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Combined clean hydrogen production and bio-active compounds recovery from spent coffee grounds. A multi-perspective analysis

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ABSTRACT

This study deals with the process simulation of an integrated system for energy production and valuable compounds recovery from spent coffee ground biomass and plasmix (non-recyclable plastic waste). The devised process consists of three main units: a sub-critical water extraction column for the recovery of bio-compounds, an oxy-combustor of residual biomass and plasmix streams coupled with a production power energy unit, and a solid oxide electrolyzer (SOEC) for the production of pure H₂ and O₂. The process was exhaustively analyzed from an energy, exergy, environmental and economic point of view. The results of the analysis provided energy and exergy efficiencies higher than 60%, and the environmental analysis (CO₂-cycle analysis) demonstrated a significant advantage of the process with respect to other hydrogen production methods. Finally, the feasibility of a plant with no net Greenhouse Gas emissions was shown to markedly depend on the costs associated to renewable energy sources.

1. Introduction

The disposal of municipal and industrial solid wastes is one of the challenges of the next future and must have a key role in the energy transition, in order to reduce the carbon footprint of this industrial sector. Landfilling is the most traditional and easiest way for food waste disposal, but it is also characterized by significant impacts on the health of the planet (Melikoglu et al., 2013; Shah et al., 2021). Because of this, in the last decade, recovery of material and energy from food waste has become a key research issue, and several solutions have been studied and proposed.

One possible way of waste food conversion into hydrogen was analysed by Shin and Youn (2005) by thermophilic acidogenesis. The process gas produced by the reactor was composed of hydrogen and carbon dioxide, without formation of methane under all tested conditions, proving that a continuous generation of hydrogen, though at a laboratory scale level, is possible.

Indeed, a study carried out in Canada by Assamoi and Lawryshyn (2012), analysed the difference between landfilling and incineration in terms of carbon dioxide equivalents emitted in the atmosphere. The results clearly proved that landfilling should be avoided and replaced with waste reutilization techniques.

Wu and Williams (2010), analysed the possibility of using

pyrolysis-gasification of municipal solid plastic waste for the production of hydrogen; they partially solved the problem of coke deposition around 700 °C, typical for such a process, by the use of a Ni-Mg-Al catalyst.

Coffee is one of the most consumed and popular beverages worldwide and the coffee industry is globally responsible for producing a great quantity of waste, mainly spent coffee grounds (SCG) (la Scalia et al., 1968). Due to the large scale of production and toxicity, direct disposal of SCG can cause serious environmental problems and should be avoided (de et al., 2021), so that its re-use is a topic of interest in the technical literature.

Cho et al. (2015), used SCG as a biomass in a pyrolysis process, to study the influence of CO₂ as reaction medium. It was noticed an appreciable reduction of the tar of the biomass, (condensable hydrocarbons), as well as a notable morphologic change of the biochar.

Another study by Ciesielczuk et al. (2015), reported the possibility of valorising the waste biomass with a thermal conversion method. The authors proved the possibility of using SCG as biomass in combustion processes, e.g. as an additive to increase the heat of combustion of alternative fuels: because of its moisture content, a preliminary drying process of the biomass is required.

The possibility of direct power generation from waste coffee grounds was demonstrated by Jang et al. (2015), thanks to a carbon fuel cell

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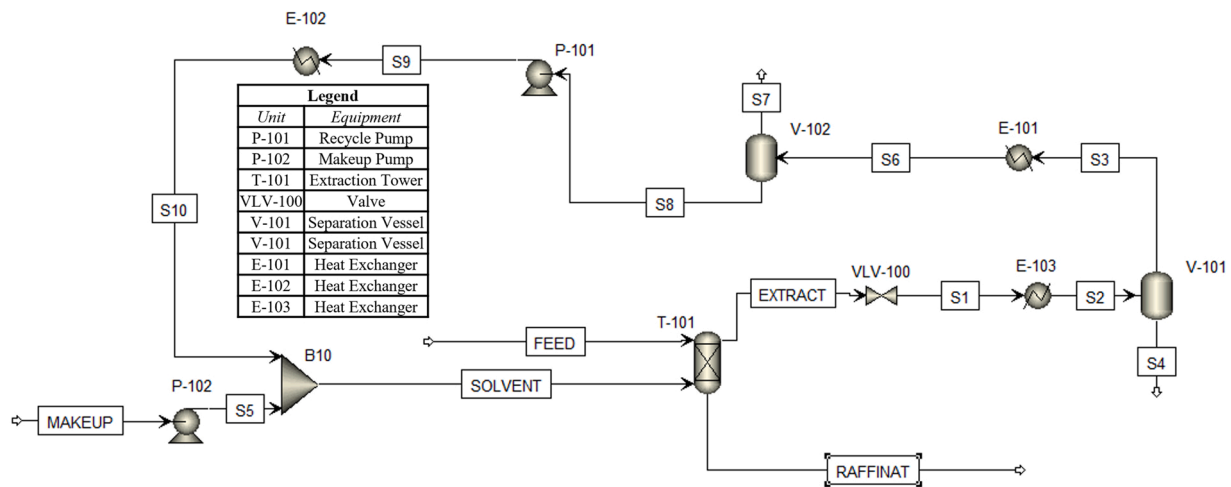


Fig. 1. Extraction process.

technology, operating at a temperature of 900 °C. This waste is particularly useful in this kind of process, due to its high lower heating value (LHV), twice that of carbon black. They demonstrated that hydrogen and other compounds contained in waste coffee grounds can be used in this technology with an “in-situ gasification”, without the necessity of a pre-reforming.

The present work addresses the possibility of combining a bioactive compounds (SCG) recovery from agro-industrial wastes, with a waste to energy (WtE) process, so as to recover energy to feed an electrolyser for pure hydrogen and oxygen production. Moreover, another energetic advantage is obtained from the combustion of Plasmix (non-recyclable plastic waste): Plasmix direct incineration is considered a valid alternative to its landfilling (Cossu et al., 2017; Rehman et al., 2020).

2. Processes description

In the devised process, SCG and non-recyclable plastics have been valorised by effectively recovering bio-active compounds (like proteins, carbohydrates, polyphenols) and energy through the waste to energy plant. The recovered energy is then used to feed a water electrolyser for the production of green hydrogen and oxygen.

The work was developed in Aspen Plus® and Aspen Hysys simulation environments. In particular, Aspen Plus® was used for the extraction process, whereas the simulation of the Solid Oxide Electrolytic Cell (SOEC), the incinerator and the waste flue gas treatment plant were carried out in Aspen Hysys® environment.

The Peng-Robinson model has been adopted as thermodynamic system for the extraction of bioactive compounds from SCG (Cornelio-Santiago et al., 2017; Dwivedi et al., 2021), while the SRK-Twu equation has been adopted for all other parts of the process (Øi and Hovland, 2018).

2.1. Water electrolysis with Solid Oxide Electrolytic Cell (SOEC)

Water electrolysis (Eq. 1) is an electrochemical reaction that forms hydrogen and oxygen from water splitting. Electrolysis of water is one of the most effective methods and has been commercialized because it is abundantly available, produces no emissions, and has only pure oxygen as a byproduct (Taipabu et al., 2022). At the cathode, charged negatively, the reduction reaction occurs (Eq. 2) while at the anode, charged positively, the oxidation reaction takes place (Eq. 3).

