Hydrogen production from residual biomass via air-steam gasification for a bioenergy-based economy in Sicily

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ABSTRACT. *This work aims at evaluating the potential impact of hydrogen production in Sicily by citrus peel air-steam gasification. The thermochemical behavior of such feedstock was evaluated in a previous work by means of a bench-scale fluidized bed reactor operate at different temperature and steam to biomass ratios. A virtual scale-up of the gasification system was developed in order to assess the combined hydrogen and power production potential. The downstream processes of syngas, i.e. hydrogen separation through Pressure Swing Adsorption (PSA) and off-gas combustion in engines for power production, were simulated considering the efficiencies reported in literature and datasheets. The results of this study show that, depending on the gasifier operating conditions, from 1,000 to 1,414 t/year of hydrogen can be produced by exploiting the totality of available citrus peel in Sicily (33,000 t/year). It has been estimated that from 927 to 15,900 MWh/year of electricity can be produced, in combination with hydrogen, by internal combustion engines and exported to the national grid, while the recovered heat may be used for the citrus peel drying.*

RÉSUMÉ. *Cet article vise à évaluer l'impact potentiel de la production d'hydrogène en Sicile par la gazéification d'air-vapeur à écorces d'agrumes. Le comportement thermochimique de cette matière première a été évalué dans un travail précédent au moyen d'un réacteur à lit fluidisé à l'échelle du laboratoire fonctionnant à différentes températures et différents rapports vapeur / biomasse. Une mise à l'échelle virtuelle du système de gazéification a été développée afin d'évaluer le potentiel combiné de production d'hydrogène et d'électricité. Les processus en aval du gaz de synthèse, à savoir la séparation de l'hydrogène par adsorption à pression modulée (APM) et la combustion des effluents gazeux dans les moteurs de production d'énergie, ont été simulés en tenant compte des rendements rapportés dans la littérature et les fiches techniques. Les résultats de cette étude montrent que, selon les conditions de fonctionnement du gazéificateur, il est possible de produire de 1 000 à 1 414 t / an d'hydrogène en exploitant la totalité des écorces d'agrumes disponibles en Sicile (33 000 t / an). Il a été estimé que de 927 à 15 900 MWh / an d'électricité peuvent être produits combinant à l'hydrogène par des moteurs* *à combustion interne et être exportés vers le réseau national, tandis que la chaleur récupérée peut être utilisée pour le séchage des écorces d'agrumes.*

KEYWORDS: *bioenergy, hydrogen, biomass gasification, citrus peel.*

MOTS-CLÉS: *bioénergie, hydrogène,gazéification de la biomasse, ecorces d'agrumes.*

