CB) (e.g. Vulcan X-72, Black Pearls 2000).

3.2. Apparatus

The experimental set-up for hydrocarbon pyrolysis consisted of three main sub-systems: (1) a thermocatalytic reactor (with temperature-controlled electric heater and pre-heater), (2) a hydrocarbon metering and delivery sub-system, and (3) an analytical sub-system. The catalytic reactors were made out of a fused quartz or ceramic (alumina) in order to reduce the effect of the reactor material on the hydrocarbon decomposition rate. The reactor was resistively heated (externally) and its temperature was maintained at a constant temperature via a type K thermocouple and Love Controls microprocessor. The amount of carbon catalysts (pre-dried) used in the experiments was 5.0 ± 0.1 g. Hydrocarbon flow rates were metered by Gilmont flow meters (for methane and propane) and Cole–Palmer syringe pump (for gasoline).

3.3. Analysis

The analysis of the products of hydrocarbon pyrolysis was performed gas chromatographically: SRI-8610A (a thermal conductivity detector, Ar-carrier gas, a silica gel column, temperature programming: 27–180 °C) and Varian-3400 (flame ionization detector, He-carrier gas, stationary

phase-Hysep D_B). The structural and surface studies of carbon products were performed by X-ray diffraction (XRD, Rigaku) and Scanning electron microscopy (SEM, Jeol) techniques.

4. Results and discussion

In this paper we demonstrate that CO_2-free production of hydrogen-rich gas and carbon byproduct can be accomplished via pyrolysis of selected hydrocarbons (propane, methane, gasoline vapor) in the presence of carbon catalysts. A great deal of efforts was directed toward the development of efficient and stable carbon catalysts for the process. Earlier we reported the data on the catalytic properties of a wide range of carbonaceous materials in methane decomposition reaction [5]. Based on these data and more recent developments, high-surface area carbons (e.g. AC and CB) were employed as catalysts in the hydrocarbon pyrolysis experiments. The hydrocarbon feedstock entered the lower section of the catalytic reactor, thermally decomposed within the catalyst layer, and the products of its decomposition (hydrogen mixed with small amounts of methane) exited via a ceramic filter located at the top section of the reactor. The reactor temperature and the hydrocarbon residence time within the catalytic zone were maintained in the range of 850–950 °C, and 20–50 s, respectively (depending on the hydrocarbon). Before the pyrolysis experiments, the reactor was purged with an inert gas (Ar) at 700 °C for 1 h to remove all the adsorbed water and air from the catalyst surface. Methane and propane were directly introduced into the reactor, whereas, gasoline was evaporated and pre-heated to 250 °C before entering the reactor. Initially, the catalyst filled approximately one-third of the reactor volume, leaving the rest of the space for the carbon to be produced during hydrocarbon pyrolysis. As the hydrocarbon

pyrolysis reaction proceeded, the produced carbon gradually filled almost whole volume of the reactor. At this moment the introduction of hydrocarbon into the reactor was cut off, the reactor let to cool down, and the carbon was dislodged from the reactor. Fig. 2 depicts the results of thermocatalytic pyrolysis of propane and gasoline over selected carbon catalysts.

The experiments demonstrated that a quasi-steady flow of hydrogen-rich gas with $[H_2] \geq 80$ vol.% (the balance-CH_4 and trace amounts of $C_2 +$ hydrocarbons) could be produced by pyrolysis of propane and gasoline over AC-based catalysts at 880–920 °C. The use of carbon black catalysts resulted in the production of the pyrolysis gas with somewhat lower hydrogen concentration (in average, 70 vol.%). Methane pyrolysis over AC (MSP-15) at 950 °C produced the gas with the average hydrogen concentration of 75 vol.% (the balance-unconverted methane). No carbon oxides were detected in the effluent gas of pyrolysis of either hydrocarbon. The production of a relatively steady flow of hydrogen-rich gas can be explained by the catalytic action of the carbon particulates produced during thermal decomposition of hydrocarbons at elevated temperatures. These experimental results are consistent with our earlier findings that at certain conditions pyrolytic carbon species exhibit relatively high catalytic activity toward hydrocarbon decomposition reactions [4,6]. XRD studies of the carbon products produced by hydrocarbon (methane or propane) pyrolysis revealed turbostratic structure of the carbon samples. In particular, the d-spacing (lattice spacing, or spacing between plates in the columnar stacking direction) is somewhat larger (by 0.147 Å) than that of the standard graphite structure.