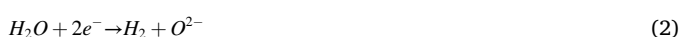


Table 1
Inlet stream composition. Extraction section.

	Unit	Feed	Makeup
Flowrate	kg/h	2421	1028
Water	w/w	0.01	1
Mannose	w/w	0.25	0
Cellobiose	w/w	0.09	0
D-Galactose	w/w	0.13	0
Arabinose	w/w	0.04	0
Linoleic acid	w/w	0.09	0
Stearic acid	w/w	0.02	0
N-hexadecanoic acid	w/w	0.05	0
Aspartic acid	w/w	0.04	0
L-Glutamic acid	w/w	0.03	0
Leucine	w/w	0.02	0
Tyrosine	w/w	0.10	0
Trans-3,4-Dihydroxycinnamic acid	w/w	0.07	0
Valine	w/w	0.04	0
Methionine	w/w	0.01	0
Carbon dioxide	w/w	0	0
Phenol	w/w	0	0
Quercetin	w/w	0.02	0



The Gibbs free energy of the reaction is expressed by Eq. 4:

$$\Delta G_r^0 = nFE_V^0 = +237.1 \frac{kJ}{mol} \quad (4)$$

where n [mol] is the number of electrons transferred, F [C/mol] is the Faraday constant and E_V^0 is the cell voltage [V].

In this work hydrogen is produced from a solid-oxide electrolyzer (SOEC). This device consists of a cathode and an anode, separated by a ceramic electrolyte (Ferrero et al., 2013), characterized by high thermal stability, mechanical resistance and notable efficiency in the conduction of the oxygen anions at high temperature (Götz et al., 2016; Laguna-Bercero, 2012). The operating temperature and pressure of a SOEC electrolyzer are 700–800 °C and 1500 kPa, respectively. These operating conditions provide this device with a very high efficiency in terms of power to hydrogen, which can also reach 100%, if the equipment works at the thermoneutral point (Laguna-Bercero, 2012; Giglio et al., 2015). The SOEC was designed to produce about 1.5 t/h of green hydrogen (see Supplementary Materials).

Table 2
SCG elemental analysis.

SCG elemental analysis (% wt)		
	Simulated	Literature (Zuorro and Lavecchia, 2013)
C	48.19	49.87 – 51.02
N	2.3	2.11 – 2.37
H	7.4	7.04 – 7.19
O	40.2	39.2 – 39.56
S	0.21	0.21 – 0.38
Ash	1.7	-

Table 3
Inlet stream properties (extraction section).

	Units of measure	Stream name in process diagram	
		Feed	Makeup
Temperature	°C	200	200
Pressure	kPa	7092.75	7092.75
Mass Flows	kg/h	2421	1027.59

2.2. Process layout

2.2.1. Extraction section

Fig. 1 shows the overall flowsheet of the extraction process.

The SCG composition was assumed based on literature data and using the compounds present in the Aspen Plus® database. Carbohydrates represent the main component in this kind of biomass, in particular as mannose, galactose, cellobiose and arabinose (Assamoi and Lawryshyn, 2012). Proteins (valine, tyrosine, aspartic acid, glutamic acid), lipids (linoleic, stearic and palmitic acids) and phenolic compounds (caffeic acid and flavonoid) are present in variable quantities depending on the origin of the SCG (Pedras et al., 2019). A water content of 0.5% was also considered. Table 1 summarizes the composition of the inlet stream to the extraction tower.

Table 2 shows the concentration ranges of carbon, hydrogen, nitrogen, oxygen and sulphur in the biomass according to literature data and those adopted in the simulations. The mass flowrate of each component used to simulate the biomass was selected so as to obtain an inlet composition in accordance with that reported in Table 2.

The following approximate formula (Chang equation), was used to determine the lower heating value (LHV) based on elemental analysis (Niessen, 2010):

$$LHV \left(\frac{kcal}{kg} \right) = 8561.11 + 179.72mh - 111.17mo - 63.89ms - 66.94mn$$

where mh, mo, mn and ms represent the content of hydrogen, oxygen, nitrogen and sulfur, respectively, expressed as mass % in the biomass.

The feed is sent to the extraction column (T-101 in Fig. 1) together with the solvent (water). The tower operates at a pressure of 7000 kPa and a temperature of 200 °C, which are the best conditions to extract the polar coffee bio compounds, soluble in water (Karimi et al., 2019; Ballesteros et al., 2017). The extraction process was then conducted according to sub-critical conditions.

From the bottom of the column the raffinate stream is obtained, that will represent the co-feed with the non-recyclable plastics to the coupled waste-to-power and hydrogen plant. On the other hand, the extract is an aqueous stream that needs to be treated to recover some bio active compounds like carbohydrates, polyphenols and proteins that, after further purification, can be sold as a product of the process.

Various literature studies (Henríquez et al., 2014a; Kieu Tran et al., 2020) showed that some bio active compounds are actually thermos-sensitive: for example, it has been reported that after 30 min of a test at 4000 kPa and 250 °C, all phenolic compounds in the SCG were degraded. For this reason, the downstream section of this unit is designed to avoid these conditions. The aqueous stream coming from the

Table 4
Heat exchanger properties.

	Units of measure	Unit number in process diagram		
		E-101	E-102	E-103
Pressure	kPa	2026.5	2026.5	7092.75
Temperature	°C	219	210.93	200

tower is firstly expanded till atmospheric pressure and then heated up till boiling temperature (102 °C) (Kieu Tran et al., 2020; Henríquez et al., 2014b). Downstream of the heat exchanger E-103, a separation vessel V-101 is provided, where all the bio compounds are recovered as liquid stream from the bottom and the water as vapour stream from the top. Then, water is condensed in the E-101 unit, pumped until the tower operating pressure and mixed with the make-up stream, before being recycled to the column. Table 3 and Table 4 report inlet stream and heat exchanger properties. Pumps (P-101 and P-102) have an efficiency equal to 0.7. The pressure drops of this portion of plant were set equal to 50 kPa.

2.2.2. Waste to energy section

After the bio-active compounds recovery section, the biomass (the residue deriving from the extraction tower) is fed together with the plasmix stream into the waste-to-energy section, represented in Fig. 2. This part of the flowsheet was carried out in the Aspen Hysys® simulation environment.

The waste to energy section is composed of 3 different processes:

- Incineration
- Power generation
- SOEC (Hydrogen production).

2.2.2.1. Incineration.

The incineration process is detailed in Figs. 3a and 3b.

The main equipment of this process is the incinerator, represented as a Gibbs reactor (R-101) in Fig. 3a. The reactor works at 100 kPa with a heat loss of 5% of the input thermal duty (Niessen, 2010).

A residual biomass flowrate of 877 kg/h and a plasmix flowrate of 2230 kg/h have been considered in the waste to energy section; this reflects in a thermal power input to the incineration reactor of 30 MW.