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1. Introduction

The great environmental impact of human activities in terms of greenhouse gas (GHG) emissions led the international community to consider the reduction of carbon emissions as one of the most important priorities. In EU, the country members are officially committed to cut the GHG emissions by acting on increasing renewable energy share in the power production sector, increasing energy efficiency in both the industrial and building sectors (D'Agostino and Parker, 2018; Cannistraro *et al*., 2015; Cannistraro *et al*., 2016, Cannistraro *et al.*, 2017), and reducing the dependence on fossil fuels in transportation (Youssef (2018)). In this political framework, researchers' efforts are focused on the development of material and technologies for energy storage, in both thermal (Mastronardo *et al*., 2017; Mastronardo *et al*., 2017) and electrical sectors (Lai *et al*., 2017; Nikolaidis and Poullikkas, 2018). Indeed, energy storage technologies are of fundamental importance for the massive deployment of renewable energy such as solar, wind and photovoltaic (del Río *et al*., 2018; Piperopoulos *et al*., 2018). Biomasses are alternative and programmable renewable sources that can be used for decentralized heat and power production (Palomba *et al*., 2017; Tagliaferri *et al*., 2018), as well as liquid biofuels (Oh et l., 2018; Maisano *et al*., 2017) and bio-hydrogen (Kraussler *et al*., 2018). In particular, biomass gasification allows producing both liquid and gaseous biofuels (Cerone *et al*., 2017; De Blasio and Järvinen, 2017). These may be used for power production by burning them in gas turbines (Brusca *et al*., 2015), internal combustion engines (Kana *et al*., 2018) or solid oxide fuel cells (Pianko-Oprych and Palus, 2017; Fragiacomo *et al*., 2018). Syngas produced during thermochemical biomass gasification can also be used for bio-hydrogen production in a sustainable way, since it would come from a renewable source. Indeed, in addition to the issue of its storage (Pedicini *et al*., 2011), one of the main limitations of hydrogen diffusion is linked to the wide use of hydrocarbon steam reforming for its production. Bio-hydrogen from biomass can be used in the chemical industry, as well as electricity production by high or low temperature fuel cells (Nicotera *et al*., 2015; Tavares *et al*., 2003; Cucinotta *et al*., 2017; Cucinotta *et al*., 2018). Further advantages can be achieved when residual biomass or wastes are used as feedstocks for the thermochemical conversion. For instance, Sicily is an Italian region where a relevant amount of agro-industrial residues could be exploited for gasification. Citrus peel is a residue of the citrus juice production, whose annual production in Sicily is estimated about 33,000 t/y (dry matter) (Paina *et al*., 2010). Prestipino *et al*. (2017) and Chiodo *et al*. (2017) observed that citrus peel from citrus juice production process could be converted into hydrogen rich syngas through air-steam and steam gasification, respectively, with very good efficiencies. Prestipino *et al.* showed that citrus peel air-steam gasification lead to cold gas efficiencies between 0.45-0.7 in the temperature range 700-850 °C (Prestipino *et al*., 2017, Chiodo *et al*., 2017). Hydrogen rich syngas can be upgraded for hydrogen separation with high purity degree through pressure swing adsorption (PSA).

Based on the experimental yields and efficiency of air-steam gasification experiments in a lab-scale equipment, the aim of this work is to assess the hydrogen potential in Sicily from citrus peel gasification. PSA performances and characteristics were obtained from literature data.

2. Materials and methods

The feedstock used in this work is citrus peel provided by a citrus juice company located in Sicily. This feedstock is the heterogeneous residue of juice extraction, consisting of skin, seeds and residual pulp. Before its characterization and testing in the gasification system, the sample has been grinded and sieved in order to reach a particle size in the range 0.4 < d < 1 mm. The ultimate and proximate analysis is conducted by means of a CHNS analyzer (CHNSO Thermo Fisher Scientific, Flash EA 1112) and a thermogravimetric analyzer (in both air and N_2 atmospheres), respectively, whose results are reported in Table 1 (Prestipino *et al*., 2017).

Table 1. Ultimate and proximate analysis of citrus peel

<table>
<tr><td colspan="8">Ultimate Analysis [$\%wt_{db}$]</td></tr>
<tr><td></td><td>C</td><td colspan="2">H</td><td>N</td><td>S</td><td>O[a]</td><td>Ash</td></tr>
<tr><td></td><td>43.0</td><td colspan="2">6.3</td><td>1.3</td><td>0.1</td><td>40.8</td><td>8.5</td></tr>
<tr><td>Moisture [%wt]</td><td colspan="2">VM [$\%wt_{db}$]</td><td colspan="2">FC [$\%wt_{db}$]</td><td>Ash [$\%wt_{db}$]</td><td>HHV_{db}[b] [MJ/kg]</td><td>LHV_{db} [MJ/kg]</td></tr>
<tr><td>8.0</td><td colspan="2">71.9</td><td colspan="2">19.6</td><td>8.5</td><td>18.0</td><td>16.6</td></tr>
<tr><td colspan="8">a. by difference;
*HHV = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.015N - 0.0211A</td></tr>
</table>

2.1. Gasification unit

The bench-scale gasification system used for determining the gasification performance of such feedstock consists of a bubbling fluidized bed gasifier that is continuously fed by a screw feeder, which connect the reactor to a vessel with a volume of about 1 l where the feedstock is stored. Downstream the reactor, the producer gas (syngas) is filtered and then cooled in order to remove solid particles (mainly ashes) and condensable components (tars, oils and water), respectively. The cleaned syngas is then analyzed by means of a micro-GC analyzer (Pollution Vega micro-CG) in order to quantify the main permanent gases. A more detailed description of the experimental set-up is reported in a previous research work (Galvagno *et al*., 2017). In this work, the system has been operated at 750 °C and 850 °C, an equivalence ration (ER) of 0.3, and steam to biomass ratio (S/B) of 0.5 and 1.25. These operative conditions were studied in order to compare their impacts on the energy efficiency of the system and the yields of the different products, i.e. cold gas efficiency of the gasifier, hydrogen yield, net electricity production, and energy efficiency of the combined power and hydrogen production system. The output from the gasifier are used as input for the downstream units.