Fig. 3 depicts the conceptual block-diagram of a power generation system comprising a pyrolytic fuel reformer combined with a fuel cell intended for mobile or portable applications. A hydrocarbon fuel (preferably, propane, or compressed NG, or gasoline vapor) is directed from a
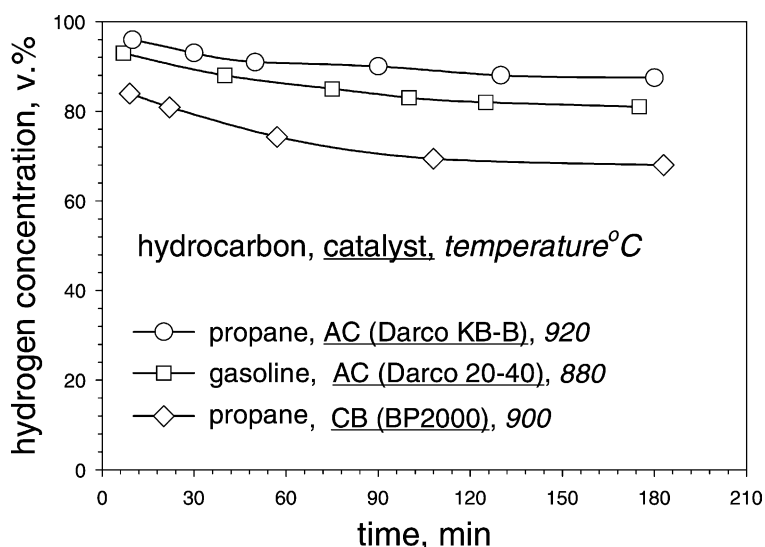

Fig. 2. Production of hydrogen-rich gas via catalytic pyrolysis of propane and gasoline vapor using carbon catalysts.
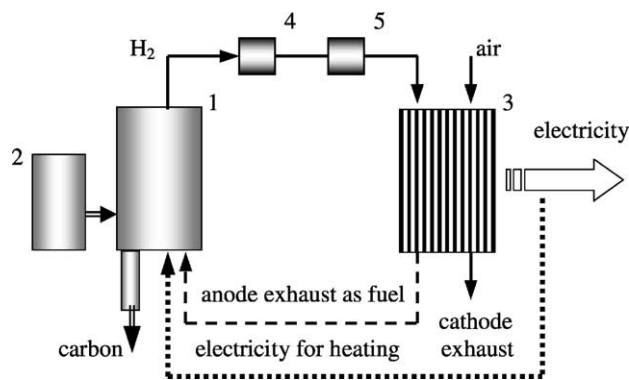
Fig. 3. Schematic diagram of pyrolytic fuel reformer coupled with PEM fuel cell (1) catalytic pyrolysis reactor, (2) fuel tank, (3) fuel cell stack, (4) sulfur trap, (5) methanator.

fuel tank (2) to the PFR (1) where it is decomposed over the carbon catalyst at 850–950 °C producing a stream of the hydrogen-rich gas with the average $[H_2] = 80$ vol.%, the balance being methane (for the comparison, POx- and ATR-reformers produce the gas with $[H_2] = 35$–40 vol.%). The hydrogen-rich gas enters the anode compartment of FC (e.g. polymer electrolyte membrane, PEM, FC) where it electrochemically reacts with oxygen (air) producing dc electricity.

