

# Hydrogen from Waste Hydrocarbons in a Compound Hydrogen Generator

## Summary

Waste streams of paper, cardboard and plastic constitute a rich source of hydrogen when gasified if a cost-effective way can be found to simultaneously extract the purified hydrogen and concentrate the carbon dioxide for sequestration. A novel approach, called H<sub>2</sub>H, is proposed for compound hydrogen generation that provides a convenient and inexpensive way to produce hydrogen from gasified hydrocarbon feedstocks, independently of the utility grid or any external source of heat or power. This concept uses a solid-state ceramic device, called a double-cell, to separate hydrogen from CO<sub>2</sub> at the high temperatures typical of hydrocarbon gasification. The technology involves partial oxidation of gasified hydrocarbon feedstocks using an electrochemical oxidation cell, EOC, to generate a hydrogen-rich gas mixture. Pure hydrogen is extracted from the resulting mixture and compressed using a protonic ceramic separation cell, PSC. The EOC and PSC are connected in electrical series in a double-cell. The power required to operate the PSC is provided by the EOC, and no external power source is required. High purity hydrogen is thus produced that is suitable for use in PEM fuel cells without additional processing. The hydrogen may be supplied directly to a fuel cell to generate electric power or transferred to external storage tanks for future use. The exhaust is nearly pure CO<sub>2</sub> suitable for sequestration. The heat required for gasification is provided by excess heat generated by the double-cell. The stand-alone system offers clean, quiet and efficient hydrogen production from a wide variety of renewable and non-renewable hydrocarbon feedstocks. The system is ideal for distributed hydrogen production where electric power is either unavailable or too costly.

## 1.0 Introduction

Hydrogen is produced industrially on a large scale today—most commonly by steam methane reforming followed by partial swing adsorption. This process is energy intensive, requiring large, centrally located plants to achieve the necessary economies of scale, and has a large CO<sub>2</sub> footprint. Alternatively, hydrogen may be generated by electrolysis of water, which requires a supply of electric power from the utility grid. Compound hydrogen generation is a method for producing

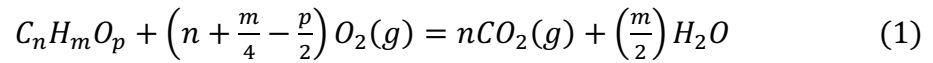
pure hydrogen from hydrocarbons in a device that does not require any external power source [1-5]. Furthermore, the system is scalable from grams of hydrogen per hour to tons per day, and is thus, suitable for distributed hydrogen production at a wide range of scales. In the system, an electrochemical oxidation cell, EOC, is used to partially oxidize a gasified hydrocarbon feedstock consisting of hydrogen, carbon monoxide, carbon dioxide, water vapor, and some low molecular weight organic compounds. The resulting hydrogen-rich mixture flows past an integrated protonic ceramic separation cell, PSC, operating in electrical series and at about the same temperature, where the hydrogen is galvanically separated and compressed. The hydrogen thus produced may be used on-site in fuel cells for generating electric power or compressed and stored for later use on-site or for delivery to some other site. The hydrogen may also be used as a reagent in chemical processes, or even run in a clean-burning internal combustion engine. **The salient feature of this hydrogen generating concept is that a self-contained, integrated system, independent of any external power source, is capable of producing pressurized hydrogen at high net energy conversion efficiency.** The energy required for fuel processing and compression is obtained by consuming some portion of the fuel enthalpy in an EOC, which makes the system portable and independent of any fixed power infrastructure. Similar to portable diesel generators, the principle difference is that a portable diesel generator produces only electric power from diesel fuel, whereas this system produces hydrogen on-site, which can either be consumed immediately to make electric power or stored for later use. This enables deployment of hydrogen fuel cells in a wide range of stationary and mobile applications from cars to trucks to trains to ships, which currently rely on fixed-based hydrogen ‘filling-stations’ or pipeline distribution networks.

The hydrocarbon feedstock may be almost any hydrocarbon containing C-H bonds. The underlying operating principle involves generating H<sub>2</sub> by breaking these C-H bonds and replacing them with C-O bonds, while excluding formation of O-H bonds. Virtually any hydrocarbon molecule can be gasified by pyrolysis in the absence of air, including coal, crop residue and municipal solid waste, etc. The only requirement is that it must be gasified into a form that is compatible with the fuel-side electrode of the EOC. In this sense, the system is practically independent of fuel selection, accepting a wide range of hydrocarbons. The system produces CO<sub>2</sub> as the principle constituent in the exhaust, which may be sequestered if necessary. Hydrogen obtained from natural gas and fossil fuels is ‘gray’ hydrogen. That is, as with all fossil fuel combustion, the exhaust contributes to global atmospheric CO<sub>2</sub> levels. Hydrogen produced from

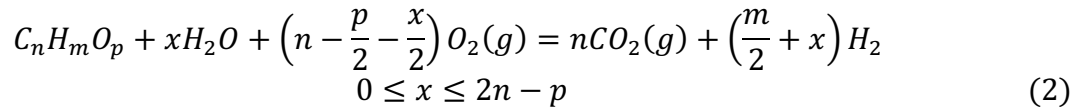
biomass is carbon-neutral with respect to atmospheric CO<sub>2</sub> as long as external power sources derived from fossil fuel combustion are not involved. On balance, living plants convert CO<sub>2</sub> back into biomass by photosynthesis. It is not possible to generate ‘green’, or zero-carbon, hydrogen using any hydrocarbon feedstock without sequestering the CO<sub>2</sub> from the exhaust stream.