2.2. PSA and power generation units

The hydrogen separation unit is based on the Pressure Swing Adsorption (PSA) technology. This process is based on the absorption of some specific gases at a determined pressure on an adsorbent material, while the purified gases flow out. In this work, the authors make use of literature-derived data for the virtual determination of pure hydrogen (99.9 %) that the gasification-PSA system is able to produce. The operating conditions and efficiencies of PSA unit are obtained from Pallozzi *et al*. (2016). In particular, hydrogen separation efficiency of 70 % and a PSA inlet pressure of 7 bara are considered. From the combination of the experimental gasification efficiencies and the literature-derived data, it is possible to assess the yield and efficiencies of the entire system, as explained in the next section. The off-gas from the PSA unit is a still a combustible gas that can be used for combined heat and power (CHP) production, e.g. by means of internal combustion engines. The real plant for hydrogen production from citrus peel gasification needs a drying unit because of high water content of such residues. In order to simplify the system's description, in this work the energy required for the drying step comes from the heat produced by the CHP unit, consuming almost the total amount of heat that can be recovered. Indeed, in a previous work the authors calculated that a citrus peel gasification-CHP plant is able to produce heat that is slightly more than the required one for the drying step of the feedstock that feeds a gasifier with the same efficiency of the one in lab scale (Pallozzi *et al*., 2016). The electrical and thermal efficiencies of the CHP unit that has been considered in this work are 0.37 and 0.44, respectively. These data were provided by the constructor of wood-gas engines.

2.3. Calculations

Using experimental data for the gasification unit, and literature-derived data for the PSA and CHP units, the yearly potential of hydrogen production as energy carrier in Sicily has been obtained according to Eq.1:

$$\dot{m}_{H2} = Y_{PSA} \cdot Y_{syn} \cdot d_{syn} \cdot \dot{m}_{biom} \tag{1}$$

where Y_{PSA} [g/kg$_{syn}$] is the yield of pure hydrogen per kg of syngas introduced in the PSA unit, Y_{syn} [Nm^3/kg$_{biom}$] is the syngas yield in the gasification unit, d_{syn} [kg/Nm^3] is the syngas density and $\dot{m}_{biom}$ [kg/y] is the annual amount of available dry biomass. With regard to the energy efficiency of the system, the CHHP efficiency

(η_{CHHP}) indicates the efficiency of the combined production of hydrogen, heat and power, which is calculated according to Eq.2.

$$\eta_{CHHP} = \frac{\dot{m}_{H2} \cdot LHV_{H2} + E_{offgas} - E_{aux} - E_{comp}}{\dot{m}_{biom} \cdot LHV_{biom}} \quad (2)$$

where LHV_{H2} and LHV_{biom} are the lower heating values of hydrogen and biomass, respectively. E_{offgas} is the annual electricity produced by the CHP unit, by burning the off-gas in the internal combustion engine, calculated according Eq.3. E_{comp} is the annual energy consumption due to syngas compression in the SPA unit, while E_{aux} is the annual energy consumption of auxiliary units of the system, excluding the PSA compressors, which accounts for about 10% of the electrical energy produced in the CHP unit.

$$E_{offgas} = \dot{m}_{offgas} \cdot LHV_{offgas} \cdot \eta_e \quad (3)$$

In this case, the heat produced from the CHP unit is not included in the calculations because it is used for biomass drying. Hence, for simplicity, the residual available heat can be neglected in these calculations (Galvagno *et al*., 2016).