If commercial hydrocarbon fuels are to be used in the power generator, then a sulfur trap (4) and a methanator (5) should be added to the scheme to prevent rapid deactivation of PEM FC by the reactive impurities (e.g. CO and H_2S) originating from moisture and sulfurous compounds potentially present in these fuels. Alternatively, the reactor could be equipped with a hydrogen-selective membrane (e.g. Pd–Ag, or ceramic membrane). The advantages of using a membrane are two-fold: the production of high purity hydrogen (>99 vol.%), and possible decrease in the maximum temperature of the process (due to the shift in the equilibrium concentration of hydrogen in the presence of a membrane).

There are several options for providing the heat input to the reactor to drive endothermic hydrocarbon decomposition reactions. These options include (in the order of minimization of CO_2 emissions): (i) catalytic combustion of a fraction of the hydrocarbon fuel (in case of propane, approximately 5% of the total amount), (ii) catalytic combustion of the anode exhaust gas (hydrogen–methane mixture), and (iii) the resistive heating of the reactor (equipped with a membrane) using a fraction of the electrical output of the FC (in case of propane, approximately 20% of the output). It is evident that the latter case presents a zero-emission option. PFR utilizes 50–60% (depending on the hydrocarbon) of the total chemical energy of the fuel leaving the remainder in the form of stored energy, i.e. carbon (rather than CO_2 byproduct). It should be noted that, although SMR process uses an entire energy of the fuel, the net energy efficiencies of both steam and pyrolytic reforming options are fairly close due to the substantial energy consumption associated with the steam reforming reaction, and CO_2 capture and sequestration (for detailed calculations see [7]). The estimated specific energy of a propane-fueled PFR is in excess of $1 kW_{th}$ h/kg (including a fuel storage).

The carbon product in the form of fine particulates remains within the reactor for the duration of a power generating cycle and is dislodged from the reactor during a refueling operation (e.g. by blowing it with nitrogen into a special container). A quarter or third of the total amount of carbon particulates produced remains in the reactor as seed particles for a new cycle of pyrolytic reforming process. The production of 1 kg of hydrogen is accompanied with the co-production of approximately 3 kg of carbon (if NG is used as a fuel) or 4.5 kg of carbon (if propane is a fuel). The carbon product collected from mobile and portable power systems is to be directed to a central carbon storage and processing facility. There are several important application areas for the carbon product, e.g. metallurgical industry (carbon electrodes for the aluminum and ferro-alloys production), tires, plastics, construction materials, etc.

5. Conclusion

The results presented in this paper prove that it is technically feasible to develop a hydrocarbon fuel reformer for mobile/portable fuel cell applications without (or drastically reduced) CO_2 emissions. The lack of bulky gas conditioning and separation stages potentially makes the reformer more compact and simple compared to conventional reformers. Furthermore, depending on the mode of operation, the pyrolytic reformer can produce either high purity hydrogen (membrane option), or CO/CO_2-free hydrogen-rich gas with the average $[H_2] = 80$ vol.%, the balance-methane (which compares favorably with the quality of reformat gas, i.e. $[H_2] = 35$–40 vol.%, produced by POx- and ATR-based reformers). Widely available and inexpensive propane is the preferred fuel for the pyrolytic reformer, however, gasoline or compressed NG could also be efficiently used for the hydrogen production.

PFR–FC-based power systems could be advantageously used in many emission-restricted application areas, e.g. mines, aerospace, recreational and emergency vehicles, etc. Potentially, their contribution to the general transportation area will increase once CO_2 becomes a regulated pollutant. Due to the lack of emissions and moving parts (i.e. lack of chemical and acoustic "signatures"), PFR–FC power systems could find an important application in military area (soldier power). Besides the use in mobile and portable devices, PFR–FC systems could be advantageous for the distributed power generation in many emission-sensitive areas, e.g. hospitals, recreational facilities, tunnels, etc.

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