Four streams are fed to the incinerator:

- Non-recyclable plastics (1)
- Biomass coming from the extraction tower (2)
- Flue gas recirculation (17)
- Oxygen from SOEC (57)

Plasmix stream was modelled as a mixture of plastic monomers, based on criteria by the European Commission's Joint Research Centre (Villanueva and Eder, 2011) and referring to a previous work (Rispoli et al., 2021). Its composition is reported in Tables 5 and 6.

The plant was simulated according to previous studies (Rispoli et al., 2021; Vilardi and Verdone, 2022): the flue gas exiting at 1200 °C was used to partially pre-heat the feed to the SOEC unit and to produce super-heated vapour in the boiler, represented as a series of three heat exchangers: E-100, E-101, E-102, i.e. the super-heater, the vaporizer and the economizer, respectively. Exchangers have a shell side pressure drop of 100 kPa (Liuzzo et al., 2007). Compressors K-101 and K-105 adjust the pressure of the recirculation and of the waste gas to the reactor, with a polytropic efficiency of 0.70 and 0.75, respectively. The oxygen stream fed to the incinerator is controlled setting an oxygen outlet content in the flue gas of 6% vol, in agreement with the European regulations (Gazzetta Ufficiale della Repubblica Italiana., 2022; Ebert et al., 1998).

The water flowrate vaporised into the heat exchangers is strictly dependent on the outgoing flue gas temperature, set at 150 °C,

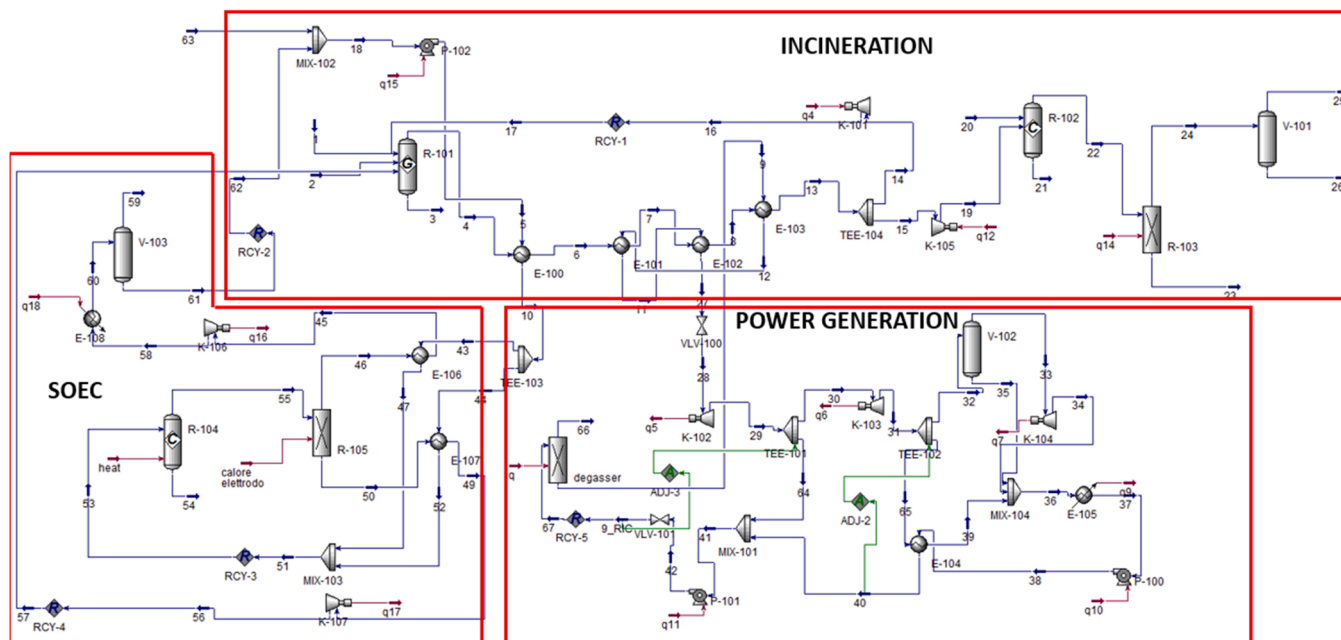


Fig. 2. General overview of the Waste to energy section.

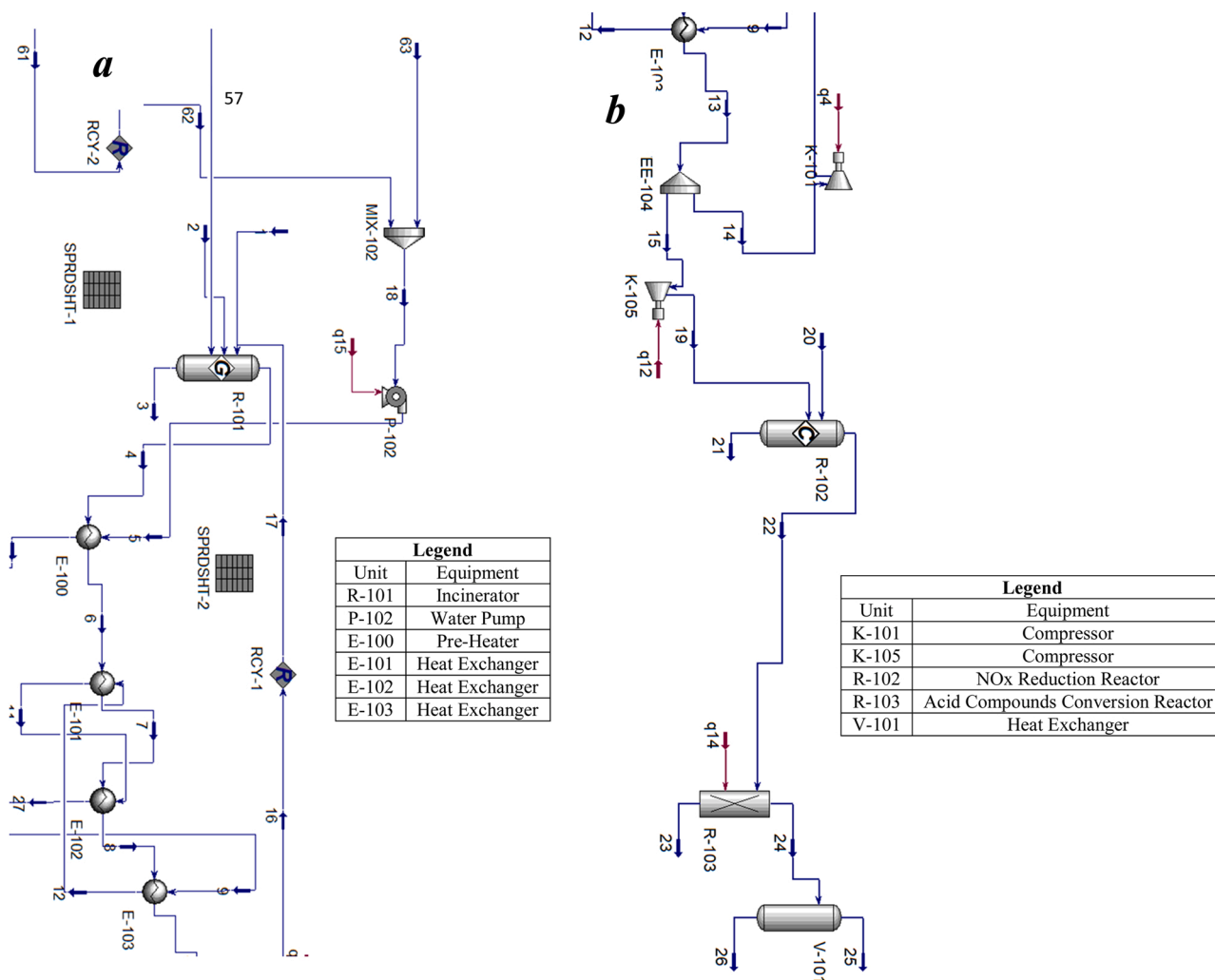


Fig. 3. a. Waste to energy section: incinerator and boiler. Fig. 3b. Waste to energy section: flue gas treatment.