3. Results and discussion

Table 2 shows syngas composition obtained from citrus peel gasification at 750 °C and 850 °C, S/B of 0.5 and 1.25, with a constant equivalence ratio of 0.3. As expected, hydrogen percentage increases as the S/B increases. Carbon monoxides decreases with S/B while carbon dioxide increases. This behavior indicates that the water-gas shift reaction is progressing, producing more hydrogen and CO_2. Another relevant reaction that is favored by increasing the steam flow is steam-carbon reaction, which produces hydrogen and carbon monoxide while consuming the solid carbon from biomass. Furthermore, the nitrogen percentage decreases, indicating that more syngas is produced. As expected, methane volume percentage decreases as the S/B ratio increases. This behavior is due to the steam reforming of methane. With regard to the effect of temperature, its increase involves the increase in the CO percentage at the expenses of CO_2, as expected. Indeed, at higher temperature the inverse Boudouard reaction is favored. In addition, it is possible to observe that the hydrogen volume percentage is slightly reduced when the temperature is increased from 750 °C to 850 °C.

Figure 1 and Figure 2 show the effect of process parameters on the syngas yield and hydrogen yield, respectively. Both are expressed per unit mass of dry biomass that enters the reactor. The first is referred to the syngas yield at the outlet of the reactor, while the second refers to the hydrogen at the outlet of the PSA unit, since its efficiency is not dependent on the gasification temperature. From these two figures, it can be observed that syngas yield increases with temperature and S/B, while the hydrogen yield is almost constant at S/B=0.5 and decreases from 750 °C to 850 °C at S/B=1.25. This means that the increase of the syngas yield does not compensate the decrease of hydrogen volume percentage when temperature is increased. A possible explanation of the observed behavior is that the high reactivity of citrus peel implies negligible differences in the kinetic of the heterogeneous char-steam reaction between 750 and 850 °C. In addition to this effect, it should be taken into account that the water-gas shift reaction is favored at lower temperatures.

Table 2. Syngas composition %vol at different temperatures and steam to biomass ratio

Temperature	750 °C		850 °C	
S/B ratio	0.5	1.25	0.5	1.25
H_2	20.0	26.4	19.6	25.2
CO_2	19.1	20.8	16.3	20.4
CO	11.4	8.3	15.6	9.8
CH_4	3.4	2.1	3.3	2.4
N_2	45.0	42.0	44.0	41.5