## 2.0 Generalized Hydrocarbon Thermochemistry

The generalized reaction for complete combustion of any hydrocarbon containing  $n$  carbon,  $m$  hydrogen and  $p$  oxygen atoms to CO<sub>2</sub> and H<sub>2</sub>O is,



Eq 1 is exothermic, and capturing the heat generated is the basis for how all heat engines work. An alternative reaction may be carried out wherein the fuel is only partially oxidized. This reaction may similarly be generalized for the case where H<sub>2</sub> and CO<sub>2</sub> are the only reaction products.



A combination of steam and oxygen reacts with the hydrocarbon fuel to produce hydrogen instead of water, so the enthalpy of formation of  $\left(\frac{m}{2} + x\right)$  moles of water is avoided. H<sub>2</sub>H uses some of the heat generated by this reaction to separate the hydrogen from the CO<sub>2</sub> and compressing it for use in a fuel cell.

In an idealized H<sub>2</sub>H system, the products consist only of CO<sub>2</sub> and H<sub>2</sub>. A further constraint is imposed because the proton flux in the PSC must be twice the oxygen-ion flux in the EOC because the current is uniform in the closed-loop series circuit. As a practical matter, a small amount of hydrogen must be slipped with the exhaust, but in an idealized H<sub>2</sub>H system all hydrogen leaves the fuel channel as protons. Oxygen may enter the fuel channel in three ways; as molecular oxygen incorporated in the fuel, as water, or as oxygen ions coming from the EOC. The oxygen ion source and protons are explicitly included in Eq. 3, where ions are enclosed in braces—a notation intended to denote that these atoms, which participate in the global reaction, entered the fuel channel as ions. The reaction is not charge-balanced. Electrons are generated at the electrodes which pass to the external circuit.

$$C_nH_mO_p + xH_2O(g) + \left(\frac{m}{2} + x\right)\{O^{2-}\} = nCO_2(g) + 2\left(\frac{m}{2} + x\right)\{H^+\} \quad (3)$$

$$x = \left(n - \frac{m}{4} - \frac{p}{2}\right) \quad (4)$$

For any given hydrocarbon molecule  $x$  gives the parameter for how much additional water is required. Eq. 3 gives the constrained condition for H2H operation, where H<sub>2</sub> (as two protons) and CO<sub>2</sub> are the only reaction products. An arbitrary amount of additional water (or other inert gases) may be added to the left-hand-side, but these will appear in the exhaust unchanged. The constraint is introduced by the parameter,  $x$ , which is the mole fraction of water that actually participates in the reaction. Any additional water that may be added to prevent coke formation is not included. When  $x = 0$ , partial oxidation applies, and  $n$  moles of CO<sub>2</sub> are generated. When  $x$  assumes its maximum value,  $\left(n - \frac{m}{4} - \frac{p}{2}\right)$ , the maximum amount of reforming applies,  $n$  moles of CO<sub>2</sub> are still generated, but  $x$  moles of water are also consumed, producing  $x$  moles of additional hydrogen by endothermic reformation.

An H2H system operates adiabatically so thermal balance must be ensured. Partial oxidation is exothermic, generating  $n$  moles of CO<sub>2</sub> at 395 kJ/mol (900K). Steam reforming is endothermic, consuming 242 kJ/mol. It is seen from Eq. 4 that the reaction can never become endothermic as constrained, so some waste heat will always be generated. Some of this heat is required to gasify the fuel, to make steam and compensate for thermal losses in the system. Heat is also generated by ohmic heating due to the passage of current in the circuit.

## 6.0 Conclusions

Hydrogen is a high-value fuel for use in a PEM fuel cell. More than 60 kilograms of hydrogen, or sixty gallons of gasoline equivalents (gge) may be generated per ton of biomass. 210 kg of hydrogen can be generated per ton of polyethylene. Due to the high degree of integration of the system, a rough estimate of the physical dimensions of a filling station sized system, excluding the gasifier, with an output capacity of 1000 kg H<sub>2</sub>/day would occupy about 300 m<sup>3</sup>. Such a hydrogen generating system offers a completely new pathway for transitioning to hydrogen-based power. It has been shown that with proper thermal and electrical integration between EOC and PSC cells, gasified hydrocarbon feedstocks may be converted to hydrogen without any supplemental energy input. Biomass provides an opportunity to increase the use of carbon-neutral fuels while reducing

dependence on imported petroleum. Consuming plastic waste with CCS offers even greater potential. With the system, hydrogen may be produced remotely at almost any scale from a few grams to tons without the need for access to a power grid or natural gas pipelines.

The complete text of this manuscript may be found online at: DOI: 10.13140/RG.2.2.16681.01120

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