Table 5
Plasmix elemental analysis.

Non-recyclable plastics elemental analysis		
		Unit
C	80.87	%wt
N	0.59	%wt
H	11.58	%wt
O	6.08	%wt
S	0.05	%wt
Cl	0.41	%wt
Ash	0.42	%wt
LHV	35.58	MJ/kg

Table 6
Plasmix composition.

Non-recyclable plastics composition		
	Unit	1
Temperature	°C	25
Pressure	kPa	101.33
Mass Flow	kg/h	2230
Ethylene	w/w	0.37
Propene	w/w	0.21
S	w/w	5×10^{-3}
Caprolactam	w/w	0.02
Styrene	w/w	0.32
VinylCl	w/w	0.01
H ₂ O	w/w	0.07

according to preliminary optimization.

Downstream of the heat recovery, the flue gas is sent to a series of process units in order to reduce the concentration of polluting agents like SO_x, HCl and NO_x (Qi et al., 2004a) according to the European regulation (directive 2010/75/EU). The core of this section consists of two reactors in series where nitrogen oxides, hydrochloric acid and SO_x are removed with ammonia and NaOH as reagents.

The waste gas is fed to the first reactor (R-102), which works at 172.40 °C and 101.33 kPa, where NO_x are catalytically reduced by the reaction with ammonia (Qi et al., 2004b; Si et al., 2021) on a MnO-based catalyst:



A thorough conversion of NO was specified, based on previous

results (Rispoli et al., 2021) reporting an almost complete NO_x conversion to N₂ at 150 °C, on a Mn-X catalyst.

In the second reactor (R-103), simulated as a conversion reactor operating at 25 °C and 1500 kPa, the acid compounds (HCl and SO_x) react with NaOH generating harmless salts (Rispoli et al., 2021):



2.2.2.2. Power generation. The power generation section is represented in Fig. 4.

The core of the unit is represented by three turbines (K-102, K-103 and K-104 in Fig. 4) where power is generated by the steam expansion. Polytropic efficiencies of the turbines are 0.76, 0.79 and 0.79, respectively, while 0.95 is the overall efficiency of the alternator and related systems.

Super-heated steam (stream 27) is used to produce power for the SOEC unit. The super-heated steam is fed to the first turbine (K-102) at 418.6 °C and 3900 kPa based on previous experience (Vilardi and Verdone, 2022) and a sensitivity analysis on this specific case.

Downstream of turbines K-102 and K-103 a knockout drum (V-102) is present to separate the condensed water before entering the last turbine. Then, the condensed water collected from the drum and from condenser E-104 pass through a stripping step to close the steam cycle. Exhaust gas (stream 66) is sent to further treatment.

2.2.2.3. SOEC. The SOEC unit is represented in Fig. 5.

The feed to this unit is steam, coming from the incineration section. Its flowrate depends on the oxygen flowrate required by the incinerator, hydrogen production and process conversion.

According with the thermoneutral approach, the water feed (stream 10 in Fig. 5) is pre-heated by the outlet streams of the SOEC, until 800 °C and then further heated up to 950 °C by an electric heat exchanger, before being fed to the electrolyser (R-104 and R-105 in Fig. 5).

In fact, in order to raise the temperature of the reactant vapor to the reaction temperature, it is possible to operate the electrolysis in two ways: thermoneutral mode and exothermic mode (Patyk et al., 2013). In the first case, an external energy source is required to raise the temperature of the feed: an electrical heat exchanger must be provided for this purpose, which allows to increase the steam temperature from 800 °C to 950 °C, i.e. the operating temperature of the isothermal electrolyser. In the second case, the energy required to raise the temperature of the steam to 950 °C is supplied directly to the electrolysis

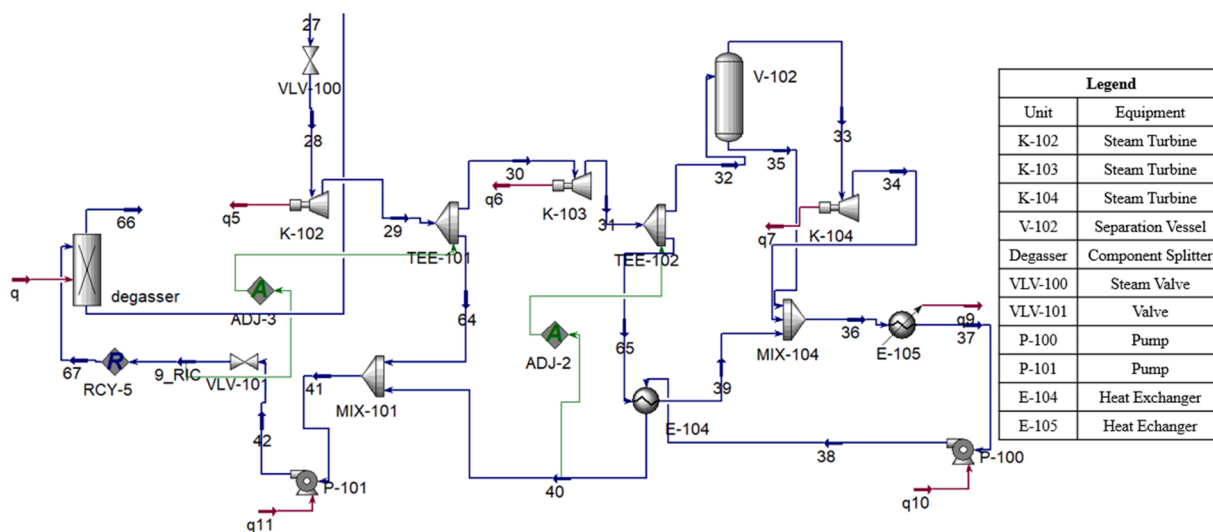


Fig. 4. Power generation unit.