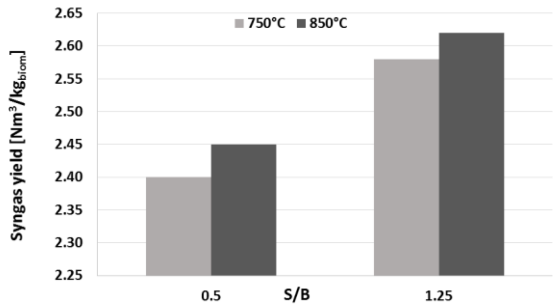

Figure 1. Syngas yield at different temperatures and S/B

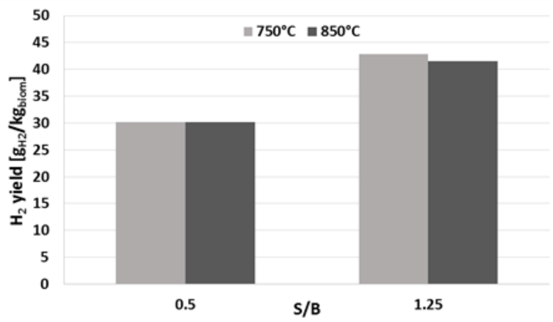

Figure 2. Hydrogen yield at different temperatures and S/B

It follows that the most favorable condition for hydrogen production can be achieved using an S/B=1.25 and a temperature of 750 °C, with a slight decrease in the hydrogen yield at 850 °C. After hydrogen purification in the PSA unit, a still burnable offgas can be used for energy production, as reported in the previous section. Figure 3 show both gross and net CHHP efficiencies, which take into account the energy share of hydrogen and the energy produced by internal combustion engine fed by offgas from PSA. The latter has very poor lower calorific values, which varies from 3.4 to 4.4 MJ/Nm3, observed at 750°C, S/B=1.25 and 850°C, S/B=0.5, respectively. As expected, the LHV of the offgass increases as the temperature increases and the S/B decreases. Indeed, these two experimental parameters contributes in an opposite way to the CO concentration in the syngas during the gasification process. This behavior is reflected in the trend of the energy efficiency of the CHHP system, which increases as temperature increases. The steam enhances the gross energy efficiency, despite the reduction of the offgas LHV, because of the increased syngas yield. As opposite, the net CHHP energy efficiency decreases notably because of the great amount of energy that is needed for the production of steam. From the net energy efficiency point of view, the best results can be achieved at 850 °C and S/B=0.5, reaching the value of 23.6 %, while the highest gross energy efficiency, equal to 37.6 %, is achieved at 850 °C and S/B=1.25. However, in this work, the heat recovery from syngas cooling has not been taken into account because it depends on the specific syngas cleaning process that is considered. For instance, the heat recovered form syngas cooling might be used for the production of steam, increasing considerably the net energy efficiency.

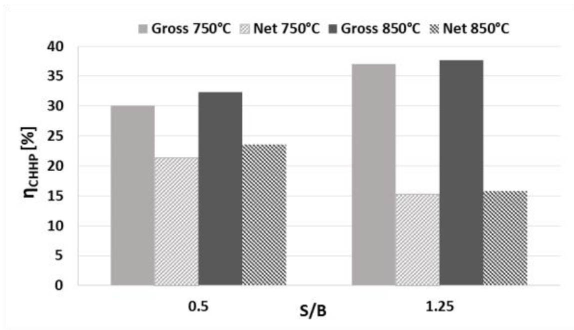

Figure 3. Gross and net CHP efficiencies at the investigated conditions

Taking into consideration that about 33,000 t/y of citrus peels (dry basis) are produced in Sicily, the annual potential of combined hydrogen and power production in Sicily is 1414 t/y of hydrogen and 9.27 GWh/y of available electricity, if the reactor is operated at 750°C and S/B=1.25. At 850°C and same S/B=1.25, the hydrogen production and electricity are 1,371 t/year and 11.55 GWh/y, respectively.

One interesting option for hydrogen utilization is the development of local public transportation based on fuel cell hybrid electric minibuses (battery/fuel cells), fed by hydrogen. The hydrogen consumption of this kind of minibus for public transportation are literature-derived from the research work of Dispenza *et al*. (2017) and Napoli *et al*. (2017). From these publications, it has been determined that the hydrogen consumption of hybrid minibuses is 0.03 kg/km. Taking into consideration a daily run of 200 km/day and 365 days per year, the annual hydrogen consumption is 2.209 t/y-bus. It follows that from 450 to 640 minibuses can be potentially fed by hydrogen obtained from citrus peel air-steam gasification in Sicily.

4. Conclusions

This work investigates the potential of combined hydrogen and electricity production in Sicily by air-steam gasification of citrus peel residues obtained as byproduct from citrus juice production. The feasibility of air-steam gasification at relatively low temperatures has been experimentally demonstrated through a fluidized bed gasification equipment at bench-scale. The investigate temperatures were 750 and 850 °C, while the steam to biomass mass ratio were 0.5 and 1.25 at both temperatures. The hydrogen purification step (Pressure Swing Adsorption unit) has been modeled by using literature data of hydrogen production from wood-syngas. By taking into account the annual production of citrus peel in Sicily, considering the experimental evidences and the system modeling, the conclusions can be summarized as follow:

Citrus peel gasification under steam atmosphere showed a very good reactivity and excellent yields even at relatively low temperatures.

The highest hydrogen yield was observed at 750 °C and S/B = 1.25, being approx. 42 g/kg_{biom}. A similar results is obtained at 850°C (41 g/kg_{biom})

The highest net combined hydrogen, heat and power (CHHP) efficiency can be achieved at 850 °C and S/B = 0.5, because of the higher syngas LHV and lower need of steam.

If the gasifiers are operated at 750 °C and S/B = 1.25, about 1414 t/y of hydrogen can produced, as well as 9.27 GWh/y of electricity by burning the offgases in internal combustion engines.

If the proposed citrus peel gasification system, coupled with PSA technology, would be spread in Sicily, it will be able to feed from 450 to 640 electrical hybrid minibuses (batteries/fuel cells). This estimation is based on field data available in literature.

