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Hydro-methane and methanol combined production from hydroelectricity and biomass: Thermo-economic analysis in Paraguay

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ABSTRACT

A thermo-economic analysis regarding large scale hydro-methane and methanol production from renewable sources (biomass and renewable electricity) is performed.

The study is carried out investigating hydrogen and oxygen generation by water electrolysis, mainly employing the hydraulic energy produced from the 14 GW Itaipu Binacional Plant, owned by Paraguay and Brazil. Oxygen is employed in biomass gasification to synthesize methanol; the significant amount of CO_2 separated in the process is mixed with hydrogen produced by electrolysis in chemical reactors to produce hydro-methane.

Hydro-methane is employed to supply natural gas vehicles in Paraguay, methanol is sold to Brazil, that is the largest consumer in South America.

The analysis is performed employing time-dependent hydraulic energy related to the water that would normally not be used by the plant, named "spilled energy", when available; in the remaining periods, electricity is acquired at higher cost by the national grid.

For the different plant lay-outs, a thermo-economic analysis has been performed employing two different software, one for the design point and one for the time-dependent one entire year optimization, since spilled energy is strongly variable throughout the year.

Optimal sizes for the generation plants have been determined, investigating the influence of electricity cost, size and plant configuration.

1. Introduction

As a developing country, Paraguay faces many challenges regarding the improvement of its energy systems. Although Paraguay has a very large hydroelectric capacity, energy demand is sustained mostly by imported hydrocarbons, especially in the transport field. Considering the low cost of electricity, compared with developed countries, the production of fuels starting from exceeding renewable energy may represent an interesting solution. One of the main actors can be hydrogen, produced by water electrolysis employing the electricity of the largest renewable production plant in the world, the 14 GW hydroelectric facility of Itaipu (owned 50% by Brazil and 50% by Paraguay, meaning that 7 GW are property of Paraguay) [1].

Hydrogen is one of the most promising energy vectors in the near future [2,3]. However, its low energy to volume ratio (compared to gasoline and diesel) represents an obstacle towards its large scale diffusion in the transportation sector. Other critical aspects are related to its distribution (pipelines and road transportation) and final use, given the high cost of fuel cells or ICE hydrogen powered vehicles [4]. Hydrogen conversion into other fuels or "chemicals" may represent a solution to bypass the limitations related to its low energy to volume ratio. In the Sabatier reaction hydrogen is mixed with carbon dioxide in order to produce methane, according to the Sabatier reaction:

$$4H_2 + CO_2 = CH_4 + 2H_2O \tag{1}$$

The reaction is highly exothermic ($\Delta H = -165$ kJ/mol) and proceeds in a temperature range between 250 and 400 °C at relatively low pressures (between 2 and 10 bar) on a catalytic bed, usually based on Nickel, Ruthenium or Aluminum [5]. Previous experimental studies [5,6] have shown that the final composition of gas, after water separation, is mainly CH_4, plus H_2 and CO_2 not reacted. The presence of hydrogen allows for classifying the gas as hydro-methane, that is a gas mixture composed mainly by methane and containing H_2 in a range from 5% to 30% in volume terms. This fuel can be transported and used with technologies similar to the ones

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Nomenclature

Abbreviation

AEC	Alkaline Electrolytic Cell
ASU	Air Separation Unit
CDE	Ciudad Del Este (Paraguay)
DC	Direct Costs
FCI	Fixed Capital Investment
HHV	Higher Heating Value
ICE	Internal Combustion Engine
LHV	Lower Heating Value
PBP	Pay Back Period
PEC	Purchased Equipment Cost
PTI	Parque Tecnologico de Itaipu
TCI	Total Capital Investment
TPG	Thermochemical Power Group
WGS	Water Gas Shift

Symbols

C	cost (€)
E	electricity flow (kW h)
M	mass flow (kg/h)

Subscript

acq	acquired
cap	capital
cons	consumed
i	*i*th time step
inst	installed
prod	produced
req	required
var	variable

employed for methane, bypassing the problems related to hydrogen. In particular, hydro-methane can be employed in traditional natural gas ICE powered vehicles that are significantly cheaper compared to fuel cells powered vehicles.