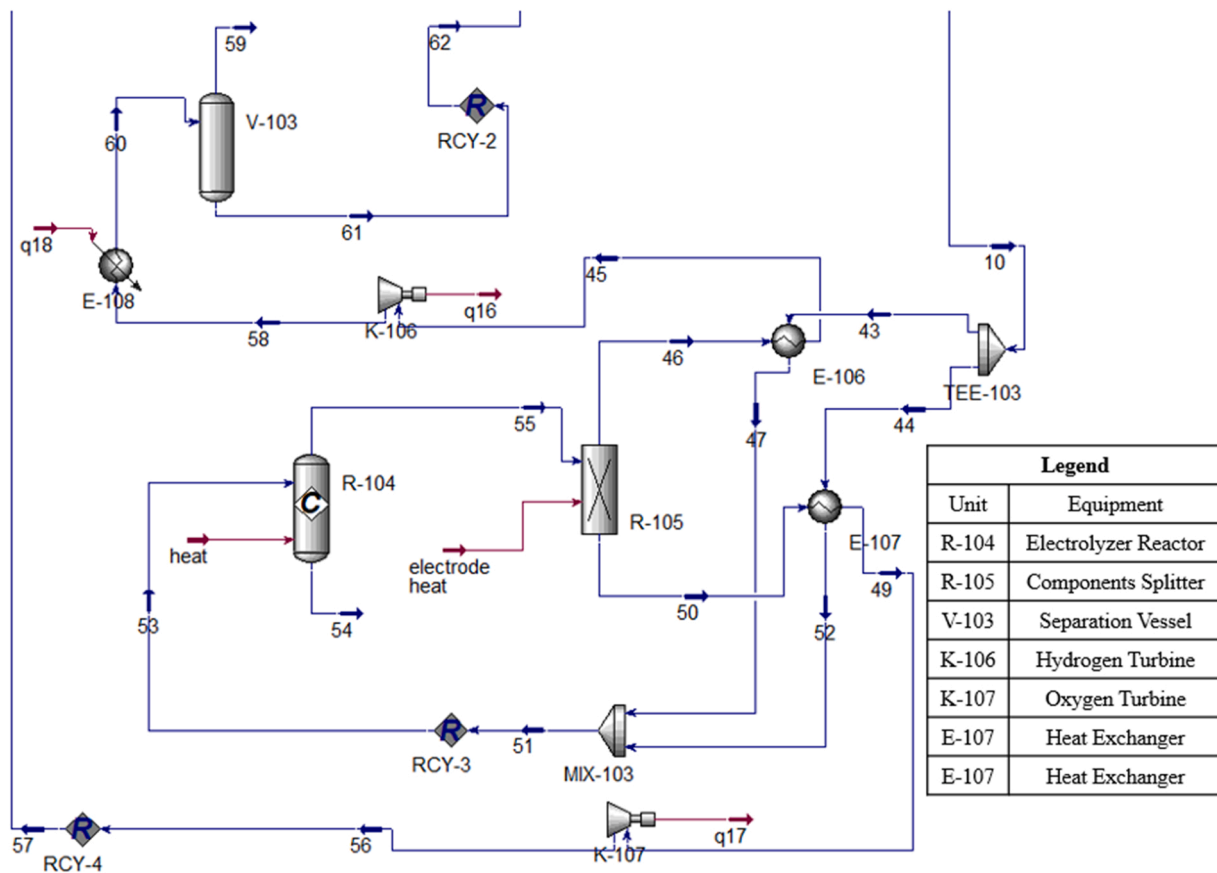


Fig. 5. SOEC unit.

Table 7
Inlet stream properties for SOEC unit.

Stream number in process diagram		
	Unit	10
Vapour Fraction		0.77
Temperature	°C	201.58
Pressure	kPa	1600
Mass Flow	kg/h	15079.58
H ₂ O	w/w	1

cell. Consequently, the power supplied to the electrolyser is greater than in the case of the thermoneutral mode, where only the power needed to make the electrolysis happen is required. The SOEC electrolyser was modelled as a conversion reactor (R-104), in which the electrolysis reaction takes place, and a components splitter (R-105), to separate cathodic and anodic chambers (Patyk et al., 2013). The system operates at 950 °C and 1500 kPa with a H₂O conversion of 70%, while the pressure drop inside the reactor is neglected (Ferrero et al., 2013; Patyk et al., 2013). The products of the reaction are an oxygen stream and a water – hydrogen mixture. The water-hydrogen stream is expanded into turbine K-106 down to atmospheric pressure and then separated in vessel V-103, whereas K-106 is used to expand the oxygen stream. Turbines K-106 and K-107 both have a polytropic efficiency of 0.78. Inlet water conditions are reported in Table 7, and optimization of the electrolyser (number of cells and sizing) is reported in the Supplementary Materials.

3. Analysis background

The devised process has been studied from several perspectives, and in the following subsections the main quantitative parameters adopted

for the analysis will be introduced, while their discussion will be presented in Section 4.

3.1. Exergy analysis

Exergy analysis is based on the second principle of thermodynamics and allows to identify irreversibilities and exergy waste streams leaving a plant (Assamoi and Lawryshyn, 2012).

The exergy content of every stream is divided into two contributions: chemical and physical. Physical exergy is evaluated in Aspen Plus® simulation environment, according to the following equation (Assamoi and Lawryshyn, 2012):

$$Ex_{in/out}^{ph} = M_{in/out} [(H - H_0) - T_0(S - S_0)] \quad (9)$$

where $Ex_{in/out}^{ph}$ [kW] is the inlet/outlet physical exergy, M is the molar flowrate of the stream (kmol/h), H and S are the molar enthalpy and entropy of the stream at its P and T , H_0 and S_0 the molar enthalpy and entropy at $P = 100$ kPa and $T = T_0 = 25$ °C, i.e. the pressure and temperature of the dead state (Kotas, 2012), respectively.

On the other hand, the chemical exergy was evaluated according to the following equation:

$$Ex_{in/out}^{ch} = M_{in/out} \left(\sum_i^n x_i ex_i^{ch} + RT_0 \sum_i^n x_i \ln(x_i) \right) \quad (10)$$

where $Ex_{in/out}^{ch}$ [kW] is the inlet/outlet chemical exergy, n is the number of chemical species, x_i is the mole fraction of i species, ex_i^{ch} (kJ/kmol) is the standard chemical exergy of i species at $P = 100$ kPa and $T_0 = 25$ °C taken from (Gharagheizi et al., 2018; Morris and Szargut, 1986) or calculated with the procedure reported by Gharagheizi and co-workers (Gharagheizi et al., 2018), R [kJ/K·mol] is the ideal gas constant.

Table 8
Utilities cost.

Utilities cost		Unit
Cooling water	0.378	\$/GJ
Refrigerated water	4.77	\$/GJ
NH ₃	200	\$/t
Process water	0.067	\$/t
Deionized water	1	\$/t
Electricity from mixed energy sources	60	\$/MW
Electricity from renewable sources only	225	\$/MW
O&M SOEC	0.028	\$/KWh
Solid waste disposal	36	\$/t
Wastewater treatment	43	\$/1000 m ³

This analysis gives back as a result an exergy efficiency and a value of the destroyed exergy, that represent the real losses of the process (Assamoi and Lawryshyn, 2012):

$$\eta = \frac{Ex_{prod}^{tot}}{Ex_{feed}^{tot}} = 1 - \frac{Ex_d^{tot}}{Ex_{feed}^{tot}} \quad (11)$$

where Ex_{prod}^{tot} and Ex_{feed}^{tot} are the total exergy of the product and the feed, respectively. The total exergy feed also includes the Net Power, which is the difference between power energy consumed and produced. The destroyed exergy can then be divided in exergy lost for irreversibility and as waste. The exergy associated to fluid machinery (pumps and compressors) was equal to the unit power, whereas the exergy associated to heat transfer can be calculated multiplying the heat power by the Carnot efficiency ($Ex_{q,unit}$) as reported elsewhere (Kotas, 2012).