References

Brusca S., Galvagno A., Lanzafame R., Garrano A. M. C., Messina M. (2015). Performance analysis of biofuel fed gas turbine. *Energy Procedia*, Vol. 81, pp. 493-504. https://doi.org/10.1016/j.egypro.2015.12.123

Brusca S., Lanzafame R., Garrano A. M. C., Messina M. (2015). Dynamic analysis of combustion turbine running on synthesis gas. *International Journal of Applied Engineering Research*, Vol. 10, No. 21, pp. 42244-42253. ISSN: 09734562

Cannistraro G., Cannistraro M., Galvagno A., Trovato G. (2017). Analysis and measures for energy savings in operating theaters. *International Journal of Heat and Technology*, Vol. 35, Special Issue 1, pp. S442-S448. https://doi.org/10.18280/ijht.35Sp0160

Cannistraro G., Cannistraro A., Cannistraro M., Galvagno A., Trovato G. (2016). Reducing the demand of energy cooling in the CED, Centers of Processing Data. with use of free-cooling systems. *International Journal of Heat and Technology*, Vol. 34, No. 3, pp. 498-502. https://doi.org/10.18280/ijht.340321

Cannistraro G., Cannistraro M., Cannistraro A., Galvagno A., Trovato G. (2015). Evaluation on the convenience of a citizen service district heating for residential use. A new scenario introduced by high efficiency energy systems. *International Journal of Heat and Technology*, Vol. 33, No. 4, pp. 167-172. https://doi.org/10.18280/ijht.330421

Cerone N., Zimbardi F., Contuzzi L., Prestipino M., Carnevale M. O., Valerio V. (2017). Air-steam and oxy-steam gasification of hydrolytic residues from biorefinery. *Fuel Processing Technology*, Vol. 167, pp. 451-461. https://doi.org/10.1016/j.fuproc.2017.07.027

Chiodo V., Urbani F., Zafarana G., Prestipino M., Galvagno A., Maisano S. (2017). Syngas production by catalytic steam gasification of citrus residues. *Int J Hydrogen Energy*, Vol. 42, No. 46, pp. 28048-28055. https://doi.org/10.1016/j.ijhydene.2017.08.085

Cucinotta F., Guglielmino E., Sfravara F. (2017). Frequency of ship collisions in the strait of messina through regulatory and environmental constraints assessment. *J. Navig.*, Vol. 70, pp. 1002-1022. https://doi.org/10.1017/S0373463317000157

Cucinotta F., Paoli A., Risitano G., Sfravara F. (2018). Optical measurements and experimental investigations in repeated low-energy impacts in powerboat sandwich composites. *Proc. Inst. Mech. Eng. Part M J. Eng. Marit. Environ.*, Vol. 232, pp. 234-244. https://doi.org/10.1177/1475090217720619

D'Agostino D., Parker D. (2018). A framework for the cost-optimal design of nearly zero energy buildings (NZEBs) in representative climates across Europe. *Energy*, Vol. 149, pp. 814-829. https://doi.org/10.1016/j.energy.2018.02.020

De Blasio C., Järvinen M. (2017). Supercritical water gasification of biomass in encyclopedia of sustainable technologies. *Abraham M*, pp. 171-195. https://doi.org/10.1016/B978-0-12-409548-9.10098-3

del Río P., Peñasco C., Mir-Artigues P. (2018). An overview of drivers and barriers to concentrated solar power in the European Union. *Renew Sustain Energy Rev*, Vol. 81, pp. 1019-1029. https://doi.org/10.1016/j.rser.2017.06.038

Dispenza G., Sergi F., Napoli G., Randazzo N., Di Novo S., Micari S., Antonucci V., Andaloro L. (2017). Development of a solar powered hydrogen fueling station in smart cities applications. *Int J Hydrogen Energy*, Vol. 42, pp. 27884-27893. https://doi.org/10.1016/j.ijhydene.2017.07.047

Fracastoro G. V. (2018). Being the energy manager in a technical university. *IJES 2018*, Vol. 61+1, No. 2, pp. 97-101. https://doi.org/10.18280/ijes.620207