The considerable amount of carbon dioxide (5.5 kg for each kg of H_2) for the Sabatier reaction is obtained from biomass gasification, employing the large amount of pressurized O_2 produced in electrolyzers as gasification agent. As mentioned in a previous study [7], the syngas obtained by biomass gasification, after cleaning and WGS section, is composed of H_2 and CO_2; after mixing with H_2 produced in electrolyzers, the gas has the optimal composition for the Sabatier reaction, in order to synthesize hydro-methane [7].

One of the innovative aspects of this study is the combined production of hydro-methane and methanol in the same plant. Methanol production by biomass gasification is a well known process, as reported in [8,9]: during the process, large amounts of CO_2 have to be separated in a Selexol unit. The remaining syngas, made of H_2 and CO, is sent to methanol reactor, where the following reaction takes place:

$$2H_2 + CO \rightarrow CH_3OH \qquad (2)$$

Methanol is widely used in several current industrial applications. Although in Paraguay its demand is actually limited, Brazil is one of the largest consumers of methanol of the world: its homeland production satisfies only 30% of the internal demand, therefore it represents an ideal market for methanol exportation [10].

In the first part of the work a design point thermo-dynamic and energetic analysis of the plant for hydro-methane and methanol combined synthesis is performed. The results of this analysis (in terms of energy and mass flows) are employed to perform a time-dependent thermo-economic analysis during an entire one-year period in order to evaluate the plant optimal size and management, for different electricity cost scenarios in Paraguay.

The thermo-economic optimization is carried out using two different software, one for the design point thermodynamic and chemical analysis, named WTEMP (Web-based Thermo-Economic Modular Program) and one for time-dependent plant management optimization, named WEPoMP (Web-based Economic Poly-generative Modular Program), both developed by the TPG at University of Genoa.

2. Design point thermodynamic analysis of the process

The thermodynamic plant analysis and optimization at the design point is carried out employing the WTEMP software, developed by TPG at University of Genoa in the last 25 years [11,12]. WTEMP adopts a modular approach and a standard component interface, that allows the user to build complex cycle configuration in a short time. This approach maintains the flexibility and the extendibility of the library components (more than 90 modules are available at the moment), allowing users to add new components without modifying the core of the code [13,14]. Each component is described by three subroutines, that define its thermodynamic, exergetic and thermo-economic properties at the design point. This paper focuses on the thermodynamic analysis of the methanol and hydro-methane synthesis.

The simplified plant layout, not including heat exchangers, is shown in Fig. 1. Oxygen and hydrogen are produced by 1 MWe commercially available alkaline electrolysers, operating at 80 °C and 30 bar, with an electrical consumption of 4.7 kW h/N m^3 of H_2 corresponding to an efficiency of 75% based on HHV [15]. Higher efficiencies could be achieved with proton exchange membrane or solid oxide electrolysers, but they are not available on the market at competitive costs, in particular for large sizes investigated in this work: for these reasons, alkaline electrolysers (AECs) are chosen.

Oxygen, produced at 30 bar, is employed for biomass gasification; the syngas exiting the gasifier at 1000 °C, is cooled and sent to a cleaning section including a scrubber and a Water Gas Shift (WGS). During the gas cooling, super-heated steam needed for WGS and biomass gasification is generated, without need for an external boiler, as reported in [8].

After the cleaning process, the gas is cooled and water is separated, therefore the syngas is made of H_2, CO and CO_2 mainly. In order to obtain stoichiometric conditions at the inlet of methanol reactor, CO_2 must be removed in a Selexol unit, in order to obtain the composition reported in Eq. (2). The gas obtained in this way is compressed to 100 bar before entering the methanol synthesis reactor, operating at 240 °C: at the outlet, the gas is cooled and methanol is condensed downstream the reactor, while the most of the remaining syngas (85%) is sent back to the reactor.

The process described above is quite well known and commercially available: it is worth noting that, in the present configuration, O_2 for biomass gasification is available from water electrolysis, therefore the installation of an Air Separation Unit, normally used in this kind of plants, is avoided. The innovative aspect of this process is that CO_2 separated by Selexol is mixed with H_2 produced by pressurized alkaline electrolysers and then sent to Sabatier reactors to produce hydro-methane, according to Eq. (1). Since Sabatier reaction is highly exothermic, heat