3.2. Energy analysis

The energy analysis reflects the global energetic efficiency of the process, and it is represented by the energy efficiency, calculated as reported in the following equation (Islam, 2018):

$$\eta = \frac{E_{prod}^{tot}}{E_{feed}^{tot}} \quad (12)$$

where E_{prod}^{tot} and E_{feed}^{tot} [kW] are the total energy produced from the system and fed to the system.

3.3. Environmental analysis

The simplified environmental analysis evaluates the carbon footprint of the process, expressed as CO₂ emitted into the atmosphere per unit of product mass.

In order to quantitatively evaluate this parameter, the real CO₂ emitted from the process (for example due to methane burning in the boiler) is added to the equivalent CO₂ required by the plant operation (e. g. associated to electrical energy consumption).

This analysis has become fundamental in the recent years in view of the energy transition and economic perspective. Moreover, the carbon tax, that is the tax proportional to CO₂ emitted in the atmosphere by a given process is becoming more and more significant for the economics of a Company.

3.4. Economic analysis: operative expenditure

The Operative Expenditure (OpEx) represents the overall annual costs of the plant.

The manpower present in the plant represents the first cost element: the manpower cost is the salary of the operators multiplied by the number of shifts required for the process (Peters and Timmerhaus, 1980).

The other cost items of the economic analysis are utilities, feedstocks,

Table 9
Outlet stream properties extraction section.

Stream name in process diagram	Raffinate	S4	S7
Temperature	199.98	219	210.93
Pressure	7092.75	2026.50	0
Mass Flows	943.66	2484.36	20.58
Water	0.05	0.39	0.75
Mannose	0	0.24	0
Cellobiose	0	0.09	0
D-Galactose	0	0.13	0
Arabinose	0	0.04	0
Linoleic acid	0.23	0	0
Stearic acid	0.05	0	0
N-hexadecanoic acid	0.13	0	0
Aspartic acid	0.10	0	0.05
L-Glutamic acid	0	0.03	0
Leucine	0.05	0	0.02
Tyrosine	0.25	0	0.12
Trans-3,4-Dihydroxycinnamic acid	0	0.07	0
Valine	0.10	0	0.05
Methionine	0.03	0	0.01
Quercetin	0	0.02	0

Table 10
Inlet streams results for the incinerator.

Stream number in process diagram	Unit	2	17	57
Temperature	°C	200	158.62	26.08
Pressure	kPa	101.33	104.80	101.33
Mass Flow	kg/h	944	62529.45	9452.51
SO ₂	w/w	0	2×10^{-3}	0
S	w/w	5×10^{-3}	0	0
Oxygen	w/w	0	0	1
Nitrogen	w/w	0.05	4×10^{-3}	0
1C16oicAcid	w/w	0.25	0	0
StearicAcid	w/w	0.1	0	0
Linoleic Acid	w/w	0.25	0	0
CO ₂	w/w	0	0.68	0
H ₂ O	w/w	0.2	0.26	0
HCl	w/w	0	1×10^{-3}	0
Phenol	w/w	0.15	0	0

maintenance and waste disposal, and their costs are reported in Table 8 (Peters and Timmerhaus, 1980). The OpEx analysis has been carried out considering either the cost of electrical energy from the national mix (both fossil and renewable sources) and from renewable sources only.

4. Results and discussion

4.1. Process simulation

4.1.1. Extraction section results

As mentioned before, the aim of this section is to recover the bioactive polar compounds from the biomass with subcritical water stream, thanks to their solubility in water. This operation was found useful for this kind of plant both for its low impact on the expenditures (the main feed, i.e. the solvent, is simple water) and for its yield. According to the process flowsheet described in the previous paragraphs, by using a pressure drop and a cooler after the extraction tower, about 94% wt of the solvent (stream S3 in Fig. 1) and almost 100% of the bioactive compounds (stream S4) have been recovered (Table 9).

The elemental analysis of the raffinate sent to incineration, shows that the mass % of C, H, O, S and N are 59.7%, 9.8%, 26%, 0.5% and 4%, respectively, and its LHV is 30.4 MJ/kg, while SCG has a LHV of 23 MJ/kg. This implies that the heat per unit mass released by combustion of the raffinate is greater than that which would be provided by direct combustion of coffee grounds. Direct use of SCG in incineration, without the preliminary extraction treatment, would involve a high value

Table 11
Heat exchanger properties.

	Unit	E-100	E-101	E-102
Duty	MW	9.5	14.5	3.2
UA	kJ/C-s	10.2	38.4	72.3
Tube Side Pressure Drop	kPa	1	1	1
Tube Side Delta T	°C	-286.7	-473.3	-114.5
Shell Side Delta T	°C	176.5	-1.4	166.7
LMTD	°C	936.2	377.2	44.0
Ft Factor		0.9	1	1

Table 12
Compressors results.

	Unit	K-101	K-105
Delta T	°C	9.21	22.58
Delta P	kPa	7.48	17.68
Power	kW	191.7	95.23

Table 13
Turbines results power generation unit.

		Unit number in process diagram		
	Unit	K-102	K-103	K-104
Power	kW	3876.82	1193.33	2009.08
ΔT	°C	-260.59	-57.98	-57.16
ΔP	kPa	3596.025	202.65	92.72

compounds loss, and higher equipment volume (blowers, turbines, furnace, heat exchangers). Consequently, it is preferable to avoid the direct use of SCG in incineration even from an energetic and economic point of view.

The simulation returned a duty for the exchangers (E-101, E-102, and 103) of 1.04, 1.01 and 3.27 MW, respectively.

4.1.2. Incineration section results

Table 10 shows the properties of the inlet streams to the incinerator while in Table 12 the compressors results are reported. As mentioned before, the core of this section, the incinerator, converts the entering thermal power of 30 MW into 7.07 MW of electrical power. This is generated in part from the plastic stream (22 MW) and the remaining part from the biomass (8 MW). Starting from this and taking into account the necessity of having 6%vol oxygen concentration in the outlet gas stream according to environmental regulations, the oxygen flowrate was calculated to be equal to 9.4 t/h. The presence of the electrolyser allows to have pure oxygen fed to the reactor, classifying the process as an oxy-combustion process. The use of pure oxygen, among other well-known advantages, guarantees the substantial decrease of the total Nox concentration in the flue gas, reduce the ignition delay of the waste, improves the control of the combustion process and reduces soot formation in the exit gas stream (Vilardi and Verdone, 2022).

Finally, the enthalpy of this gas stream is used to vaporize 30 t/h of water in the boiler. Table 11 reports the boiler parameters. The final conditions of the steam leaving this section are 410 °C and 4100 kPa.