Fragiacomo P., Corigliano O., De Lorenzo G., Mirandola F. A. (2018). Experimental activity on a 100-W IT-SOFC test bench fed by simulated syngas. *Journal of Energy Engineering*, Vol. 144, No. 2, pp. 04018006. https://doi.org/10.1061/(ASCE)EY.1943-7897.0000526

Galvagno A., Prestipino M., Chiodo V., Maisano S., Brusca S., Lanzafame R. (2017). Energy performance of CHP system integrated with citrus peel air-steam gasification: A comparative study. *Energy Procedia*, Vol. 126, pp. 485-492. https://doi.org/10.1016/j.egypro.2017.08.233

Galvagno A., Prestipino M., Zafarana G., Chiodo V. (2016). Analysis of an integrated agro-waste gasification and 120 kW SOFC CHP system: modeling and experimental investigation. *Energy Procedia*, Vol. 101, pp. 528-535. https://doi.org/10.1016/j.egypro.2016.11.067

Kana X., Zhou D., Yang W., Zhai X., Wang C. (2018). An investigation on utilization of biogas and syngas produced from biomass waste in premixed spark ignition engine. *Appl Energy*, Vol. 212, pp. 210-222. https://doi.org/10.1016/j.apenergy.2017.12.037

Kraussler M., Binder M., Schindler P., Hofbauer H. (2018). Hydrogen production within a polygene ration concept based on dual fluidized bed biomass steam gasification. *Biomass and Bioenergy*, Vol. 111, pp. 320-329. https://doi.org/10.1016/j.biombioe.2016.12.008

Lai C. S., Jia Y., Lai L. L., Xu Z., McCulloch M. D., Wong K. P. (2017). A comprehensive review on large-scale photovoltaic system with applications of electrical energy storage. *Renew Sustain Energy Rev*, Vol. 78, pp. 439-451. https://doi.org/10.1016/j.rser.2017.04.078

Maisano S., Urbani F., Mondello N., Chiodo V. (2017). Catalytic pyrolysis of Mediterranean Sea plant for bio-oil production. *Int J Hydrogen Energy*, Vol. 42, pp. 28082-28092. https://doi.org/10.1016/j.ijhydene.2017.07.124

Mastronardo E., Bonaccorsi L., Kato Y., Piperopoulos E., Lanza M., Milone C. (2017). Strategies for the enhancement of heat storage materials performances for $MgO/H_2O/Mg(OH)_2$ thermochemical storage system. *Appl. Therm. Eng*., Vol. 120, pp. 626-34. https://doi.org/10.1016/j.applthermaleng.2017.04.004

Mastronardo E., Kato Y., Bonaccorsi L., Piperopoulos E., Milone C. (2017). Thermochemical storage of middle temperature wasted heat by functionalized $C/Mg(OH)_2$ hybrid materials. *Energies*, Vol. 10, Article number 70. https://doi.org/10.3390/en10010070

Napoli G., Micari S., Dispenza G., Di Novo S., Antonucci V., Andaloro L. (2017). Development of a fuel cell hybrid electric powertrain: A real case study on a Minibus application. *Int J Hydrogen Energy*, Vol. 42, pp. 28034-28047. https://doi.org/10.1016/j.ijhydene.2017.07.239

Nicotera I., Angjeli K., Coppola L., Enotiadis A., Pedicini R., Carbone A., Gournis D. (2015). Composite polymer electrolyte membranes based on Mg-Al layered double hydroxide (LDH) platelets for H_2/air-fed fuel cells. *Solid State Ionics*, Vol. 276, pp. 40-46. https://doi.org/ 10.1016/j.ssi.2015.03.037

Nikolaidis P., Poullikkas A. (2018). Cost metrics of electrical energy storage technologies in potential power system operations. *Sustain Energy Technol Assess*, Vol. 25, pp. 43-59. https://doi.org/10.1016/j.seta.2017.12.001

Oh Y. K., Hwang K. R., Kima C., Kim J. R., Lee J. S. (2018). Recent developments and key barriers to advanced biofuels: A short review. *Bioresource Technology*, pp. 519-525. https://doi.org/10.1016/j.biortech.2018.02.089

Paina A., Piccinini E., Rossi L. (2010). Studio sull'utilizzo di biomasse combustibili e biomasse rifiuto per la produzione di energia. ISPRA, Rapporti 111/2010, ISBN 978-88-448-0440-4. http://www.isprambiente.gov.it/it/pubblicazioni/rapporti/studio-sull2019utilizzo-di-biomasse-combustibili-e-biomasse-rifiuto-per-la-produzione-di-energia.

