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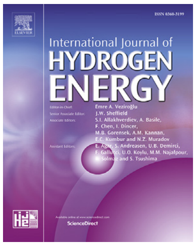

Cogeneration of power and substitute of natural gas using electrolytic hydrogen, biomass and high temperature fuel cells

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ABSTRACT

Energy storage from renewable sources is one of the main current goals for the energy sector, and the production of a substitute of natural gas could be a good solution to solve the problem in the short term, helping the transition to hydrogen in the long term.

Renewable energy sources usually generate variable electric power or medium/low energy content gas. This paper proposes a way to upgrade these products through the use of electrolytic hydrogen. By using electrolytic oxygen as an oxidant for biomass partial oxidation and for high temperature fuel cells, the exhaust gas after post-combustion is an almost pure mixture of water and carbon dioxide. Once such a gas is dehydrated, the carbon dioxide can be mixed with electrolytic hydrogen to obtain methane through the Sabatier process.

Four layouts based on molten carbonate fuel cells and solid oxide fuel cells has been investigated. The results obtained are very similar: the conversion efficiency is close to 60% and the mix of energy output consist of fuel for about 75% and electric power for about 25%.

Introduction

Energy storage from renewable sources is one of the main current goals for the energy sector. Storage as chemical energy should be the best option under several aspects and hydrogen, in particular, thanks to its flexibility and low environmental impact, should be the best long term option when produced from exceeding electric energy through water electrolysis. Apart from some niche applications, the use of hydrogen requires to implement a completely new energy system for production, storage, distribution and final use. Production technologies are available and could be gradually implemented wherever there is exceeding energy from renewable sources, whereas storage and distribution are the bottleneck and limit the use to local supply. The need for significant investment in the distribution infrastructure does not allow the exploitation of the whole potential of hydrogen production.

The Sabatier process allows to convert carbon dioxide into methane by using hydrogen (e.g. Ref. [1]):

$$CO_2 + 4H_2 \Rightarrow CH_4 + 2H_2O$$

Supplying an over-stoichiometric flow of hydrogen, the almost whole conversion of carbon dioxide can be achieved so that the final dry gas obtained contains methane and hydrogen, plus not significant percentage of other substances. It is called substitute of natural gas (SNG), or sometimes synthetic natural gas, because its characteristics

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Nomenclature

Symbols

E°	standard potential
F	Faraday constant
n	number of electrons transferred
p	pressure
R	gas constant
T	temperature
V	voltage
x	molar fraction

Subscripts

6	working at 6 bar
30	working at 30 bar
an	anodic
base	referred to the base case
c	chemical
cat	cathodic
e	electric
η	efficiency

Acronyms

HHV	Higher Heating Value
MCFC	Molten Carbonate Fuel Cell
NG	Natural Gas
POX	Partial OXidation
SNG	Substitute of Natural Gas
SOFC	Solid Oxide Fuel Cell
STIG	STeam Injected Gas turbine

are very similar to those of natural gas (NG) and therefore, can be distributed, stored and used exactly as we do with NG. The amount of hydrogen allowed for distribution through existing NG infrastructure can be up to 20% [2]. SNG can be used for combustion just like NG and can be used directly into internal combustion engines resulting in performance improvement [3].

Converting electrolytic hydrogen to a substitute of natural gas could be a solution, given the fact that such a gas can be distributed and utilised just as we do with natural gas.

In this way the production of hydrogen from renewable energy sources could be largely developed postponing investments for storage and distribution infrastructure. Also fossil fuels, and coal in particular, could be used as a carbon source for Sabatier process [4–6]. And, obviously, a mix of coal, biomass and wastes could be suitable.

A system like the one shown in Fig. 1 has been analysed in previous papers [7,8] where a gas turbine or an internal combustion engine are considered as a power unit. In this paper the option to use high temperature fuel cells is investigated using AspenONE® v8.4 for simulation.

The goal of the system is to obtain valuable electric power and valuable fuel, starting from renewable variable electric power, biomass and/or wastes. Though other kinds of biomass and other processors can be suitable, a lignocellulosic biomass (Table 1) has been considered for partial oxidation (POX) into a gasifier, like in the previous papers cited. The hydrogen required for the Sabatier process is generated by an electrolyser, using exceeding power from renewable energy sources. An interesting issue is that the electrolytic oxygen generated is used, in part for the biomass partial oxidation, and in part for the cathodic fuel cell stream. Since the oxygen produced by electrolysis exceeds the amount required by the process, the remaining could be sold for several different uses given its particular high purity. By replacing air with electrolytic oxygen, water and carbon dioxide are the unique relevant components of combustion products, while the amount of nitrogen is almost negligible. Therefore, a stream of almost pure carbon dioxide can be easily obtained and fed to the Sabatier process.

Topping system layouts

Just as in the systems previously investigated, the schematics of the biomass process (Fig. 2) and of the Sabatier process (Fig. 3) do not change when changing the power unit. The electrolysis is assumed to be carried out at 30 bar in order to favour the methanation process. Also the POX reactor operates at such a pressure due to the availability of pressurised electrolytic oxygen.

Concerning the Sabatier process, even the flows do not change, because the amounts of hydrogen and carbon dioxide do not change. There could be only changes of the water contents when changing the power unit, but they are negligible. The situation of the biomass process is different because the flow of electrolytic oxygen depends on the working temperature and pressure of the fuel cells and therefore, flow and composition of the syngas change.

The Sabatier process is supplied with electrolytic hydrogen and carbon dioxide recovered from the exhaust gas downstream the fuel cell stack. The process is carried out in three intercooled steps in order to reduce the water content and to supply the syngas at 300 °C to the following step. Moreover, the first step includes a partial recycle of the outlet gas, according to the typical layout of methanation process from Haldor Topsoe [9].

For the power unit both molten carbonate fuel cells (MCFC) with internal reforming and solid oxide fuel cells (SOFC) has been considered with two different layouts. The first one is based on fuel cell stacks working at the same pressure of the POX, while in the second one the pressure of the fuel cell stacks is lower and work is recovered also by gas turbines.

Four cases were examined:

- MCFC working at 30 bar (MCFC30);
- SOFC working at 30 bar (SOFC30);
- MCFC working at 6 bar (MCFC6);
- SOFC working at 6 bar (SOFC6).

The first layout is simpler because the topping power system is made up by the fuel cell stack and the afterburner only (Fig. 4) and there is no need for re-compressing the exhaust gas before sending to the methanators. All the thermal energy recoverable is converted in a bottoming power system.

The second layout is more complex and requires three gas turbines and three compressors. Two gas turbines precede the fuel cell stack to lower the pressure of syngas and oxygen to

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