4.1.3. Power Generation Unit results

The conversion of thermal/potential energy of steam into mechanical (and then electrical) is carried out through turbines K-102, K-103 and K-104 (Fig. 4-Table 13).

The steam, entering at 410 °C and 4100 kPa, is fed to the high-pressure turbine (K-102) where it is expanded to 300 kPa, obtaining 3.87 MW of power. Then, the steam is fed into a splitter (knock-out drum) and the liquid phase is recirculated into the heater; the separated stream is fed to the second turbine to recover 1.2 MW. Finally, water, now at 100 °C and 100 kPa, is fed to the last turbine to recover 2 MW

Table 14
Results stream properties SOEC section.

		Stream number in process diagram	
	Unit	59	62
Vapour Fraction		1	0
Temperature	°C	25	25
Pressure	kPa	101.33	101.33
Mass Flow	kg/h	1535.83	4216.48
H ₂ O	w/w	0.03	0.999
Hydrogen	w/w	0.97	0

Table 15
Turbines results SOEC section.

		Unit number in process diagram	
	Unit	K-106	K-107
Power	kW	1624.48	535.75
Delta T	°C	-178.51	-216.44
Delta P	kPa	1397.68	1397.68

Table 16
Total exergy of inlet and outlet streams.

Inlet stream total exergy		
Stream number	Exergy	Unit
63 (H ₂ O)	159.26	kW
SCG	7767.58	kW
Plasmix	24531.95	kW
20 (NH ₃)	0.53	kW
Cooling water	2513.51	kW
Total	34.97	MW
Outlet stream total exergy		
Waste stream total exergy		
Stream number	Exergy	Unit
21 (H ₂ O)	52.10	kW
26 (H ₂ O)	45.49	kW
25 (CO ₂)	825.89	kW
68 (CO ₂)	65.20	kW
Cooling water	2256.96	kW
Product stream total exergy		
59 (H ₂)	38722	kW
Total	41.96	MW

power, thus providing a total value for the plant of 7.07 MW of power produced.

It must be noticed in this section the presence of a degassing unit, necessary to remove oxygen and other gases from water before feeding it to the boiler.

4.1.4. SOEC results

The SOEC electrolyser is modelled in Aspen Hysys® as a reactor coupled with a separator, where the electrolysis reaction happens producing oxygen and a hydrogen-water stream. Table 14 reports the outlet streams results.

The oxygen stream (1500 kPa and 950 °C) is expanded in turbine K-107 (Fig. 5) to atmospheric pressure and 26 °C, to be recycled to the incinerator. In this turbine 0.54 MW are recovered in addition to that obtained from the power generation unit (Table 15).

According to Aspen Design Spec, since the oxygen required is 9.4 t/h, the water flowrate fed into the system is 15 t/h.

The water – hydrogen mixture is expanded into turbine K-106 to atmospheric conditions, recovering additional 1.6 MW, in order to be separated into vessel V-103; from this equipment a hydrogen-rich gaseous stream is recovered, while the liquid water stream is recycled to the SOEC electrolyser.

The total power absorbed from the SOEC was 37.87 MW (see Supplementary Materials for more details).

Table 17
Power energy consumption and production.

Power consumption		
	Power	Unit
<i>Pumps</i>		
P-102	8.86	kW
P-101	51.14	kW
P-100	3.77	kW
<i>Compressors</i>		
K-100	454	kW
K-101	191.70	kW
K-105	95.23	kW
SOEC	37.87	MW
Total	38.67	MW
Power production		
	Power	Unit
<i>Turbines</i>		
K-102	3877	kW
K-103	1193	kW
K-104	2009	kW
K-106	1624	kW
K-107	536	kW
Total	9.23	MW

4.2. Process analyses

4.2.1. Exergy and energy analysis

Table 16 reports the total exergy of the main streams.

The chemical exergy of solids inlet feeds is equal to 29583.63 kJ/kg for SCG and 42288 kJ/kg for Plasmix.

Based on the above results, energy and exergy efficiencies equal to 0.63 and 0.60 have been calculated, respectively. These values are strongly affected by the high energy consumption. Although turbines recover an appreciable amount of energy, the energy required by the SOEC is still high: producing hydrogen using the electrolyser alone is a very energy intensive process.

The power recovered by the turbines represents about 22.5% of the plant total energy demand, and this helps increase the energy and exergy efficiencies (Table 17). Without this additional energy recover, only 7.07 MW would have been produced from the incinerator, thus reducing the energy efficiency at 0.55, and the exergy efficiency at 0.53, so that the recovered power would cover only 18% of the plant total energy demand.

In terms of specific (i.e. per unit product mass flow rate) energy consumption and production, the following values were calculated: energy consumption is around 91.22 MJ/kg, while the specific energy

production was around 2.25 MJ/kg.

The exergy analysis also quantified the different components of the destroyed exergy: exergy lost as irreversibility and as waste. Fig. 6 shows the destroyed exergy divided in its components: it can be seen that most of the destroyed exergy is due to irreversibility, that is a contribute thermodynamically impossible to reduce without a plant upgrading; indeed, the waste exergy, that represents the losses of the process that may be actually reduced by process optimization, were only 3.25 MW, i. e. 12.2% of the total exergy destroyed.

4.2.2. Economic analysis

Table 18 displays the unitary costs of reagents and the results of the OpEx analysis.

Electricity cost represents the largest contribution to the total OpEx: about 50% when using fossil energy and 80% for renewable energy scenario. Therefore, attempting to achieve zero impact by employing alternative sources only is still very expensive, especially for these two highly electrified plants: operating costs increase by 158%, using renewable power only.

Finally, the operational costs have been normalized with respect to the hydrogen produced, always distinguishing the only renewable and fossil fuels cases (Fig. 7). Hydrogen costs result higher if compared with hydrogen produced from Steam Gas Reforming (SMR), which is 2.08 \$/kg and 2.27 \$/kg with Carbon Capture System (CCS) (Kayfeci et al., 2019; Shehabi et al., 2021). This difference becomes relevant especially in the case of use of renewable sources. However, this gap is expected to shrink with time if the price of CO₂ emissions (e.g. in the form of carbon

Table 18
Production costs.