Pallozzi V., Di Carlo A., Bocci E., Villarini M., Foscolo P. U., Carlini M. (2016). Performance evaluation at different process parameters of an innovative prototype of biomass gasification system aimed to hydrogen production. *Energy Conversion and Management*, Vol. 130, pp. 34-43. https://doi.org/10.1016/j.enconman.2016.10.039

Palomba V., Prestipino M., Galvagno A. (2017). Tri-generation for industrial applications: Development of a simulation model for a gasification-SOFC based system. *Int J Hydrogen Energy*, Vol. 42, pp. 27866-27883. https://doi.org/10.1016/j.ijhydene.2017.06.206

Pedicini R., Saccà A., Carbone A., Passalacqua E. (2011). Hydrogen storage based on polymeric material. *International Journal of Hydrogen Energy*, Vol. 36, pp. 9062-9068. https://doi.org/10.1016/j.ijhydene.2011.04.176

Pianko-Oprych P., Palus M. (2017). Simulation of SOFCs based power generation system using Aspen. *Polish Journal of Chemical Technology*, Vol. 19, No. 4, pp. 8-15. https://doi.org/10.1515/pjct-2017-0061

Piperopoulos E., Mastronardo E., Fazio M., Lanza M., Galvagno S., Milone C. (2018). Enhancing the volumetric heat storage capacity of $Mg(OH)_2$ by the addition of a cationic surfactant during its synthesis. *Appl Energy*, Vol. 215, pp. 512-522. https://doi.org/10.1016/j.apenergy.2018.02.047

Prestipino M., Chiodo V., Maisano S., Zafarana G., Urbani F., Galvagno A. (2017). Hydrogen rich syngas production by air-steam gasification of citrus peel residues from citrus juice manufacturing: Experimental and simulation activities. *Int J Hydrogen Energy*, Vol. 42, No. 43, pp. 26816-26827. https://doi.org/10.1016/j.ijhydene.2017.05.173

Tagliaferri C., Evangelisti S., Clift R., Lettieri P. (2018). Life cycle assessment of a biomass CHP plant in UK: The Heathrow energy centre case. *Chemical Engineering Research and Design*, Vol. 133, pp. 210-221. https://doi.org/10.1016/j.cherd.2018.03.022

Tavares A. C., Dubitsky Y. A., Zaopo A., Pedicini R., Gatto I., Passalacqua E. (2003). New sulfonated polysulfone co-polymer membrane for low temperature fuel cell. *Journal of New Materials for Electrochemical Systems*, Vol. 6, pp. 211-215. ISSN: 14802422

Youssef A. M. (2018). Operations of electric vehicle traction system. *Mathematical Modelling of Engineering Problems*, Vol. 5, No. 2, pp. 51-57. https://doi.org/0.18280/mmep.050201

Nomenclature

B	dimensionless heat source length
CP	specific heat, J. kg^{-1}. K^{-1}
E	Electricity, MWh
ER	Equivalence Ratio, mol/mol
FC	Fixed Carbon, $\%_{wt}$
HHV	Higher Heating Value, kJ/kg
LHV	Lower Heating Value, kJ/kg
$\dot{m}$	Annual mass flow rate; kg/y
PSA	Pressure Swing Adsorption

S/B	Steam to biomass ratio, wt/wt
VM	Volatile matter, $\%_{wt}$
Y	Mass Yield, g/kg; Nm^3/kg
Greek symbols	
η	Energy efficiency
Subscripts (related to)	
aux	Auxiliaries (pumps, fan, blowers, motors, etc.)
biom	Biomass
CHHP	Combined Hydrogen Heat and Power
comp	Compressors
e	Electrical
offgas	Residual offgas after hydrogen separation in the PSA unit
PSA	Pressure Swing Adsorption
syn	syngas