OpEx (\$/y)	
Labour	1330,000
Cooling water	32,376.37
Refrigerated water	57,362.72
NH ₃	552.81
Deionized water	3742.27
O&M SOEC	9035,104.88
Waste gas treatment	877,389
Wastewater treatment	1113,851.59
Renewable power energy	63,365,579.14
Fossil power energy	15,207,738.99
Total (renewable energy)	75,815,958.78
Total (fossil energy)	27,658,118.63

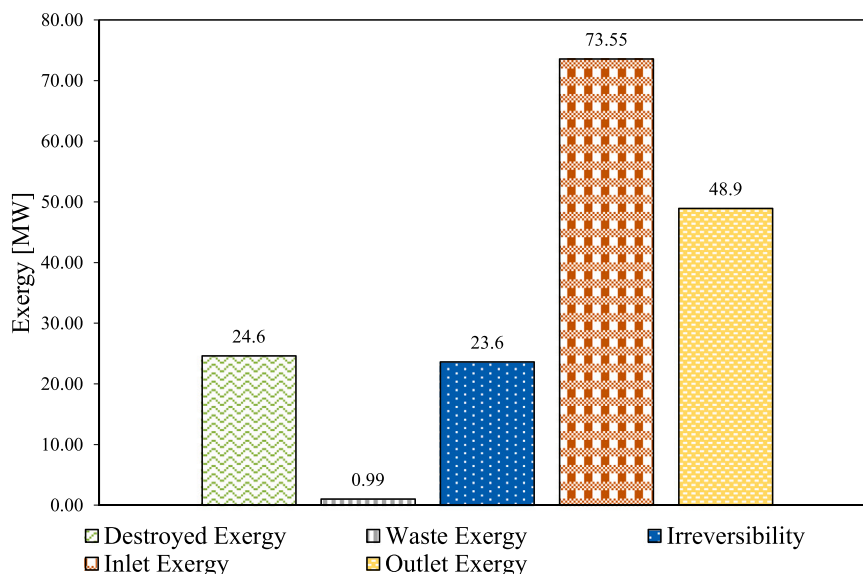


Fig. 6. Inlet, outlet and destroyed exergy.

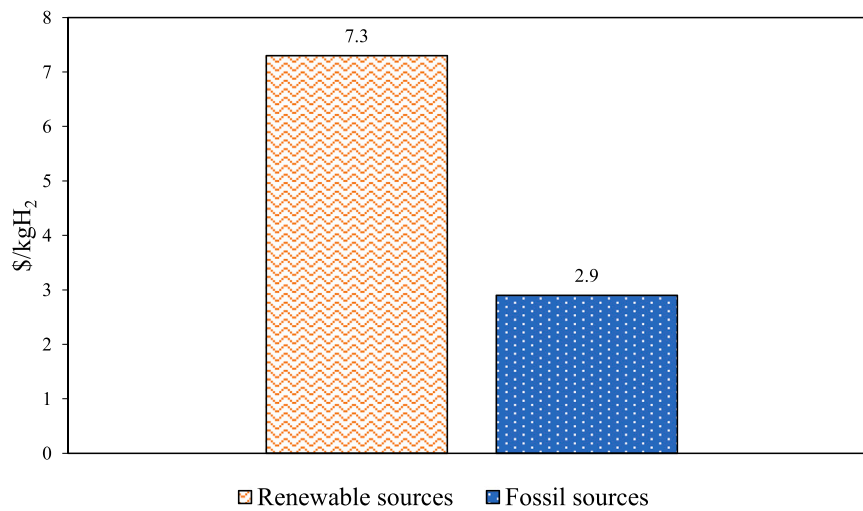


Fig. 7. Specific production costs.

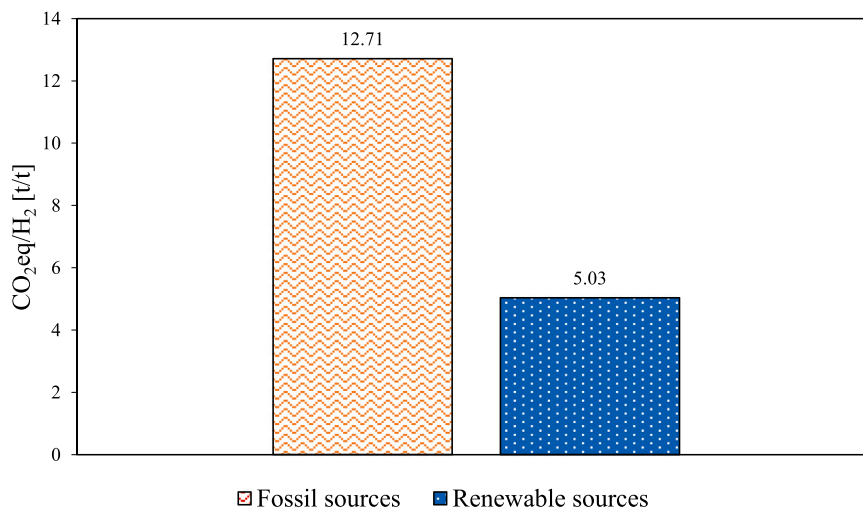


Fig. 8. CO₂ emissions per t of hydrogen produced.

tax) will further rise (Masoudi Soltani et al., 2021).

4.2.3. Environmental analysis

Finally, carbon footprint, expressed as tons of CO₂ (tCO₂) emitted per hydrogen unit mass (Fig. 8), was evaluated. The use of renewable energy sources allows to considerably decrease CO₂ emissions by up to 93%, despite a higher production cost.

For comparison, SMR is characterized by higher emissions of carbon dioxide, about 7 kg of CO₂ per 1 kg of hydrogen produced (Bassani et al., 2020), while CCS allows high CO₂ capture rate (>90%) (Ali Khan et al., 2021). However, according to the International Energy Agency (IEA), the amount of CO₂ emissions generated during the capture process using common absorption technologies (such as amine scrubbing) can range from 0.3 to 0.5 tonnes of CO₂ per tonne of CO₂ captured, depending on the efficiency of the process and the source of energy used (I. Energy Agency, 2015). The IEA also estimates that the overall increase in CO₂ emissions from the power plant due to the capture process can range from 11% to 14%, again depending on the efficiency of the process and the energy source used.

As a further comparison, methane pyrolysis emits 2.5 kgCO₂/kgH₂ (Parkinson et al., 2018), markedly higher than the value reported here assuming renewable sources use only.

5. Conclusions

In this study an integrated Waste to Energy process has been analysed for the recovery of bioactive compounds from agro-industrial wastes, and their successive incineration together with a plasmix stream to generate power required by a SOEC electrolyser to produce “green” hydrogen. The innovation of the proposed cycle is the development of an integrated hydrogen production process with lower greenhouse gases emission than alternative common processes. Furthermore, some of the products recovered from the agro-industrial wastes, in this case from spent-coffee ground, can still have a high value of interest for the cosmetic, pharmaceutical and food industries.

The simulations carried out showed the feasibility of recovering the bio-active compounds from the biomass with a subcritical water stream, thanks to their solubility in water. From the waste to energy section of the plant, 1.54 t/h of a hydrogen/water mixture was obtained, from a feed of 2421 kg/h of biomass, and with the energy coming from the incineration of the residual portion of biomass. The whole cycle allowed to achieve the total recovery of the waste streams, in terms of both energy (used for the production of a green energy vector) and high-value bio active compounds.

The energetic and exergetic analyses showed remarkable results, since the efficiency of the plant was higher than 60% in both cases.

Finally, the environmental and economic analyses allowed to assess the impact of the process in terms of carbon footprint: the use of 100% renewable energy significantly reduces the emission of greenhouse gases, even if compared with alternative methods, but at the moment this can be accomplished only with an increase of the total costs of around 158%. From this result, it is apparent that, in order to move forward on the energy transition pathway, significant efforts are still required to reduce the cost of 100% renewable energy sources, to allow the adoption of really “green” processes.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.psep.2023.03.005](https://doi.org/10.1016/j.psep.2023.03.005).

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